

## Photoluminescence Properties of Azo-Containing Schiff Bases Metal Complexes

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**ABSTRACT:**The Schiff base ligand containing -N=N- group, 4-((E)-(4-bromophenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol (L<sup>1</sup>H) (Fig. 1), and its Co<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup> and Fe<sup>III</sup> complexes have been prepared and characterized in previous study. According to analytical, UV-visible and IR data, the metal complexes are formed by coordination of the N, O atoms of the ligands and metal:ligand ratio was found to 1:2 for all the complexes. In this study, photoluminescence properties of L<sup>1</sup>H and its metal complexes were investigated.

**Keywords:** Schiff Base complexes; azo compounds, photoluminescence

### Azo Grubu İçeren Schiff Baz Metal Komplekslerinin Fotolüminesans Özellikleri

**ÖZET:** Daha önceki çalışmada 4-((E)-(4-bromophenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol (L<sup>1</sup>H) ligandı ve bu ligamndın Co<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup> ve Fe<sup>III</sup> komplekslerinin sentezi ve karakterizasyonu yapılmış olup komplekslerin metal:ligand oranı 1:2 olacak şekilde oluştuğu gözlenmiştir. Bu çalışmada sentezi ve karakterizasyonu yapılan ligand ve komplekslerinin fotolüminesans özellikleri incelenmiştir.

**Anahtar Kelimeler:** Schiff bazı kopmleksleri, azo bileşikleri, fotolüminesans

## 1. INTRODUCTION

Among the various ligands, Schiff base ligands have significant importance because Schiff base ligands are potentially capable of forming stable complexes with metal ions [1]. By attaching donor atoms of Schiff bases, they can coordinate various metals and stabilize them in different oxidation states; such complexes are used as catalysts in many important processes [2, 3]. The N=N bonds in azo compounds are good electron/hydrogen acceptors [4]. The molecule bears the azoimine (-N=N-C=N-) functional group, and is an efficient p-acid system for stabilization of low oxidation state metal ions [5]. Synthesis of metal complexes with luminescence properties has attracted much attention in recent years due to their importance in designing sensors and optical materials [6]. Azo compounds and their complexes are of interest for application in detection of ions in solution. Although, a few azo ligands have been utilised as chemosensors for anions and cations [7-15] but there are scarcity of luminescent metal complexes incorporating azo ligands which can act as efficient sensors for anions. Metal complexes of Schiff bases have been extensively studied at scientific applications as catalysts due to their attractive chemical and physical properties.

In our previous study, the synthesis and characterization of L1H and its complexes were done [16]. Ligand and complex structures were confirmed by, elemental analysis, FTIR, 1H-, 13C- NMR, and UV/Vis spectroscopy, mass spectrometry, thermal analysis, molar conductivity. Single-crystal X-ray analysis were performed for ligand (L<sup>1</sup>H) (Figure 3) and its Zn complex (Zn(L<sup>1</sup>)<sub>2</sub>) (Figure 4). The analytical data shows that the ratio of metal to ligand in the mononuclear Schiff Base complexes is 1:2.

Due to the importance of the various properties of Schiff base metal complexes, we herein reported the luminescence properties of L<sup>1</sup>H and its metal complexes.

## 2. EXPERIMENTAL

### 2.1. Materials and measurements

The single-photon fluorescence spectra of the ligand (H<sup>1</sup>L) and their metal complexes (Cu(II), Co(II), Ni(II), Zn(II) and Fe(III)) were collected on a Perkin Elmer LS55 luminescence spectrometer. All the samples were prepared in spectrophotometric grade solvents and analyzed in a 1 cm optical path quartz cuvette. The solution concentrations of the ligand and complexes in DMF solvents were 4.8 x 10<sup>-5</sup> mol L<sup>-1</sup>.

The different concentrations studies were done in the  $1 \times 10^{-3}$ - $1 \times 10^{-7}$  M range and in the DMF solution.

## 2.2. Synthesis of (E)-5-((4-bromophenyl)diazenyl)-2-hydroxybenzaldehyde

(E)-5-((4-bromophenyl)diazenyl)-2-hydroxybenzaldehyde was prepared according to the literature method [17].

## 2.3. Synthesis of 4-((E)-(4-bromophenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol (L<sup>1</sup>H)

4-((E)-(4-bromophenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol (L<sup>1</sup>H) (Figure 1) was synthesized as follow; 10 mmol (3.05 g) of (E)-5-((4-bromophenyl)diazenyl)-2-hydroxybenzaldehyde and 10 mmol (0.93 g) of aniline were condensed by refluxing in 70 cm<sup>3</sup> of absolute ethanol for 3 h. The solution was left at room temperature. 4-((E)-(4-bromophenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol was obtained as orange micro crystals; the micro crystals were filtered off, washed with 10 cm<sup>3</sup> of absolute ethanol and then recrystallized from DMF.

## 2.4. General procedure for the synthesis of metal complexes

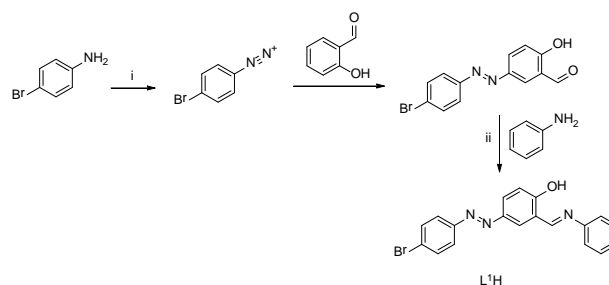
L<sup>1</sup>H (20 mmol) dissolved in 40 cm<sup>3</sup> absolute EtOH was mixed with 10 mmol Cu(Ac)<sub>2</sub>.H<sub>2</sub>O or Co(Ac)<sub>2</sub>.4H<sub>2</sub>O in 20 cm<sup>3</sup> EtOH. The stirred mixture was refluxed for 24 h, then evaporated to 15–20 cm<sup>3</sup> in vacuum and left to cool to room temperature. The compounds were precipitated after adding 5 cm<sup>3</sup> EtOH. The products were filtered in vacuum, washed with a small amount of MeOH and water. Zn(L<sup>1</sup>)<sub>2</sub> recrystallized from DMF. The products are soluble in solvents such as CHCl<sub>3</sub>, DMF and DMSO.

## 3. Result and Discussion

### 3.1. Synthesis of the compounds

The Schiff base ligand, L<sup>1</sup>H was prepared by the condensation of (E)-5-((4-bromophenyl)diazenyl)-2-hydroxybenzaldehyde with aniline, (1:1 molar ratio) in EtOH as shown in Fig. 1. The level of the purity of the ligand was checked by T.L.C. on silica gel-coated

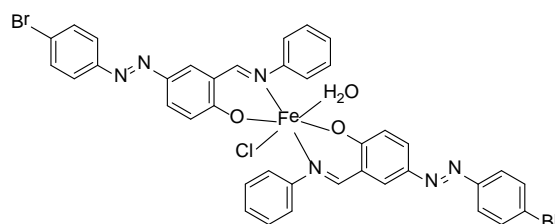
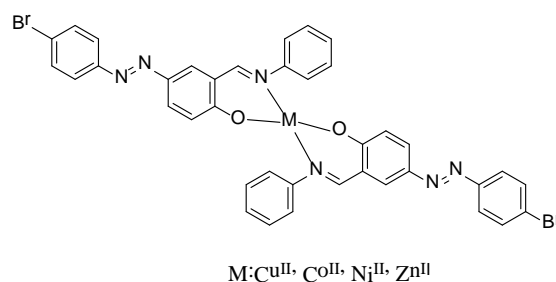
plates. CoII, CuII, NiII, ZnII and FeIII complexes of L<sup>1</sup>H were prepared.



i. HCl/NaNO<sub>2</sub>, salicylaldehyde, 0–5 °C and (ii) Ethanol, 3 h, reflux.

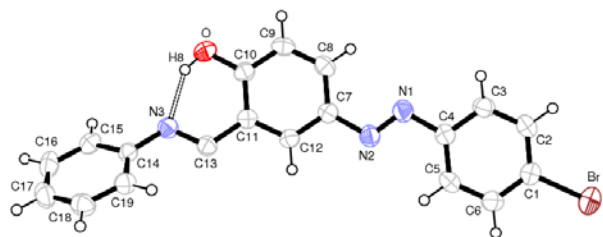
**Figure 1.** General synthesis of azo-containing ligand.

The ligand is stable at room temperature and soluble in common organic solvents such as EtOH, MeOH, DMF and CH<sub>2</sub>Cl<sub>2</sub>. The complexes are also stable at room temperature. The complexes have oxygen and nitrogen atoms as  $\pi$  donors and the metal ions allow  $\pi$  electronic delocalization as shown in Figure 2.



**Figure 2.** Proposed structures of metal complexes

The structures of the complexes were further characterized by FTIR, UV-visible spectra and elemental analyses. The experimental elemental analyses results of the complexes are in good harmony with the theoretical values. The data show the complexation ratio of formulae [M(L)<sub>2</sub>] is 1:2 [Metal : Ligand]. Single crystals of L<sup>1</sup>H which is shown in Figure 3 and was grown from DMF solutions by slow evaporation.



**Figure 3.** The molecular structure of L1H ligand, with atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. Dashed lines indicate the intramolecular hydrogen bond.

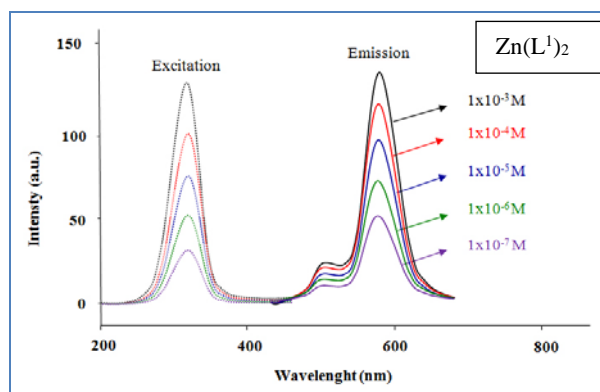
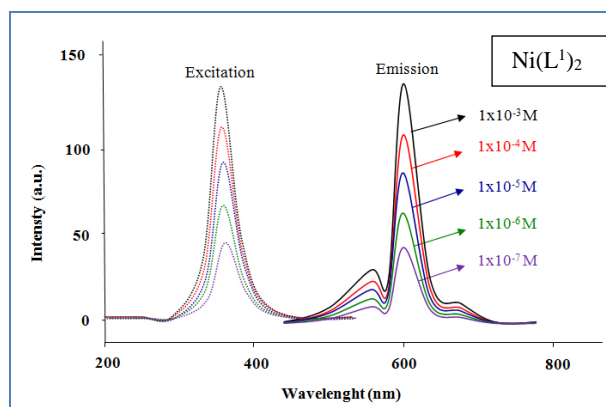
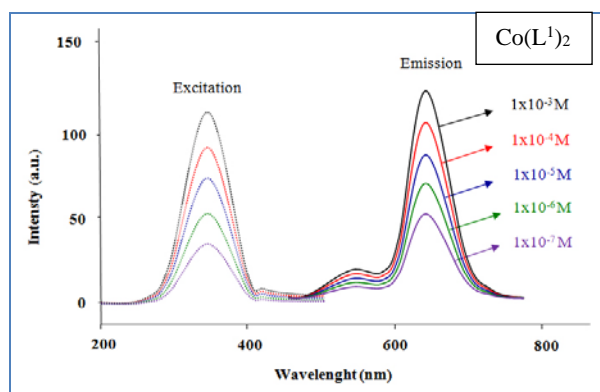
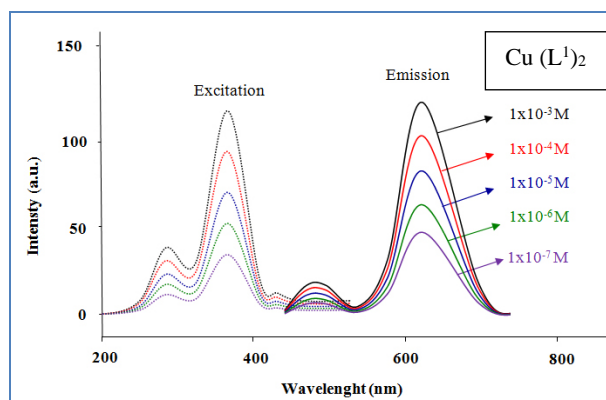
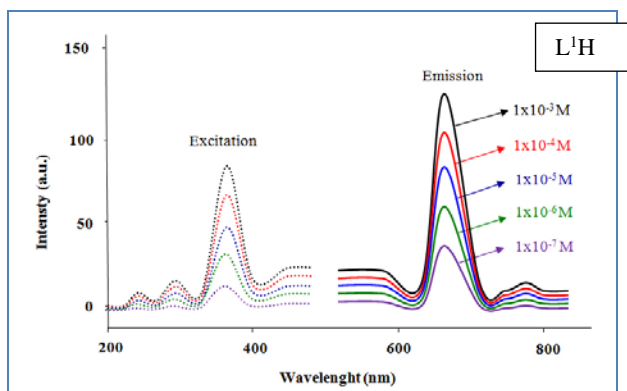
Also single crystals of Zn complex which is shown in Figure 4 and was grown from DMF solutions by slow evaporation too.

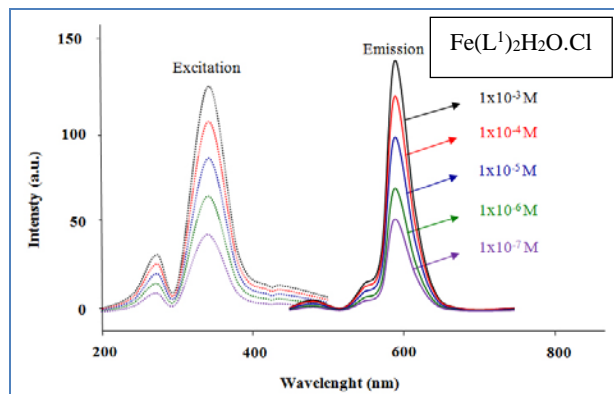


**Figure 4.** The molecular structure of complex  $(Zn(L^1)_2)$ , with atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

### 3.2. The effect of different solvent on the photoluminescence properties of the Schiff base ligands

The photoluminescence properties of the ligand ( $L^1H$ ) and their metal complexes ( $Cu(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Zn(II)$  and  $Fe(III)$ ) were studied in DMF solvent using  $1 \times 10^{-3}$ - $1 \times 10^{-7}$  solutions and obtained data are given in Table 1. At room temperature, the ligand and metal complexes exhibit similar emission spectra in the UV-vis region. The emission and excitation spectra of the ligand and metal complexes in different concentrations are shown in Figure 5.





**Figure 5.** Photochemical spectra of L1H and its metal complexes in different concentrations.

The spectra of the ligand show one emission band in the 680-684 nm range shorter wavelength (SW)

region in  $1 \times 10^{-3}$  M concentration and the other in the 680-684 nm range longer wavelength (LW) region. The photoluminescence emission peaks of the ligand (L1H) apparently produce red shift with the introduction of the accepting and donating electron groups such as  $-\text{OH}$  and Br. As shown also from Table 1, the introduction of the electron donating groups by mesomeric and inductive effects causes the fluorescence characteristic emission peaks of the ligand to red-shift in the range of 5 nm. The reason is that the electron density of the OH-group is increased with the unpaired electron pair effect. The ligand with hydroxyl and brom substituents possesses  $p \rightarrow \pi$  conjugation that can increase their photoluminescence emission intensity [18].

The excitation spectra of the ligand and their metal complexes was investigated in DMF and different concentrations ( $1 \times 10^{-3}$ - $1 \times 10^{-7}$ ) obtained data are given in Table 1.

**Table 1.** UV-visabsorption, emission and excitation spectral data of ligand and their metal complexes.

	Concentration(M)	$(\lambda_{\text{max}})$				$\lambda$
		Excitation	Intensity	Emission	Intensity	
L <sup>1</sup> H	$1 \times 10^{-3}$	375	21	680	39	224, 277, 335, 390
	$1 \times 10^{-4}$	376	38	681	60	
	$1 \times 10^{-5}$	377	48	682	75	
	$1 \times 10^{-6}$	378	65	683	110	
	$1 \times 10^{-7}$	379	86	684	124	
Cu (L <sup>1</sup> ) <sub>2</sub>	$1 \times 10^{-3}$	382	36	610	42	236, 275, 335, 366, 425, 642
	$1 \times 10^{-4}$	383	50	612	64	
	$1 \times 10^{-5}$	384	67	613	79	
	$1 \times 10^{-6}$	385	92	614	103	
	$1 \times 10^{-7}$	386	119	615	121	
Co(L <sup>1</sup> ) <sub>2</sub>	$1 \times 10^{-3}$	375	30	625	50	237, 279, 348, 366, 458, 552
	$1 \times 10^{-4}$	376	50	626	65	
	$1 \times 10^{-5}$	377	75	627	75	
	$1 \times 10^{-6}$	378	90	628	105	
	$1 \times 10^{-7}$	379	120	629	120	
Ni(L <sup>1</sup> ) <sub>2</sub>	$1 \times 10^{-3}$	380	40	602	45	283, 375, 490, 539
	$1 \times 10^{-4}$	381	65	603	65	
	$1 \times 10^{-5}$	382	85	604	80	
	$1 \times 10^{-6}$	383	120	605	120	
	$1 \times 10^{-7}$	384	142	606	143	
Zn(L <sup>1</sup> ) <sub>2</sub>	$1 \times 10^{-3}$	319	25	595	50	283, 333, 399, 457
	$1 \times 10^{-4}$	320	50	596	75	
	$1 \times 10^{-5}$	321	75	597	100	
	$1 \times 10^{-6}$	322	100	598	115	
	$1 \times 10^{-7}$	323	125	599	130	
Fe(L <sup>1</sup> ) <sub>2</sub> H <sub>2</sub> O.Cl	$1 \times 10^{-3}$	373	40	598	46	270, 330, 350, 375, 610
	$1 \times 10^{-4}$	374	60	599	62	
	$1 \times 10^{-5}$	375	80	600	98	
	$1 \times 10^{-6}$	376	110	601	132	
	$1 \times 10^{-7}$	377	125	602	145	

The spectra of the ligand are given in Figure 5. Similar properties were shown also for excitation peaks of the metal complexes. In the  $1.0 \times 10^{-3}$  M concentration, the ligands have highest excitation peaks in the 319-386 nm range. In the  $1.0 \times 10^{-7}$  M concentration, the excitation peaks of the ligands have both lowest intensity and also shift to the lower regions (319 nm).

#### 4. Conclusions

Photoluminescence properties of the schiff base ligand containing -N=N- group, 4-((E)-(4-bromophenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol (L<sup>1</sup>H) and its Co<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup> and Fe<sup>III</sup> complexes prepared studied.

According to the analytical and IR data, the metal complexes are formed by the coordination of N, O atoms of the ligands.

The photoluminescence studies showed that, the ligand with hydroxyl and brom substituents possesses p→π conjugation that can increase their photoluminescence emission intensity.

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