

Synthesis, characterization of *N,N'*-bis(2-hydroxynaphthalidene)phenylene-1,2-diamine with M(II) (M = Ni, Zn and Fe) Schiff-base complexes and their non-linear optical studies by z-scan technique

H.C. Sampath Kumar^a, B. Ramachandra Bhat^{a,*}, B.J. Rudresha^a, R. Ravindra^a, Reji Philip^b

^a Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasanagar 575 025, India

^b Raman Research Institute, Sadashivanagar, Bangalore 560 080, India

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ABSTRACT

Schiff-base complexes of *N,N'*-bis(2-hydroxynaphthalidene)phenylene-1,2-diamine ligand with metal M (M = Ni(II), Zn(II) and Fe(II)) have been synthesized and characterized by their UV, FT-IR, NMR, elemental analysis and magnetic susceptibility measurements. Non-linear optical measurements carried out using nanosecond laser pulses at 532 nm show that these complexes can be used for optical limiting applications.

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1. Introduction

Of late, much interest has been aroused in the exploration of new materials with large third-order optical nonlinearities, not only from the perspective of understanding non-linear optical (NLO) phenomena [1,2], but also from their potential technological applications related to telecommunications, optical computing, optical storage, and optical information processing [3–5]. New non-linear optical (NLO) materials are essential for the advancement of various optoelectronic and nano technologies, e.g. optical communications, high speed electro-optical information processing, light modulation and switching, and high density data storage. In the past non-linear optical research has primarily focused on purely inorganic semiconductors, organic molecules, and conjugated polymers [6–8]. However, after the report by Green et al. [9], in which good second-harmonic generation (SHG) efficiency was revealed for a ferrocenyl derivative, attention has been paid to metal complexes also as potential NLO materials [10–12]. Thus various classes of metal complexes and organometallic compounds [13] have systematically been explored for new and optimized NLO materials. Early and more recent review articles on NLO of metal complexes indicate the breadth of active research in this field. Despite these efforts, the vast potential of organometallic and coordination complexes as NLO materials still remain largely untapped. Moreover, the design and preparation of new NLO active materials required for practical devices is still a challenging task [14–16].

In organic compounds the increase of the optical response is due not only to high level of the π conjugated charge transfer but also to the increase of the conjugation length which plays a determining role in the delocalisation of π -electrons under light excitation. As result the values of χ^3 and β increase with the number of branches of the molecule [17]. In proceeding to organometallic, one hopes to combine the advantages of organic molecules which possess design flexibility, fast response with those of inorganic salts which possess properties of mechanical strength and thermal stability. The flexibility available for organometallic is metal variation, ligand variation, coordination geometry, oxidation state, electron donating/withdrawing capabilities of the metal or ligand and stabilization of unstable organic fragments can all, in principle, be modified to optimize targeted responses [18,19]. In particular, transition metal Schiff-base complexes have attracted considerable attention recently since metal ions can play a central role in many fields such as materials research, photonics and biology [20]. Schiff bases are widely used as analytical reagents because they allow simple and inexpensive determination of several organic and inorganic substances [21]. They also form stable complexes with metals that perform an important role in biological systems [22]. Schiff bases derived from salicylaldehyde are well known as polydentate ligands [23], coordinating as deprotonated or neutral forms. There are many reports available for metal complexes with bidentate or tridentate ligands.

In the present work, the synthesis, characterization and NLO measurements of metal M (M = Ni(II), Zn(II) and Fe(II)) complexes of Schiff base derived from 1,2-diaminobenzene and 2-hydroxynaphthaldehyde are being reported.

* Corresponding author. Fax: +91 824 2474033.

E-mail address: chandpoorna@yahoo.com (B. Ramachandra Bhat).

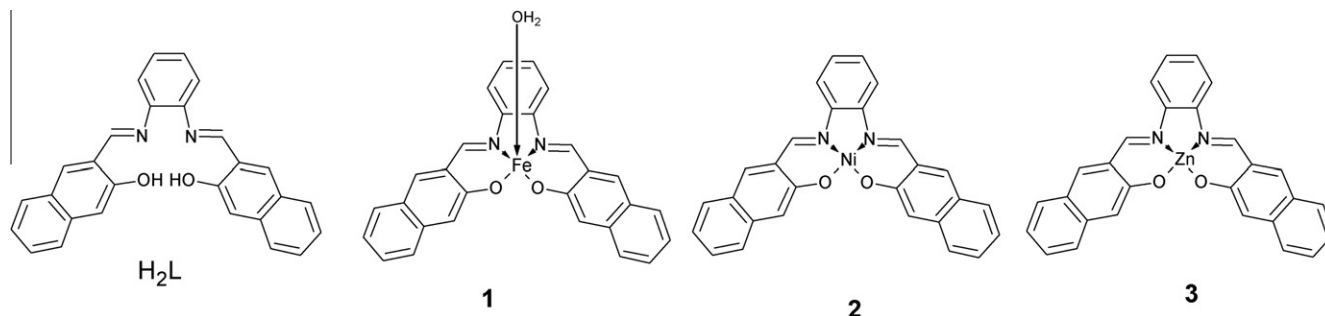


Fig. 1. Structure of the ligand (H_2L) and complexes (1–3).

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. Solvents were purified and dried according to standard procedure [24]. $NiCl_2 \cdot 6H_2O$ was purchased from Merck, $ZnCl_2$ and $FeCl_3$ was procured from NICE chemicals, and were used without further purification.

2.2. Synthesis of ligand

The Schiff base ligand N,N' -bis(2-hydroxynaphthalidene)phenylene-1,2-diamine (H_2L) was prepared in 85–95% yield by condensation between 1,2-diaminobenzene and 2-hydroxynaphthaldehyde in methanol at room temperature [25]. The structure of the ligand is given in Fig. 1. Yield: 0.53 g (86%). M.P. 231 °C. Anal. Calc. for $C_{28}H_{20}N_2O_2$ (416.47): C, 80.75; H, 4.84; N, 6.73. Found: C, 80.51; H, 4.77; N, 6.65%. IR (KBr, cm^{-1}): 3658(m), 1617(m), 1323(m), 1083(m), 750(m), 826(m), 1H NMR (400 MHz, DMSO): 9.68 (d, 2H) (OH), 8.51 (d, 2H) (–C–N–), 7.96–7.04 (m, 16H) (aromatic), UV–Vis: λ_{max} (nm) intraligand interactions: 320, 400.

2.3. General procedure for the synthesis of complexes

The complexes (1–3) were prepared by refluxing an equimolar quantity of respective metal salts ($FeCl_3$, $NiCl_2 \cdot 6H_2O$ and $ZnCl_2$) and the ligand (H_2L) in (4:1) acetone–methanol solvent mixture for 2 h. The complexes were filtered, washed with methanol followed by hexane and dried in vacuo. The structures of the complexes are given in Fig. 1.

2.3.1. Iron complex (1)

Yield: 0.56 g (78%). M.P. >330 °C. Anal. Calc. for $C_{28}H_{22}FeN_2O_4$ (488.31): C, 68.87; H, 4.13; N, 5.74. Found: C, 68.62; H, 4.05; N, 5.65%. IR (KBr, cm^{-1}): 3450(m), 1595(s), 750(m), 830(w), 554(m), 421(m). UV–Vis: λ_{max} (nm) intraligand interactions: 343, 389, d → d forbidden transition: 454.

2.3.2. Nickel complex (2)

Yield: 0.56 g (80%). M.P. >330 °C. Anal. Calc. for $C_{28}H_{20}N_2NiO_2$ (473.14): C, 71.08; H, 3.83; N, 5.92. Found: C, 70.97; H, 3.80; N, 5.86%. IR (KBr, cm^{-1}): 1607(s), 1317(m), 750(m), 830(w), 565(m), 423(m). 1H NMR (400 MHz, DMSO): 8.55 (d, 2H) (–C–N–), 7.97–7.04 (m, 16H) (aromatic), UV–Vis: λ_{max} (nm) intraligand interactions: 330, 387, d → d forbidden transition: 484.

2.3.3. Zinc complex (3)

Yield: 0.62 g (88%). M.P. >330 °C. Anal. Calc. for $C_{28}H_{20}N_2ZnO_2$ (479.86): C, 70.08; H, 3.78; N, 5.84. Found: C, 69.92; H, 3.71; N, 5.80%. IR (KBr, cm^{-1}): 1591(s), 1353(s), 755(m), 832(m), 551(m),

463(m). 1H NMR (400 MHz, DMSO): 8.54 (d, 2H) (–C–N–), 7.97–6.97 (m, 16H) (aromatic), UV–Vis: λ_{max} (nm) intraligand interactions: 332, d → d forbidden transition: 415, 463.

2.4. Physical measurements

Electronic spectra of the complexes in the 200–800 nm range were measured on a GBC UV–Vis double beam spectrophotometer in N,N -dimethylformamide solution. FT-IR spectra were recorded on a Thermo Nicolet Avatar FT-IR spectrometer as KBr powder in the frequency range 400–4000 cm^{-1} . The C, H, N and S contents were determined by Thermoflash EA1112 series elemental analyzer. 1H NMR spectra were recorded in Bruker AV 400 instrument using TMS as internal standard. Thermal analysis, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurements were recorded on SII-EXSTAR6000-TG/DTA6300 thermal analyzer with heating rate of 10 °C/min. Magneto-chemical measurement was recorded on a Sherwood Scientific instrument.

3. Results and discussion

3.1. Spectral analysis

Microanalysis data is matching with the proposed structure of the complexes. The electronic spectra of ligand and complexes (1–3) are depicted in Fig. 2. Bands in the region 250–350 nm corresponding to intraligand transition whereas the region 390–490 nm corresponds to forbidden d–d transitions. IR absorption band due

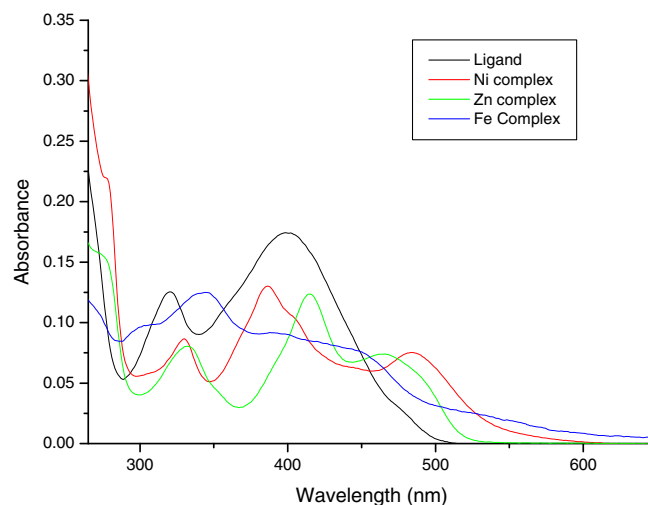


Fig. 2. UV–Vis spectrum of the complexes.

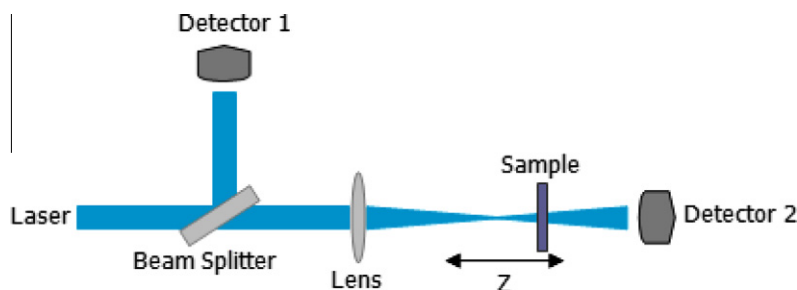


Fig. 3. Schematic of the open aperture z-scan experiment.

to $\nu(\text{C}=\text{N})$ of the free ligand appears in the region $1610\text{--}1620\text{ cm}^{-1}$. For all complexes, $\nu(\text{C}=\text{N})$ undergoes a negative shift by $5\text{--}25\text{ cm}^{-1}$ indicating the coordination of azomethine nitrogen to the metal [26,27]. The band in the region $1315\text{--}1330\text{ cm}^{-1}$ which is assigned to phenolic $\nu(\text{C}=\text{O})$ in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion [26,28,29]. The bands around 550 cm^{-1} and 470 cm^{-1} in the complexes are assigned to $\nu(\text{M}=\text{O})$ and $\nu(\text{M}=\text{N})$, respectively [30]. In Fe(II) complex, a band in the region 3450 cm^{-1} observed is assigned to $\nu(\text{O}=\text{H})$ of coordinated water, which is confirmed from the TGA and DTA analysis. These results show that only Fe(II) complex contain one coordinated water molecule [31,32]. ^1H NMR spectral data of the complexes nickel(II) and zinc(II) complex exhibits a multiplet around $6.9\text{--}7.9\text{ ppm}$ which has been assigned to the protons of phenyl groups present in Schiff base ligand. A peak observed at 8.5 ppm in the complex has been assigned to azomethine proton ($-\text{C}=\text{N}-$) [33–35]. The absence of a resonance due to phenolic hydrogen indicates the deprotonation of the Schiff base.

Magnetic susceptibility measurement shows Ni(II) and Zn(II) complexes are diamagnetic whereas Fe(II) complex is found to be paramagnetic in nature.

3.2. Non-linear optical measurements

Open-aperture z-scan measurements were performed to determine the non-linear transmission of laser light through the samples. The z-scan is a widely used technique developed by Sheik Bahae et al. [36] to measure optical nonlinearity of materials, and the open aperture z-scan gives information about the non-linear absorption coefficient. A schematic of the open aperture z-scan experiment is given in Fig. 3. Here a laser beam which is spatially Gaussian is focused using a lens and passed through the sample.

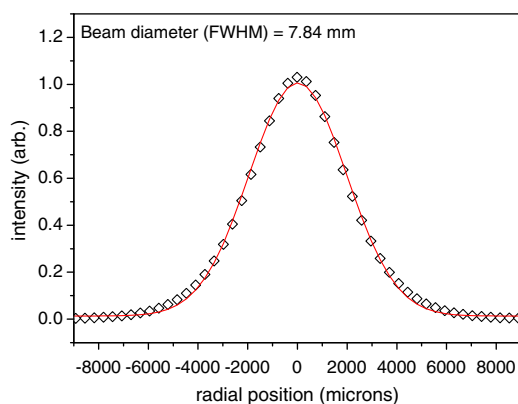


Fig. 4. Spatial profile of the Nd:YAG laser beam used for the z-scan experiment, measured using the knife-edge technique. The solid line is a Gaussian fit to the measured data.

The beam's propagation direction is taken as the z-axis, and the focal point is taken as $z = 0$. The beam will have maximum energy density at the focus, which will symmetrically reduce towards either side for the positive and negative values of z . The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of z), and measuring the corresponding light transmission. The graph plotted between the sample position z and the normalized transmittance of the sample $T(\text{norm.})$ (transmission normalized to the linear transmission of the sample) is known as the z-scan curve. For a Gaussian beam, each z position corresponds to an input laser energy density of $F(z) = 4\sqrt{\ln 2} E_{in} / \pi^{3/2} \omega(z)^2$, and intensity of $I(z) = F(z) / \tau$, where E_{in} is the input laser pulse energy, $\omega(z)$ is the beam radius, and τ is the laser pulsewidth. The curve drawn between $F(z)$ (or $I(z)$) and $T(\text{norm.})$ is known as the non-linear transmission curve. The non-linear absorption coefficient of the sample can be numerically calculated either from the z-scan curve or the non-linear transmission curve.

In our experiment, samples taken in 1 mm cuvettes were irradiated by laser pulses of 7 ns width at the wavelength of 532 nm, available from an Nd:YAG laser (Quanta Ray, Spectra Physics) provided with the second harmonic option. The laser beam is spatially Gaussian, as found from a knife-edge measurement (Fig. 4). The beam diameter (FWHM) is found to be 7.84 mm. The Rayleigh range in our experiment was 1.9 mm. The z-scan and non-linear transmission curves are shown in Figs. 5–7. As seen, the transmission is reduced at higher intensities, showing that the samples behave as optical limiters. Maximum nonlinearity was found in nickel complex (2) and minimum in iron complex (1). It is well known that optical limiters have potential applications in protecting human eyes and other light sensitive devices like cameras from accidental exposure to intense light.

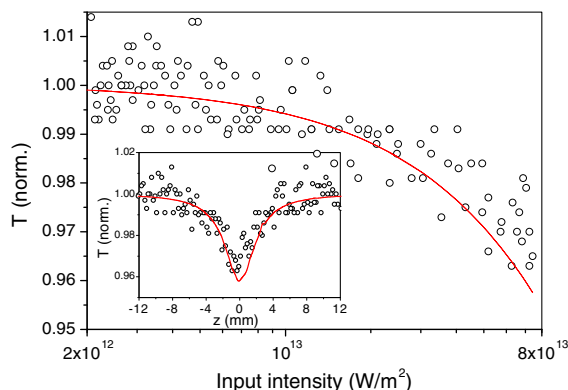


Fig. 5. Non-linear transmission curve of iron complex (1). Inset shows the open aperture z-scan curve. Linear transmission of the sample (corresponding to $T(\text{norm.}) = 1$) is 75%. Circles are data points while solid curves are numerical fits using Eq. (1).

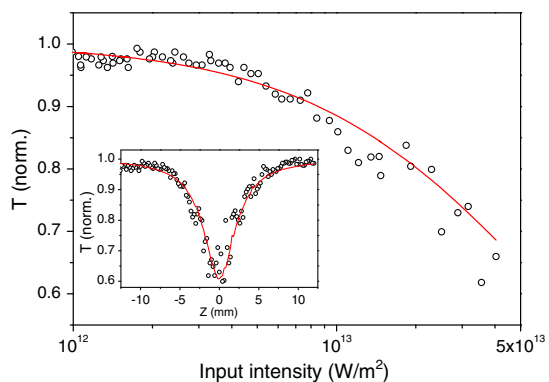


Fig. 6. Non-linear transmission curve of nickel complex (**2**). Inset shows the open aperture z-scan curve. Linear transmission of the sample (corresponding to T (norm.) = 1) is 60%. Circles are data points while solid curves are numerical fits using Eq. (1).

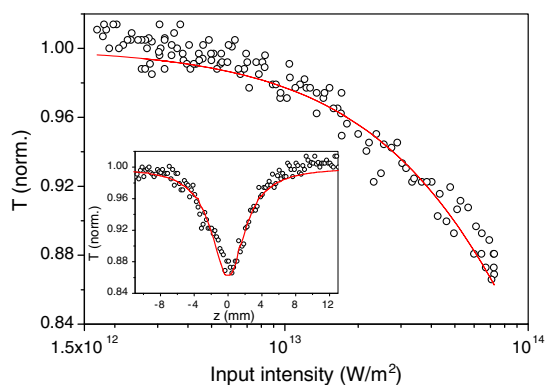


Fig. 7. Non-linear transmission curve of zinc complex (**3**). Inset shows the open aperture z-scan curve. Linear transmission of the sample (corresponding to T (norm.) = 1) is 70%. Circles are data points while solid curves are numerical fits using Eq. (1).

It was found that numerically, a two-photon absorption (TPA) type process gives the best fit to the obtained open aperture z-scan data. In the present context strong two-step excited state absorption also will happen concurrently with genuine TPA, and hence the effect is an effective TPA process. The data obtained are fitted to the non-linear transmission equation for a two-photon absorption process, given by [37]:

$$T = \left((1 - R)^2 \exp(-\alpha L) / \sqrt{\pi q_0} \right) \int_{-\infty}^{+\infty} \ln \left[\sqrt{1 + q_0 \exp(-t^2)} \right] dt \quad (1)$$

where T is the sample transmission given by T (norm.) \times linear transmission of the sample, and L and R are the length and surface reflectivity of the sample, respectively. α is the linear absorption coefficient. q_0 is given by $\beta(1 - R)I_0L_{\text{eff}}$, where β is the effective TPA coefficient, and I_0 is the on-axis peak intensity. L_{eff} is given by $1 - \exp(-\alpha l/\alpha)$. The calculated values of the effective TPA coefficient are $5 \times 10^{-11} \text{ m W}^{-1}$ for Nickel complex (**2**), $8 \times 10^{-12} \text{ m W}^{-1}$ for zinc complex (**3**), and $2 \times 10^{-12} \text{ m W}^{-1}$ for Iron complex (**1**). For comparison, under similar excitation conditions, NLO materials like Cu nanocomposite glasses had given effective TPA coefficient values of 10^{-10} – $10^{-12} \text{ m W}^{-1}$ [38], Bismuth nanorods gave $5.3 \times 10^{-11} \text{ m W}^{-1}$ [39], and CdS quantum dots gave $1.9 \times 10^{-9} \text{ m W}^{-1}$ [40], respectively. This shows that the present samples have a com-

parable optical nonlinearity, so that they can find potential applications in optical limiting devices.

It may be worthwhile here to consider whether over and above the effective TPA mechanism, any thermal effect is contributing to the observed optical limiting behavior. In general, when excited with laser pulses of nanoseconds duration, the possibility of sample heating cannot be excluded. However, this will contribute to the optical limiting action only if substantial non-linear scattering takes place in the system. We measured non-linear scattering using a photodiode attached at an angle to the beam path in front of the sample, but it did not give any appreciable signal. Another aspect of the experiment is that since we used detectors having large apertures, even if the sample shows any non-linear refraction it will not contribute to the observed optical limiting behavior. Therefore it is clear that the nonlinearity arises mostly from two-step excited state absorption in the system, which is the cause behind the effective TPA mechanism.

4. Conclusions

In this work we have synthesized and characterized the Schiff-base complexes of N,N' -bis(2-hydroxynaphthalidene)phenylene-1,2-diamine with metal M ($M = \text{Ni(II)}, \text{Zn(II)}$ and Fe(II)). Ni(II) and Zn(II) complexes are diamagnetic whereas Fe(II) complex is found to be paramagnetic in nature. On the basis of above studies and keeping in view the preferred geometries, square planar structure have been proposed for the Ni(II) and Zn(II) complexes and square pyramidal geometry for Fe(II) complex. Non-linear optical measurements of the complexes carried out at 532 nm using nanosecond laser pulses show optical nonlinearity. Among the samples, nickel complex displaying maximum optical limiting capability. Being optical limiters, these samples can have potential applications in optoelectronics and photonics.

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