



# Metal-induced efficient enhancement of nonlinear optical response in conjugated azo-based iminopyridine complexes



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## ABSTRACT

The nonlinear optical (NLO) properties of conjugated azo-based iminopyridine complexes with zinc and silver metal cations were studied. The processes of second and third harmonic generations in guest-host polymeric films were investigated and NLO parameters were extracted. Obtained second and third order NLO susceptibilities of zinc containing complex exceeds the latter of silver containing one. Using the Z-scan technique the NLO refractive index, NLO absorption coefficient, second order hyperpolarizability and NLO absorption cross section for the azo-based iminopyridine zinc (II) and silver (I) complexes were obtained and analyzed. Estimated nonlinearity/loss figure of merit of these complexes show promise for optical device applications.

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## 1. Introduction

The development of efficient organic and/or hybrid organic/inorganic NLO materials for optoelectronic applications, which are promising for high-speed information processing and telecommunications, has drawn considerable attentions over the last decades. Although various perspective materials have been demonstrated, the improvement of practical devices still requires further materials development. The optimization of molecular structural properties is essential prerequisite to the design of efficient material with high nonlinearities [1]. One of the mostly applied strategies to tailor the NLO properties of conjugated systems is to insert electron donating and/or accepting groups. Relationship between the molecule structure and its hyperpolarizabilities are of prime importance to get the nonlinearities of larger values. Establishing predictive structure-property relationship could help to get the materials with sufficiently large NLO parameters which are desired in telecommunication industry [2] and holographic data storage [3].

Azobenzenes that are functionalized with an electron-donor and/or electron-acceptor groups have attractive optical and

nonlinear optical properties [4–7]. Due to photoinduced trans-cis isomerization, azobenzenes are interesting for a variety of novel and useful applications: photopoling, optical storage, grating formation [8–10]. In our investigation for efficient materials for NLO applications, we have been recently interested in the use of electroactive and photoactive ligands and the effect of the metal complexation on the resulting NLO performances. We have thus demonstrated the positive effect of the metal cation complexation of tetrathiafulvalene (TTF) based ligands, in which the NLO absorption have been switched from reverse saturable absorption (RSA) in ligand to saturable absorption (SA) in iron (II) and ruthenium (II) metal complexes [11]. For the iminopyridine based TTF ligand we have shown an important enhancement of the NLO response upon zinc (II) complexation [12]. In the case of photoactive ligands we have prepared four azo-based iminopyridine ligands and described their corresponding NLO properties [13]. In addition for the dimethylaminosubstituted ligand we have clearly shown a dramatic enhancement of the NLO response upon zinc (II) complexation [14]. Motivated by the aforementioned results we describe herein an approach to tune second and third order NLO properties of nitrosubstituted azo-based iminopyridine ligands by coordination of zinc (II) and silver (I) metal cations. This complexation has a beneficial influence on the second order hyperpolarizability compared to pure ligand and this research work can be seen as the continuation of our NLO study of azo-based iminopyridine zinc (II) complex. In addition, a focus is made in order to study the effect of the electron accepting substituent (nitro

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group) as well as the effect of the metal cation (zinc (II) or silver (I)) used for ligand complexation and to establish relationship between the molecular structure and its NLO response.

## 2. Experimental details

In the framework of our study two azo-based iminopyridine metal complexes were synthesized with  $\text{ZnCl}_2$  and  $\text{AgNO}_3$  metal cations. Their chemical structures as well as ligand structure are shown in Fig. 1. Recently we have reported on the preparation of series of azobenzene-based iminopyridine ligands as well as silver metal complexes of the monosubstituted ones with dimethylamino group for **L1** and nitro group for **L2** [15]. As a continuation of this work, we report herein the synthesis of a new complex of ligand **L2** using zinc chloride as metal cation precursor. Thus, (E)-4-((E)-(4-nitrophenyl)diazenyl)-N-(pyridin-2-ylmethylene)aniline zinc chloride (**L2ZnCl<sub>2</sub>**) complex was prepared by following the same procedure as used for the **L2AgNO<sub>3</sub>** complex. In a test tube, a solution of ligand **L2** (10 mg 0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was mixed with a solution of  $\text{ZnCl}_2$  (3 mg 0.02 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) and ultrasonicated for 5 min. On top of the resulting solution a layer of diethylether was added, which lead to the formation of single crystals of complex **L2ZnCl<sub>2</sub>** after three days. Yield: (75%). MALDI-TOF MS for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}_2\text{ZnCl}$  calcd:  $m/z = 432.16$  Da found:  $m/z = 430.2$ . HR-MS (M): for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}_2\text{ZnCl}$ : 430.0049. Found 430.0060, Selected IR bands ( $\text{cm}^{-1}$ ):  $\nu = 1581, 1533, 1336, 1318, 841, 546$ .  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ )  $\delta/\text{ppm}$ : 193.7, 156.2, 154.4, 150.2, 146.7, 143, 137.7, 128.4, 126.5, 124.9, 122.4, 121.8, 113.6.

For the films preparation the solution of PMMA (Sigma-Aldrich, Mw = 350000 g/mol) dissolved in 1,1,2-trichloroethane at concentration of 50 g/L was prepared as a host system. The concentration of the compositions was 40  $\mu\text{mol}$  towards 1 g of PMMA. The glass plates were washed in distilled water using ultrasonic bath, acetone, and ethanol and then dried. The solutions were deposited on glass substrates using the spin-coater (SCS G3) at 1000 rpm. Obtained guest-host polymer films were kept at room temperature during two days in order to eliminate any remaining of solvent. The

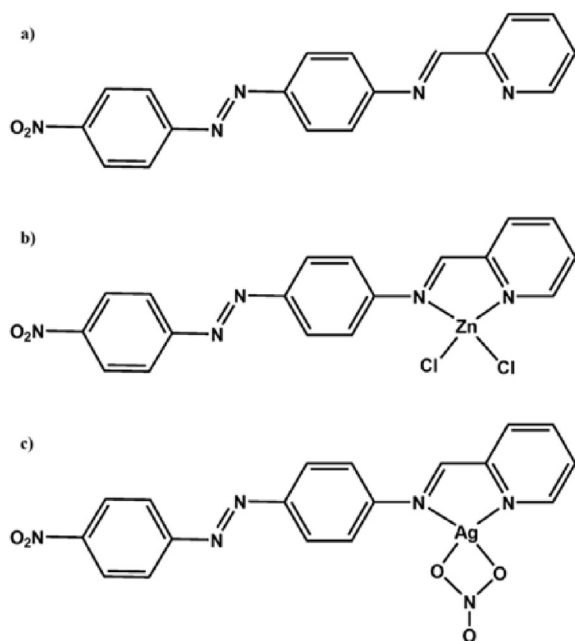


Fig. 1. Structures of the iminopyridine azo-based ligand and complexes: a) **L2**; b) **L2ZnCl<sub>2</sub>**; c) **L2AgNO<sub>3</sub>**.

thickness of deposited films was estimated with the profilometer (Dektak 6M, Veeco) to be about 700 nm. Absorption spectra of the films and solutions were measured by means of Lambda 950 UV/Vis/NIR spectrophotometer (PerkinElmer) in the range 200–800 nm. The pure PMMA film on glass plate and the cuvette filled only with solvent were used on the way of reference beam in spectrometer for the measurements of absorption spectra of our compounds in films and solutions, respectively.

Second and third harmonic generation (SHG and THG) measurements were carried out by means of the rotational Maker fringe technique in the transmission scheme for the *s*- and *p*-polarized fundamental laser beam. A *y*-cut crystalline quartz plate has been used as a reference material for SHG measurements and fused silica plate for THG measurements. As a fundamental beam, we used the output beam of a mode-locked Nd:YAG/YVO<sub>4</sub> laser (EKSPLA) generating at  $\lambda = 1064$  nm with 30 ps pulse duration and 10 Hz repetition rate. The input laser pulses energy was controlled by laser power/energy meter (LabMax TOP, COHERENT) to be 90  $\mu\text{J}$  for SHG and 150  $\mu\text{J}$  for THG measurements. Nonlinear refraction and nonlinear absorption were investigated by means of Z-scan technique [16,17] using the frequency doubled exit of a 30 ps mode-locked Nd:YAG/YVO<sub>4</sub> laser (EKSPLA) with a repetition rate of 10 Hz at 532 nm. Two different series of measurements were simultaneously carried out giving access to different information: the “open aperture” (OA) Z-scan, where the totality of the transmitted light is collected, and the “closed aperture” (CA) Z-scan where a small part of the transmitted light is collected after passing through a small circular diaphragm. The detailed setups description which was used in SHG, THG and Z-scan measurements can be found elsewhere [18].

## 3. Results and discussion

The absorption spectra of **L2ZnCl<sub>2</sub>** and **L2AgNO<sub>3</sub>** complexes embedded in PMMA films at the concentration 40  $\mu\text{mol/g}$  are given in Fig. 2. Due to the small thickness (about 700 nm) and low molecules concentration the absorbance of the films is quite low, less than 0.1. The spectra of both films exhibit wide absorption band with maximum at 435 nm. This absorption band corresponds to a ligand centred (LC,  $\pi-\pi^*$  and  $n-\pi^*$ ) transitions [15]. At the wavelengths more than 600 nm the samples show high optical transparency.

The measurements of SHG in **L2ZnCl<sub>2</sub>** and **L2AgNO<sub>3</sub>** guest-host polymeric films were performed by rotational Maker fringe

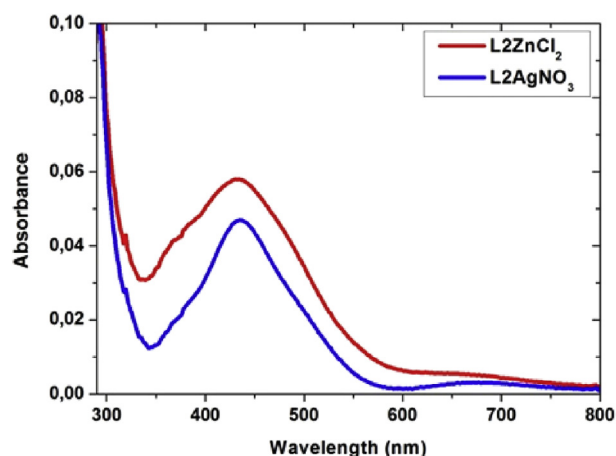


Fig. 2. UV–vis absorption spectra of the **L2ZnCl<sub>2</sub>** and **L2AgNO<sub>3</sub>** complexes embedded in PMMA films.

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