

# Metal Oxide – Schiff Base Nanofibers as Novel Optical Sensors for Different Metal Ion Detection in Aquatic Environment

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## Summary:

Schiff base derivatives of 2,4-dihydroxybenzaldehyde and o-phenylenediamine are potential candidate for fluorescent chemosensors because their metal oxide – Schiff base composites can exhibit fluorescence properties and can be sensitive to the metal ions in the aquatic environment. The spectroscopic properties of the ligand crystalized in MeOH and ethyl acetate were investigated by <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H<sup>13</sup>C NMR, IR, UV-Vis, and fluorescent properties, along with sensitivity tests of its zinc(II) and copper(II) complexes. The morphology and composition of new materials were determined using SEM/EDS and AFM microscopy. The emission of new materials was noted.

**Keywords:** Schiff base, photoluminescence, chemosensors, ZnO composites, ESIPT.

## Introduction

Many mental illnesses, including Alzheimer's disease, Parkinson's disease, epilepsy, etc., have been caused by the imbalance of Zinc ions[1]. Zinc ion causes severe environmental pollution due to their widespread use in electroplating [2]. Thus, a highly selective detection probe for zinc ions and other transition metal ions is needed. Schiff bases are a potential candidate due to their fluorescence properties, which can be used to detect metal ions[3-4]. Optical chemosensors caused a revolution in the sensing field due to their high specificity, sensitivity, and fast detection features. Optical sensors, based on absorbance and photoluminescence for metal ions detection, are simple, low cost, and can be integrated into one system. Optical SB sensors have shown good sensitivity to metal ions, such as Zn<sup>2+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, etc. The change of optical properties of the SB after interaction with metal ions and the sensing mechanism is explained by the isomerization of chemical bonds (C=N, -CH=N, etc.) and donor-acceptor photo-induced electron transfer[9].

The new ligand **L1**, sensitive to various ions, was obtained. It also showed an excited-state intramolecular proton transfer (ESIPT) mechanism, which provides an attractive material platform for fabricating optoelectronic devices. **L1** was also

coupled with ZnO tetrapods to enhance its sensitive properties. The ionosensor was also obtained from Zinc oxide (nf/tp) and Schiff bases, which were selective towards various metal ions.

## Method

2,4-dihydroxybenzaldehyde (98%) and o-phenylenediamine (analytical grade) were purchased from Sigma Aldrich and used without further purification. **L1.MeOH** and **L1.EA** ligand was obtained and was analyzed for its sensor properties. (Fig.1)

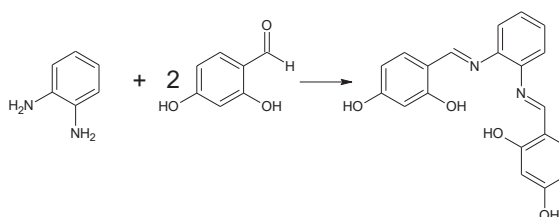


Fig. 1. Scheme of synthesis of ligand **L1**.

## Results

Sensor tests of the ligand have been performed in ethanol. The sensitivity of the ligands was investigated by adding the metal ion probes to the ligand ethanol solution. Initially, the equilibrium of the intensity was achieved, and the probe was

added. Full PL spectra were measured before the injection and after setting the equilibrium between adsorption and desorption. The interactions of both the ligands **L1.MeOH** and **L1.EA** with various metal ions were studied. It was found that **L1.MeOH** was sensitive towards  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Co^{2+}$  and  $Mn^{2+}$  ions, whereas **L1.EA** towards  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Al^{3+}$ .

The interaction between metal ions and the ligand in ethanol led to decreased photoluminescence intensity. The sensor's response time has been studied by measuring photoluminescence kinetics at fixed wavelengths (380 and 432 nm).

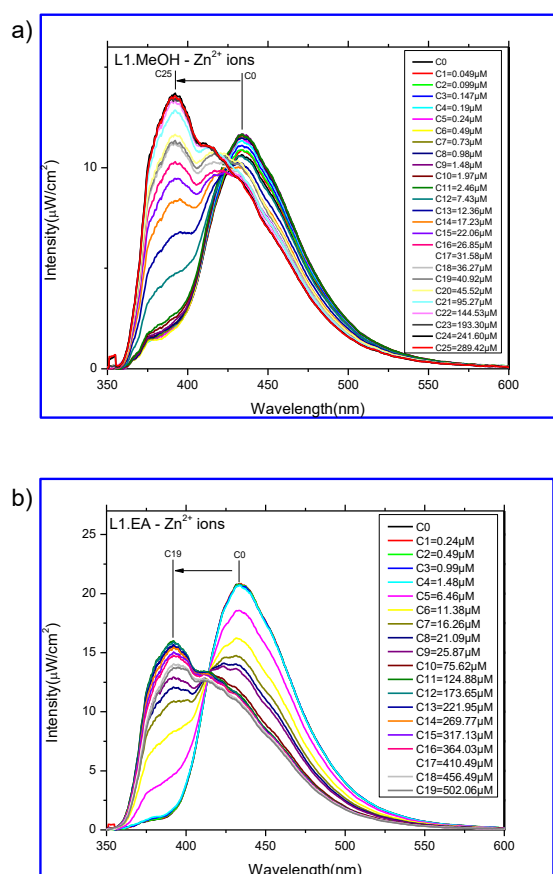


Fig.2. The photoluminescence spectra of **L1.EA**. Each spectrum corresponds to the additional concentration of  $Zn^{2+}$  ions, (a) for ligand **L1.MeOH** (b) for ligand **L1.EA**

It was found that the sensor response to metal ions increased with the ion concentration (Fig.2). The changes in emission intensity upon the addition of metal ions can result from the photoinduced charge transfer mechanism (PCT). The intramolecular charge transfer (ICT) from the donor to the acceptor was observed upon excitation.

The ligand crystallized in two different forms, **L1.MeOH** has methanol and **L1.EA** has ethyl acetate in the crystal structure.

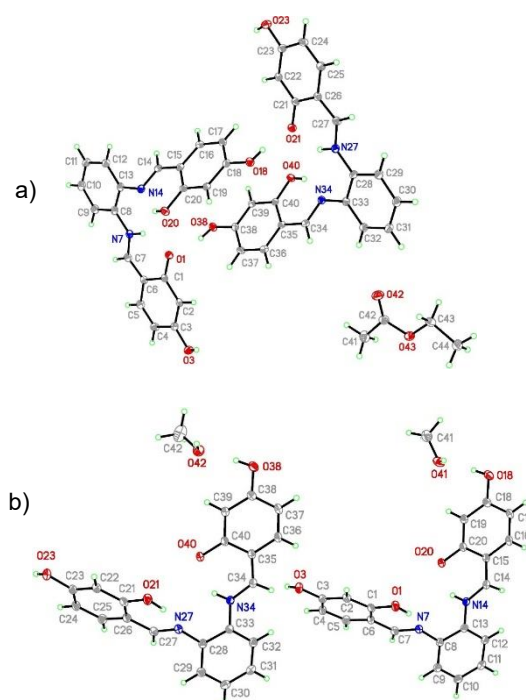


Fig.3. ORTEP of a) **L1.EA** and b) **L1.MeOH** with two crystallographically independent Schiff bases in the asymmetric unit and molecule of solvent.

## References

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