

Short communication

## Third-order optical nonlinear studies of Cobalt (II) Schiff base complex bearing triphenylphosphine using Differential Optical Kerr Gate and Z-scan studies

Rudresha Bada Jayappa<sup>a</sup>, Badekai Ramachandra Bhat<sup>a,\*</sup>, Dileep Ramakrishna<sup>a</sup>, John Kiran Anthony<sup>b</sup>, Fabian Rotermund<sup>b</sup>

<sup>a</sup> Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasanagar 575025, Mangalore, Karnataka, India

<sup>b</sup> Division of Energy Systems Research, Ajou University, Suwon 443749, South Korea

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### ABSTRACT

The third-order optical nonlinearity of the composite film of coordination complex [CoLPPH<sub>3</sub>Cl] (L = N-(2-pyridyl)-N'-(salicylidene)hydrazine) and PMMA has been investigated by using Differential Optical Kerr Gate (DOKG) and Z-scan measurements. Large value of the third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ) of the order of  $10^{-10}$  esu was measured and its nonlinear response time was found to be faster than or comparable to the laser pulse width (90 fs) used. The single beam Z-scan technique was used to investigate the nonlinear absorption property of the composite near 800 nm. The sample exhibit saturable absorption. The nonlinear absorption coefficient of sample is found to be  $-32$  cm/GW.

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### 1. Introduction

With the rapid development of optical communication, some novel materials with large and ultrafast nonlinear optical responses are essential for fabricating the ultrafast optical switching and processing devices [1–5]. For these purposes, many materials, including semiconductors, polymers, nanomaterials and inorganic materials, have been researched. In recent years,  $\pi$ -conjugated organic materials have received considerable interest for their high nonlinear optical (NLO) properties and fast response time of the nonlinearity [6]. Among various methods to enhance the third-order nonlinearity of organic materials, incorporating metals into NLO systems adds a new dimension and introduces many new variables. Organometallic and coordination chemistry can offer a very large variety of molecular and bulk NLO materials, in relation to the metal nd configuration, oxidation state, spin state and high NLO properties of organics with good transmittancy, temporal and thermal stability of inorganics. The central metal atom of an organometallic and coordination complexes can readily coordinate to conjugated ligands and undergo metal–ligand orbital overlap facilitating effective electronic communication and electronic transitions between metal and ligand leading to large dipole moment changes between the excited states [7].

In this paper, we report the third-order optical nonlinearity of the coordination complex [CoLPPH<sub>3</sub>Cl] using the time-resolved Differential Optical Kerr Gate and Z-scan measurements. Here we used the composite film of compound and PMMA for measurement of third-order optical nonlinearity. From DOKG experiment third-order NLO susceptibility  $\chi^{(3)}$  of composite film of complex was derived to be very large as  $3.6 \times 10^{-10}$  esu and open aperture Z-scan measurement shows the sample exhibit saturable absorption. The nonlinear absorption coefficient of sample is found to be  $-32$  cm/GW.

### 2. Experimental

#### 2.1. Synthesis of [CoLPPH<sub>3</sub>Cl] complex

The complex (Fig. 1a) was prepared according to the procedure reported recently by our group [8]. The complex was prepared by refluxing a dichloromethane solution of [CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and N-(2-pyridyl)-N'-(salicylidene) hydrazine in a 1:1 molar ratio for 3 h. The complex was dark green. The complex was soluble in CH<sub>3</sub>OH, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>6</sub>, DMSO and DMF. The electronic spectrum was measured on a GBC Cintra 101 UV–vis double beam spectrophotometer in CH<sub>3</sub>OH solution of the complex in the 200–600 nm range. The electronic spectra (Fig. 1b) showed many bands in the region 250–490 nm. The bands appeared in the region 250–350 nm have been assigned to intraligand transitions. A less intense band in the range, 390–490 nm, cor-

\* Corresponding author. Tel.: +91 824 2474000x3204; fax: +91 824 2474033.  
E-mail address: [chandpoorna@yahoo.com](mailto:chandpoorna@yahoo.com) (B. Ramachandra Bhat).

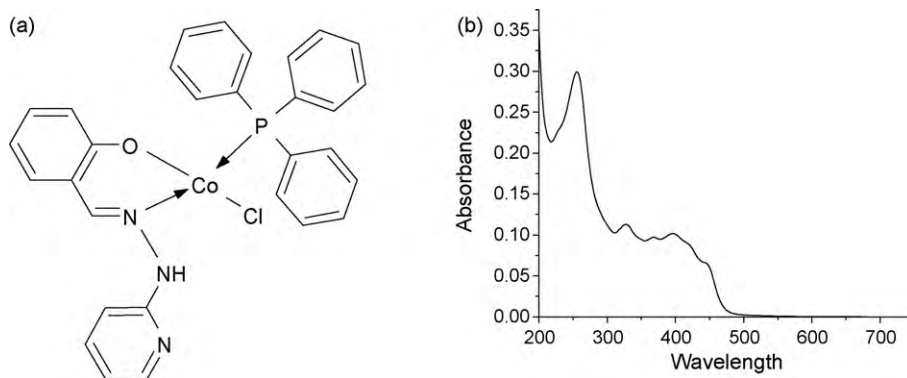


Fig. 1. (a) Molecular structure of [CoLPPh<sub>3</sub>Cl] (b) Absorption spectra of the complex.

responds to Laporte forbidden electronic transition between *d* orbitals.

## 2.2. Film preparation

In order to prepare composite of complex and PMMA, 250 mg of PMMA (M.W. 140,000) and 2 mg of complex were dissolved in 2.5 mL of dichlorobenzene (DCB). The concentration of compound in the solution was 0.001 mol/L. The solution was mixed thoroughly by stirring and via ultrasonication to ensure homogenous mixing. The solution was subsequently spin coated at 1200 rpm on a glass substrate and the coated film was dried in a vacuum oven at 100°C for about 20 h. The film thickness (*L*) of complex film was measured to be 1.40 μm, by an Alpha-step surface profiler (Tencor P-10).

## 2.3. Differential Optical Kerr Gate and Z-scan measurements

The time-resolved DOKG [9] experiment with a Ti:sapphire laser delivering 90 fs pulses at a repetition rate of 92 MHz at 800 nm was used to investigate the third-order optical nonlinearity of the composite. The laser beam was divided into pump and probe beams with 20:1 intensity ratio by a beam splitter. The polarization of the probe beam was set to 45° with respect to that of the pump beam by a half wave plate. Two beams were focused on the sample by a convex lens of focal length of 7 cm. The time delay of the probe with respect to the pump was controlled by a PC-driven linear translator (PI, M-014.D01). At the zero time delay, the two beams overlap spatially and temporally, and the probe beam polarization rotates due to the birefringence induced in the sample by the pump beam. The pump beam, after passing through the sample, was blocked and the probe beam was passed through a quarter wave plate. The circularly polarized probe beam was then split into two beams by a polarizing cube beam splitter and the two beams were detected by a photo detector pair connected to a lock-in amplifier. CS<sub>2</sub> was used to check the reliability of the setup as well as to estimate the  $\chi^{(3)}$  of the sample. Additionally, single beam Z-scan technique [10] was used to investigate the nonlinear absorption property of the composite near 800 nm. An optical parametric oscillator synchronously pumped with a Ti:sapphire laser operating at 92 MHz (800 nm, 110 fs), was employed in the study. The laser beam was focused by a convex lens on the sample. The beam waist at 800 nm was estimated to be 16 μm, by the knife edge method.

## 3. Results and discussion

The result of the DOKG experiment performed at 800 nm is depicted in Fig. 2. The optical kerr effect (OKE) signal is symmetric about the zero time delay, shows that the nonlinear response time of the sample is faster than or comparable to the laser pulse

width used (90 fs). Such an ultrafast response originates in this compound due to the effective electronic communication between  $\pi$ -conjugated Schiff base ligand and triphenylphosphine through central Cobalt (II) atom and also because of effective overlapping of metal orbitals with the ligand orbitals. CS<sub>2</sub> was used as the reference and its optical kerr signal was recorded. CS<sub>2</sub> exhibited a biexponential nonlinear response curve (inset of Fig. 2) with response times of 0.2 and 1.8 ps, respectively. These values agree well with the previously reported values [11]. Response time of our investigated complex is comparable with porous anodized aluminum oxide (AAO) nanostructures [12], copolymers containing fluorine and tetraphenyldiamineobiphenyl units in backbones [13], cross-conjugated isopolydiacetylene oligomers [14], hybrid silica gel glasses [15] and chloro(1,10-phenanthroline-N,N')(triphenylphosphine)copper(I) dichloromethane [16]. Maximum signal is observed at zero probe delay times, suggesting that the ultrafast electronic response is the dominant contributor to the observed nonlinearities. The magnitude of  $\chi^{(3)}$  of the sample can be estimated by comparing its OKE signal amplitude with that of CS<sub>2</sub> using the following equation [9].

$$\chi_s^{(3)} = \chi_r^{(3)} \left( \frac{I_s}{I_r} \right)^{1/2} \left( \frac{n_s}{n_r} \right)^2 \left( \frac{L_r}{L_s} \right) \frac{\alpha L_s}{\exp(-\alpha L_s/2) \cdot [1 - \exp(-\alpha L_s)]}$$

where the subscripts *s* and *r* represent the sample and the reference, *I* the absolute magnitude of OKE signal, *n* the refractive index, *L* the thickness and  $\alpha$  the linear absorption coefficient, respectively. The

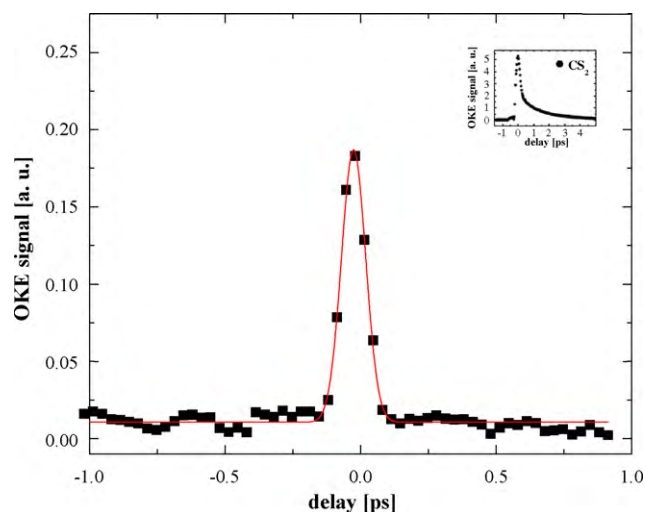


Fig. 2. Optical Kerr signal for [CoLPPh<sub>3</sub>Cl] at 800 nm. The nonlinear response time is faster than or equal to the laser pulse width 90 fs. The reference OKE signal of CS<sub>2</sub> is shown as an inset.

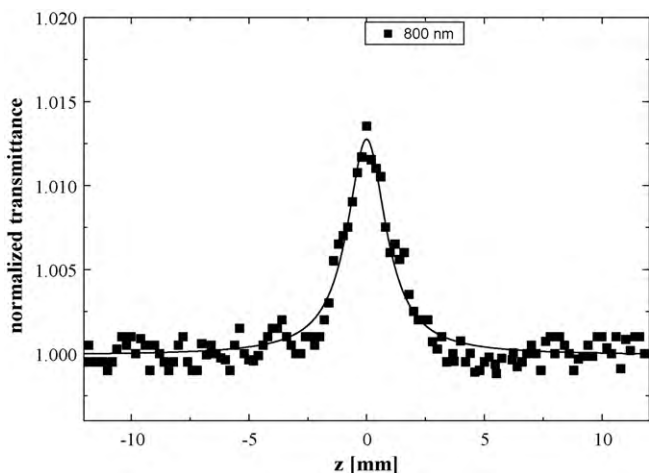


Fig. 3. Nonlinear absorption by [CoLPPPh<sub>3</sub>Cl]. The input intensity is 8 GW/cm<sup>2</sup>.

$\chi_r^{(3)}$  of CS<sub>2</sub> was taken as  $1 \times 10^{-13}$  esu [12] and that of the composite film of complex was derived to be  $3.6 \times 10^{-10}$  esu.

The following conclusions are drawn from the experimental determinations. Combining the conjugated triphenylphosphine ligand with its electron accepting character ( $d$  to  $\sigma^*$ ) [17,18], which facilitating effective electronic communication and CT transitions between metal and ligands leading to large dipole moment changes between the excited states [19] and also which makes circulation of electrons throughout the distorted inorganic tetrahedral center. Several reports on complexes containing phosphine [20–23] and Schiff base [24–26] ligands exhibit large nonlinear coefficient and the absorption coefficient. The existence of strong intramolecular CT excitations in a noncentrosymmetric molecular environment is the key to the NLO activity. The first criterion can be satisfied by considering a polarizable molecular system (e.g.  $\pi$ -conjugated pathway) having an uneven or asymmetric charge distribution. The simplest way to achieve this is to have a donor (D)–acceptor (A) system with a bridge (D– $\pi$ –A) which can help the electronic communication between donor and the acceptor. Most metal complexes can be envisaged within an above mentioned D– $\pi$ –A system, in which donor and/or acceptor, or the bridge moieties are selectively replaced by an organometallic group. This is because metal complexes possess intense, low energy MLCT, LMCT, or intraligand charge transfer (ILCT) excitations. Therefore they can effectively behave as donor and/or acceptor groups of the D– $\pi$ –A system, or as constituents of the polarisable bridge [19]. Metal ions make an important contribution to the NLO properties. The strength of the NLO properties can be altered by the  $\pi$ -back-donation capacity of the metal ions to the ligands, and the increased  $\pi$ -back donation capacity of the metal ions to the ligands may enhance the extension of the electronic  $\pi$  system and improve the NLO properties [27]. For example, in the reported polymers [Co(bbtt)<sub>2</sub>(NCS)<sub>2</sub>]<sub>n</sub>, [Mn(bbtt)<sub>2</sub>(NCS)<sub>2</sub>]<sub>n</sub> and [Cd(bbtt)<sub>2</sub>(NCS)<sub>2</sub>]<sub>n</sub>, [Co(bbtt)<sub>2</sub>(NCS)<sub>2</sub>]<sub>n</sub> possesses the strongest NLO properties just because the electronic  $\pi$  back-donation capacity of Co<sup>2+</sup> is the largest among the three kinds of ions [28]. This phenomenon is also observed in other reported compounds of chromium, zinc, cadmium, lead molybdenum and tungsten [29–31]. From these results it is clear that the resonance and structural effects, which determine the electronic polarization properties, will modulate the observed nonlinearity.

Open aperture Z-scan studies show that composite film of complex near 800 nm exhibit saturable absorption. The result is displayed in Fig. 3. The nonlinear absorption coefficient of sam-

ple is found to be  $-32$  cm/GW. This observed value is comparable to previously reported polyads based complexes of ruthenium and osmium [32] and thiol based copper (II) complexes [33,34].

#### 4. Conclusions

In this work, we have reported systematic investigation of the third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ) of the complex [CoLPPPh<sub>3</sub>Cl] by using DOKG. From this experiment third-order NLO susceptibility  $\chi^{(3)}$  of composite film of complex was derived to be very large as  $3.6 \times 10^{-10}$  esu. Open aperture Z-scan measurement, shows the sample exhibit saturable absorption. The nonlinear absorption coefficient of sample is found to be  $-32$  cm/GW. This type of material is suitable candidate for pulse compression technological applications.

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