



# Enhanced photostability and optical nonlinearity of nickel and cobalt organometallic complexes

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## ABSTRACT

Nonlinear optical and limiting properties of nickel, cobalt metal-organic complexes and ligand (L) {L = N,N'-o-phenylenebis (4-hydroxy-salicylideneimine)} were studied using Z-scan technique using Q-switched Nd: YAG laser with nanosecond pulses at 532 nm. The results reveal that metal complexes exhibit large negative nonlinear refractive index ( $n_2$ ) of the order of  $10^{-11}$  esu. The metal complexes displays large nonlinearity than the ligand due to effective charge delocalization between metal ion and ligand. The magnitude of ground state absorption cross section is small compared to the effective excited-state absorption cross section implying the observed nonlinearity is due to reverse saturable absorption. Further, metal-organic complexes exhibit enhanced optical limiting behaviour at nanosecond laser pulses.

## 1. Introduction

The important application of nonlinear optical materials has been the development of optical limiting (OL) materials with strong optical nonlinearity. All optical sensors including human eye have damage threshold above which sensor will be damaged. Sensors with high damage threshold are desirable for practical applications. The simplest method to enhance the damage threshold is place an OL material in front of the sensor. The ideal optical limiters are highly transmissive at low intensity but become increasingly absorptive at high intensity while retaining the sensitivity of the sensors [1–3]. OL behaviour in the materials has been realized by exploiting different nonlinear absorption (NLA) mechanisms which include reverse saturable absorption (RSA), two-photon absorption (2 PA), multi-photon absorption, and molecular excited state absorption (ESA) and nonlinear refraction (NLR) and scattering (NLS) [4,5].

Recently, metal-organic or organometallics have gained considerable interest due to their large optical nonlinearity and its applications in photonic devices [6–9]. Strong optical nonlinearity, ease in molecular structural changes, low cost and flexible synthetic approach has

made these materials more attractive for nonlinear optical (NLO) applications. Metal-organic materials are obtained by adding the transition metal ion to the organic systems. The inclusion of the metal ion creates more sub-levels in the energy levels, which enables more electronic transitions and leads to a large optical nonlinearity [10]. Further, NLO properties can be altered by modifying the centre metal ion and/or surrounding organic chromophores [10–12].

In this paper, we are reporting the effect of central metal ion on optical nonlinearity of free ligand, nickel and cobalt metal-organic complexes using popular Z-scan technique. OL characteristic of the complexes was carried out using energy dependent transmission technique. The results indicate metal-organic complexes possess enhanced optical nonlinearity and OL property as compared to ligand.

## 2. Experiment

Syntheses of metal-organic complexes nickel [NiL], cobalt [CoL] metal-organic complexes and ligand (L) {L = N,N'-o-phenylenebis (4-hydroxy-salicylideneimine)} were reported in elsewhere [13]. N,N-Dimethylmethanamide (DMF) solvent was used to prepare liquid samples

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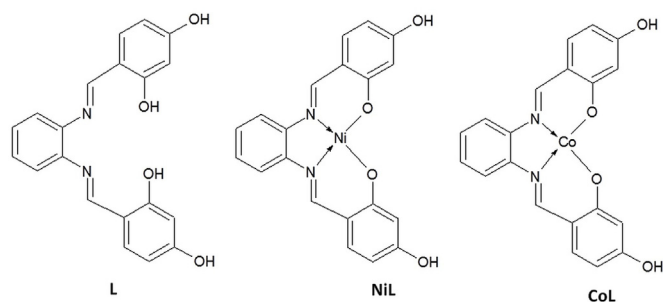


Fig. 1. Molecular structure of the ligand (L) and Nickel (NiL) and Cobalt (CoL) metal-organic complexes.

of ligand and metal organic complexes and maintained 1 m-mol/L of concentration. The linear refractive indices ( $n_0$ ) of the samples were measured using digital refractometer RX-7000 $\alpha$ , Atago Co. Ltd. Z-scan technique was used to determine third-order optical parameters of ligand and metal-organic complexes [9,14]. The OL performance of the ligand and metal-organic complexes were investigated by energy dependent transmission experiments.

### 3. Results and discussions

#### 3.1. UV-Vis spectra

Molecular structure and UV-Vis absorption spectra of the ligand and metal-organic complexes are shown in Fig. 1 and Fig. 2 respectively. The linear absorption spectra of the samples were recorded on UV-visible fiber optic spectrometer (Model SD2000, Ocean Optics Inc.) using  $10^{-3}$  mol dm $^{-3}$  solutions in DMF. The complexes exhibit absorption band around 270 nm and at 400 nm due to intra-ligand electronic transition and forbidden d-d electron transition. There are two absorption bands, assigned to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions in the electronic spectrum of the ligand. These transitions are also found in the spectra of the complexes (intra-ligand transition), but they are shifted towards lower and higher frequencies, confirming the coordination of the ligand to the metallic ions.

The energy levels for tetrahedral cobalt (II) is  $^4A_2$ ,  $^4T_2$  and  $^4T_1(F)$ , derived from  $^4F$  of the free ion,  $^4A_2$  being the ground state. Besides, the excited  $^4P$  term of the free ion changes its notation to  $^4T_1(P)$ . The spin allowed transitions expected are  $^4A_2(F) \rightarrow ^4T_2(F)$ ,  $^4A_2(F) \rightarrow ^4T_1(F)$  and  $^4A_2(F) \rightarrow ^4T_2(P)$ . The transition  $^4A_2(F) \rightarrow ^4T_2(F)$  is occurs in the near IR region and usually not observed. The electronic spectrum of the Co(II) complex in DMF, in the present case suggests tetrahedral configuration

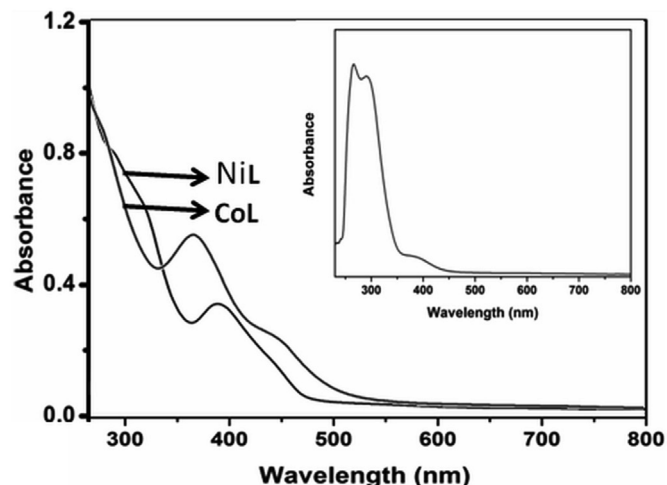


Fig. 2. UV-Vis spectra of the NiL and CoL. Inset UV-Vis spectrum of L.

for the complex. The spectrum shows two broad band transitions assignable to  $^4A_2(F) \rightarrow ^4T_2(P)$  and  $^4A_2(F) \rightarrow ^4T_1(F)$ . The electronic spectrum of the Nickel (II) complex in DMF, in the present case suggests tetrahedral configuration for the complex. Tetrahedral nickel (II) complex exhibit two transitions  $^3T_1(F) \rightarrow ^3A_2(F)$  and  $^3T_1(F) \rightarrow ^3T_1(P)$ . Tetrahedral complexes are characterized by comparatively high intensity for the electronic transitions [15,16]. The linear absorption coefficient ( $\alpha$ ) of the samples were calculated using the formula  $\alpha = \{\ln(100/(\%T))/d$ . Where T is the percentage of transmittance at 532 nm and d is the thickness of the sample.

#### 3.2. NLO measurements

Z-scan experiments on free ligand, nickel and cobalt metal-organic complexes were carried out to investigate the role of metal ion on NLO properties. Open aperture (OA) Z-scan was performed to determine NLA coefficient ( $\beta_{\text{eff}}$ ) and imaginary part of third-order NLO susceptibility ( $\text{Im} \chi^3$ ) and are shown in Fig. 3 along with corresponding theoretical fit. The shape of the open aperture curves depicts the intensity dependent absorptive nonlinearity in the metal-organic complexes with smooth valley at  $z = 0$  confirming strong NLA at higher intensities. The corresponding normalized transmission as a function of sample position in open aperture condition is given by Refs. [14,17,18],

$$T(z) = 1 - (q_0/2\sqrt{z}) \text{for } |q_0| < 1 \quad (1)$$

where  $q_0 = \beta_{\text{eff}} I_0 (1 - \exp(-\alpha L)) / (1 + z^2/z_0^2) \alpha$ ,  $\alpha$  is the linear absorption coefficient, where L is the length of the sample,  $\beta_{\text{eff}}$  is the nonlinear absorption coefficient of the sample,  $I_0$  is the intensity of the laser beam at the focus and  $z_0$  is the Rayleigh range for the lens.

Depending on the various factors such as linear absorption of the molecules, operating wavelength, intensity and fluence of laser light, and laser pulse-width, NLA can arise from different mechanisms: reverse saturable absorption (RSA), multi-photon absorption (two-photon absorption (2PA), three-photon absorption, etc.), excited state absorption (ESA), and saturable absorption (SA). Since samples have small linear absorption at the incident wavelength 532 nm, ESA is the primary dominating mechanism for the observed NLA [17,19]. Further, at higher intensities under nanosecond laser pulses 2PA play a major role [20,21]. The normalized valley depicts the presence of RSA process in the molecules [22]. The small reduction of normalized transmission value of ligand at the focus (Fig. 3a) is due to lower NLA associated with the free ligand and z-scan data points of the free ligand not as smooth as the metal complexes this may be due to instability of the molecule at higher intensities (Fig. 3a).

Nonlinear absorption coefficient ( $\beta_{\text{eff}}$ ) of the ruthenium complex is obtained by fitting the experimental data using Eq. (1). ESA cross section ( $\sigma_{\text{exc}}$ ), ground state absorption cross section ( $\sigma_g$ ) and imaginary part of third-order NLO susceptibility ( $\text{Im} \chi^3$ ) were calculated based on the model reported in the literature [14,17] and tabulated in Table 1. Larger  $\sigma_{\text{exc}}$  as compared to  $\sigma_g$  also suggests that observed NLA is due to RSA.

Closed aperture (CA) Z-scan was performed to determine nonlinear refraction coefficient ( $n_2$ ) and real part of third-order NLO susceptibility ( $\text{Re} \chi^3$ ). The CA Z-scan curves are shown in Fig. 4 with corresponding theoretical fit [14,17]. Fig. 4 depicts the negative nonlinear refractive index (self-defocusing) associated with samples. It is observed that the peak-valley of closed-aperture Z-scan satisfies the condition of  $\Delta Z \sim 1.7 \Delta Z_0$ , thus confirming the third-order nonlinearity is due to electronic process [23]. The normalized transmittance for closed aperture condition is given by,

$$T(z) = 1 - 4\Delta\phi_0 x / (1 + x^2)(9 + x^2) \quad (2)$$

where T(z) is the normalized transmittance for the pure refractive nonlinearity at different z,  $\Delta\phi_0$  is the on-axis nonlinear phase shift and  $x = Z/Z_0$  and  $\lambda$  is the wavelength of light. The nonlinear refractive index ( $n_2$ ) is obtained by fitting the experimental data using Eq. (2). The

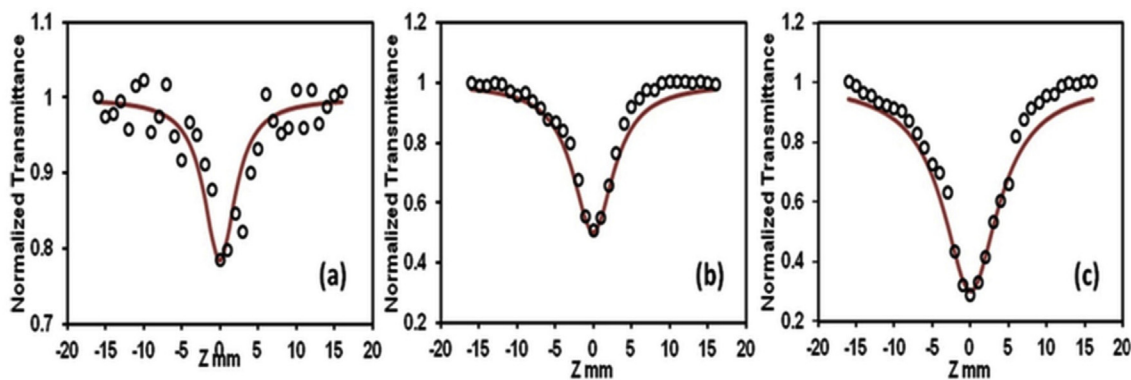


Fig. 3. Open aperture Z-scan curves of (a) L (b) NiL and (c) CoL. Solid line depicts theoretical fit.

real part of third-order nonlinear optical susceptibility ( $\text{Re } \chi^{(3)}$ ) can be determined using the relation given in the literature [17]. Measured values of  $n_2$  and  $\text{Re } \chi^{(3)}$  are tabulated in Table 1. The Z-scan experiments were obtained in single pulse mode to eliminate thermal effects in the observed nonlinearity. Further the pure nonlinear refraction curve in Fig. 4 depicts the peak-valley separation is less than  $1.7 Z_R$  (Rayleigh range) which confirms the observed nonlinearity arising from thermal effects are negligible [14]. Therefore, optical nonlinearity of the metal complexes is mainly arises from the delocalization of the electron cloud and the charge transfer mechanisms which is due to the applied electric field associated with nanosecond laser pulses [24].

Under similar experimental condition NLO parameters of the free ligand are lower compared to their corresponding complexes. This increased NLO response can be attributed to: increase in delocalization via central metal atom and donor-acceptor behaviour due to metal atom and substituent ( $-\text{OH}$ ) present at the phenyl ring. The formation of the  $\text{N} \rightarrow \text{M}$  and  $\text{O} \rightarrow \text{M}$  bonds enhances the optical nonlinearities in hetero-aromatic conjugate systems. In particular, under nanosecond pulses and at the wavelength 532 nm, the optical nonlinearity of the metal-organic complexes increased with respect to their ligand. The metal-organic complexes exhibited strong NLO properties, while NLO properties were practically lower for the free ligand. The high NLO properties for cobalt complex is may be due to more effective delocalization through  $\text{N} \rightarrow \text{M}$  and  $\text{O} \rightarrow \text{M}$  bonds because of its larger size compared nickel ion, which allows the system to stabilize the negative charge more efficiently [25,26]. Further, the addition of metal ion enhances the photo stability of the metal-organic complexes at higher intensities.

The  $\beta_{\text{eff}}$  values of the investigated metal-organic complexes are in range of  $10^{-8}$ – $10^{-9}$  cm/W, which are enhanced and comparable with hollow gold nanocages ( $5 \times 10^{-9}$  cm/W) [27]  $\text{MoS}_2$  nanosheets ( $1.5 \times 10^{-9}$  cm/W) [28] and  $\text{WS}_2$  nanosheets ( $3.9 \times 10^{-9}$  cm/W) [29] at 532 nm.

### 3.3. Optical limiting studies

Nonlinear transmittances of the metal complexes varying with input fluence were performed to explore the OL capability of the samples and also determine the OL onset values ( $F_{\text{on}}$ , fluence at which OL action begins) and OL threshold ( $F_{\text{th}}$ , fluence at which transmittance reduces to 50% of the linear transmittance). The capability of the optical limiter is decided by  $F_{\text{on}}$  and  $F_{\text{th}}$  values, sample with smaller threshold value

exhibits good optical limiting property [30].

The nonlinear optical process leading to optical limiting has different origins, such as nonlinear scattering, free carrier absorption (FCA), two-photon absorption (TPA) and reverse saturable absorption (RSA). Generally, the molecules which exhibit RSA process will have an exceedingly fast response time as it involves electronic transitions [31]. The well known reverse saturable absorbers are porphyrin complexes, fullerene (C60) and phthalocyanines [32–34]. Open aperture Z-scan measurements indicate that complexes exhibits RSA behaviour due to large value of  $\sigma_{\text{exc}}$  as compared to  $\sigma_g$  and moreover we didn't observe any scattering during the experiments. Further, RSA is the dominating nonlinear optical mechanism that responsible for optical limiting effects in metal-organic complexes [4]. Therefore, the observed optical limiting in the complexes is predominantly due to RSA process. The OL behaviour of the metal-organic complexes are shown in Fig. 5 and  $F_{\text{on}}$  and  $F_{\text{th}}$  values of the ligand and metal-organic complexes NiL and CoL are tabulated in Table 2.

The results indicate that CoL complex possesses lower  $F_{\text{th}}$  values and minimal transmittance at 532 nm, these characteristic properties make them to be possible candidates for optical limiting applications at visible region. Further,  $F_{\text{th}}$  values are comparable to those of reported benchmark OL materials like carbon-60 ( $2 \text{ J/cm}^2$ ), carbon black suspension ( $2.2 \text{ J/cm}^2$ ) [35] and better compared to  $\text{MoS}_2$  ( $11.2 \text{ J/cm}^2$ ),  $\text{WS}_2$  ( $9.3 \text{ J/cm}^2$ ) and graphene ( $15.15 \text{ J/cm}^2$ ) [36].

## 4. Conclusion

In summary, NLO coefficients (NLA, NLR,  $\text{Im } \chi^{(3)}$  and  $\text{Re } \chi^{(3)}$ ) of nickel and cobalt metal-organic complexes were estimated using Z-scan technique. Both the complexes exhibited good NLO property at these experimental conditions. Z-scan experiments reveal the negative NLR index and RSA associated with the metal-organic complexes. OL data indicates the samples exhibited good OL behaviour with lower OL threshold. This is due to strong NLA associated in the samples. Hence, investigated nickel and cobalt complexes can be potential materials in NLO applications such as optical limiting.

### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to

Table 1

Third-order nonlinear optical parameters of ligand and metal organic complexes.

Sample	$\beta_{\text{eff}}$ (cm/GW)	$\text{Im } \chi^{(3)}$ (esu) $\times 10^{-13}$	$\sigma_g$ ( $\text{cm}^2$ ) $\times 10^{-19}$	$\sigma_{\text{exc}}$ ( $\text{cm}^2$ ) $\times 10^{-18}$	$n_2$ (esu) $\times 10^{-11}$	$\text{Re } \chi^{(3)}$ (esu) $\times 10^{-11}$
CoL	16.9	2.5	8.3	2.2	−7.3	−7.6
NiL	11.7	1.7	2.3	5.3	−6.2	−6.4
L	5.1	0.7	1.6	3.2	−1.9	−1.9

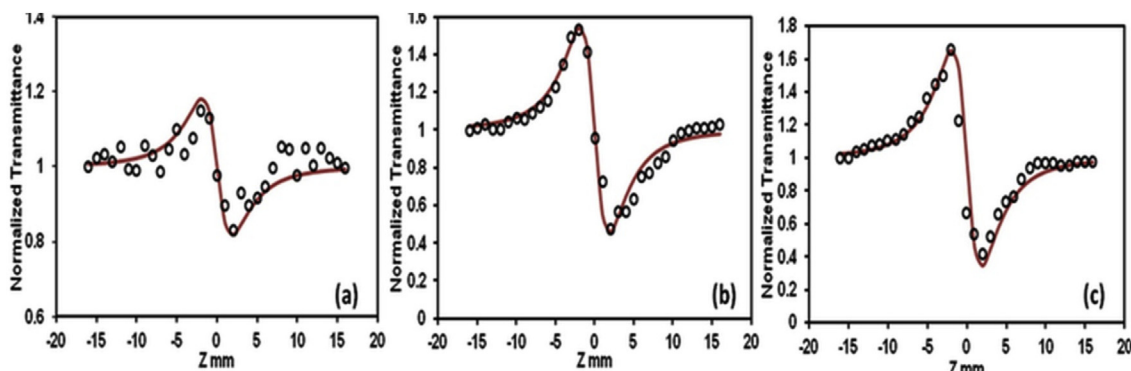


Fig. 4. Pure nonlinear refraction Z-scan curves of (a) L (b) NiL and (c) CoL. Solid line depicts theoretical fit.

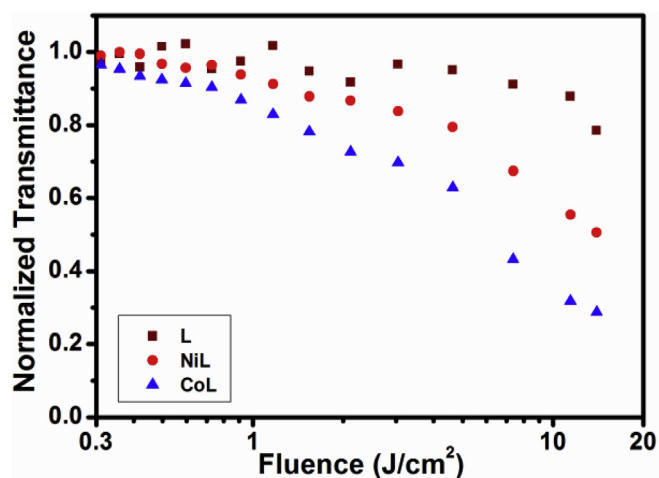


Fig. 5. Normalized optical transmittance of L, NiL and CoL as function of input fluence.

Table 2

Optical limiting onsets ( $F_{on}$ ) and optical limiting thresholds ( $F_{th}$ ) of ligand and metal-organic complexes.

Sample	$F_{on}$ ( $J/cm^2$ )	$F_{th}$ ( $J/cm^2$ )
CoL	0.3	7
NiL	1	14
L	10	–

influence the work reported in this paper.

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