



A Fluorescent Chemosensor Based on Schiff Base for the Determination of Zn^{2+} , Cd^{2+} and Hg^{2+}

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Abstract

Metal complexes were obtained by the reaction of zinc, cadmium and mercury(II) salts with Schiff base HL (N(salicylidene)benzylamine). HL was synthesized by the condensation reaction of benzylamine and 2-hydroxybenzaldehyde. The fluorescence properties of the Schiff base and its metal complexes were studied in ethanol-water solutions. HL was examined for its utility as a fluorescent chemosensor for the determination of Zn^{2+} , Cd^{2+} and Hg^{2+} in aqueous samples. The HL chemosensor was found to be sensitive to Zn^{2+} , Cd^{2+} and Hg^{2+} than some metal ions and its complexes emitted strong fluorescence at 452 nm for Zn^{2+} at 474 nm for Cd^{2+} and at 491 nm for Hg^{2+} , respectively. It was determined that HL forms complexes with a ratio of 2:1 for Zn^{2+} and Hg^{2+} and with a ratio of 1:1 for Cd^{2+} by Job plots. For the detection of Zn^{2+} , Cd^{2+} and Hg^{2+} in aqueous samples, pH, solvent type and ligand concentration were optimized for an analytical method based on HL chemosensor. HL gave a wide range of linearity with Zn^{2+} , Hg^{2+} and Cd^{2+} , the limit of detection was found to be 2.7×10^{-7} M, 7.5×10^{-7} M and 6.0×10^{-7} M, respectively.

Keywords Schiff base · Transition metal complexes · Fluorescent sensor · Chemosensor · Zn(II) · Cd(II) · Hg(II)

Introduction

In recent years, transition metal complexes produced from Schiff base ligands have a wide field of study because of their importance in coordination chemistry, especially as analytical, biochemical and antimicrobial reagents [1–6]. Schiff bases are compounds with azomethine ($-\text{CH}=\text{N}$) groups and their complexes obtained with different transition metals often exhibit extraordinary structural properties [7–10]. Many of the Schiff base ligands and metal complexes are used as a model for metal bioactive site modeling, metalloenzyme reaction centers, nonlinear optical materials, homogeneous or heterogeneous catalysts for many reactions and luminescent materials [3, 7, 11–16].

The development of luminescent sensors is related to supramolecular chemistry [17, 18]. Fluorescent sensors have become an important research topic due to their

applications in medical and environmental research fields, their practical use, high sensitivity and accuracy, different biological functions of targeted metal ions [12, 19–32]. Hence, many selective fluorescent chemosensors have been developed for detecting transition metals [33–49]. Zinc, mercury and cadmium draw attention due to their biological benefits or harm. However, selective determination of zinc, cadmium and mercury ions is difficult due to the fact that they have a closed shell d^{10} electron configuration [50–54].

Zinc exists naturally about 0.0075% in the Earth's crust, making it one of the most abundant elements [25–27, 38, 41, 43–45, 53, 55]. Zinc is one of the indispensable elements for the metabolism of all living organisms due to its diverse roles in many biological, physiological and pathological processes [24, 39, 56–58]. Infertility, acrodermatitis, neuropsychiatric disorders, breast and prostate cancer, digestive disorders and sluggish immune system are clinically caused by zinc deficiency [59].

Mercury is one of the most dangerous pollutants that can be found in the aquatic environment [60–62]. Mercury is toxic to human health, especially threatening the development of fetuses and infants. Different forms of mercury (elemental, inorganic and organic) have a

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different level of toxic effects on cardiovascular diseases, infertility, kidney damage and cancer. Exposure to mercury occurs in different ways: inhalation of elemental mercury vapors released in industrial processes, ingestion of fish and shellfish that contain methylmercury, misuse and excessive use of mercury-containing products such as skin lighteners, fungicides, antiseptics [60, 63, 64].

Among the various transition metals, cadmium requires special attention due to its excessive toxicity in nature [17, 33, 35, 61]. The United States Environmental Protection Agency (EPA) has determined that cadmium is a probable human carcinogen. Due to anthropogenic activities, its concentration in nature gradually increases over time and once absorbed by a human, cadmium accumulates in the human body throughout life [38, 44].

In this study, an ON type Schiff base ligand (E)-2-((benzylimino)methyl)phenol has been synthesized and it was investigated whether it can be used as a fluorescence chemosensor in the determination of Zn^{2+} , Cd^{2+} and Hg^{2+} in aqueous samples. Although studies related to the synthesis of (E)-2-((benzylimino)methyl)phenol have been found in the literature, the investigation of the fluorescent properties of metal complexes of this Schiff base has been the subject of the study. Parameters affecting the fluorescent properties of the prepared metal complexes were examined and the most appropriate values were determined. The results obtained in the study show that the (E)-2-((benzylimino)methyl)phenol can be used as a selective chemosensor for the Zn^{2+} , Cd^{2+} and Hg^{2+} in aqueous solution.

Materials and Methods

Reagents and Instruments

Ethanol, methanol and acetone were purchased from Sigma-Aldrich, N,N-dimethylformamide was purchased from Riedel-de Haen and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , CdCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were purchased from Merck. All chemicals and solvents were used without further purification.

Electron ionization mass spectra (EI-MS) were obtained using the direct inlet (DI) unit of the Shimadzu QP2010 Plus gas chromatography-mass spectrometer (Shimadzu, Japan). Ion source and interface temperature were set at 200 °C. Fluorescence spectra measurements were carried out using a PerkinElmer LS50B luminescence spectrometer (PerkinElmer, USA). Excitation slit and emission slit widths were set as 10 nm and 5 nm, respectively. GBC Avanta flame atomic absorption spectrometer (AAS) equipped with acetylene-air (2 L/min:10 L/min) was used for the analysis (GBC Scientific

Equipment, Australia). pH measurements were carried out using Mettler Toledo pH-meter equipped with a combined pH electrode.

Synthesis of Chemosensor

HL was prepared by the 1:1 condensation of salicylaldehyde with benzylamine (Fig. 1). To a stirred solution of salicylaldehyde (2.44 g, 0.02 mole) in 50.0 mL of hot ethanol, benzylamine (2.14 g, 0.02 mole) in 25.0 mL of ethanol was added. The reaction mixture was heated to the boiling point. After cooling, the Schiff base crystals were filtered. The synthesized HL was stored in the dark and at room temperature.

The interaction between HL and the metal ion takes place with the covalent bond established on phenolic oxygen and the coordination bond based on iminic nitrogen [65, 66].

Fluorescence Studies

The stock solution of HL chemosensor was prepared at a concentration of 3.0×10^{-3} M in ethanol. Metal ion stock solutions of Zn^{2+} , Cd^{2+} , Hg^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} and Co^{2+} were prepared at a concentration of 3.0×10^{-3} M in double distilled water from their chloride or nitrate salts. Working solutions at the desired concentration were prepared by diluting the stock metal ion solutions in double distilled water and diluting HL in ethanol.

Fluorescence spectra were recorded 40 minutes after mixing an equivalent volume of metal ion solutions (3.0×10^{-3} M) and HL (3.0×10^{-4} M) and excitation and emission wavelengths were determined. HL-M (M: Zn^{2+} , Cd^{2+} and Hg^{2+}) complex formation stoichiometry was determined by measuring the fluorescence intensities corresponding to the varying molar fractions of HL.

Analysis of Zn^{2+} , Cd^{2+} and Hg^{2+} in Synthetic Aqueous Sample

To construct the calibration graph, after mixing 6.0 mL of 3.0×10^{-4} M HL solution with increasing concentrations of metal ion solutions, the total volume was completed to 9.0 mL with double distilled water.

Fluorescence intensities were measured at 452, 474 and 491 nm emission wavelengths after adding 2 times the volume of 3.0×10^{-4} M HL on the portion taken from the synthetic aqueous sample. The amount of Zn^{2+} , Cd^{2+} and Hg^{2+} in synthetic sample were determined from the calibration graph.

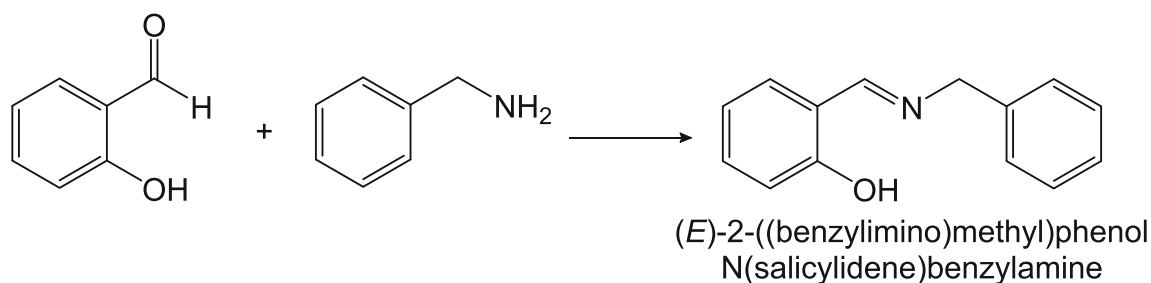


Fig. 1 Synthesis of Schiff base ligand (HL)

Results and Discussion

EI-MS Studies

Electron ionization mass spectrometry was employed for structural characterization of the Schiff base ligand. Mass spectra were obtained by using 70 eV electrons in a quadrupole mass analyzer. The pattern of the mass spectra shows the sequential degradation of the ligand. In the mass spectrum, the fragment at $m/z = 211$ corresponding to the molecular weight of the Schiff base and the fragment at $m/z = 91$ corresponding to $[C_7H_7]^+$ are dominant (Fig. 2). The ions at $m/z = 194$ and $m/z = 120$ were attributed to $[C_{14}H_{12}N]^+$ and $[C_7H_6NO]^+$, respectively. The fragment at $m/z = 194$ was thought to be formed by the removal of the hydroxyl group. The loss of C_7H_7NO (2-(iminomethyl)phenol) group from the ligand caused the formation of a fragment at $m/z = 91$.

Fluorescence Measurements

Fluorescence studies were carried out to assess the potential use of HL as a fluorescent chemosensor for the determination of Zn^{2+} , Cd^{2+} and Hg^{2+} . Since excitation and emission wavelengths of HL and ligand-metal complexes were not known, a

wavelength scan was performed. For this purpose, HL solution in ethanol at 3.0×10^{-4} M was mixed with the equivalent volume of metal ion solution (3.0×10^{-3} M in double-distilled water) (Fig. 3).

As can be shown in Fig. 4, there is a weak peak at 464 nm in the fluorescence emission spectrum of HL. The weakness of the peak indicates that the fluorescence intensity of HL is very low. The excitation spectra obtained gave a peak at 369 nm.

Fluorescence responses of HL with some metal ions were examined to assess whether HL could act as a fluorescent chemosensor. As a result of reaction with HL, significant fluorescence emission was seen for Zn^{2+} , Cd^{2+} and Hg^{2+} . These peaks were observed at 452 nm for Zn^{2+} , at 474 nm for Cd^{2+} and at 491 nm for Hg^{2+} in the emission spectra (Fig. 5).

Determination of Binding Stoichiometry

The binding stoichiometry of HL-M (M: Zn^{2+} , Cd^{2+} and Hg^{2+}) complexes was determined from the Job's plots. The fluorescence intensity at 452 nm for Zn^{2+} , at 474 nm for Cd^{2+} and at 491 nm for Hg^{2+} was measured by varying the molar fraction of HL with a total

Fig. 2 Electron ionization mass spectra of HL obtained with 70 eV electrons

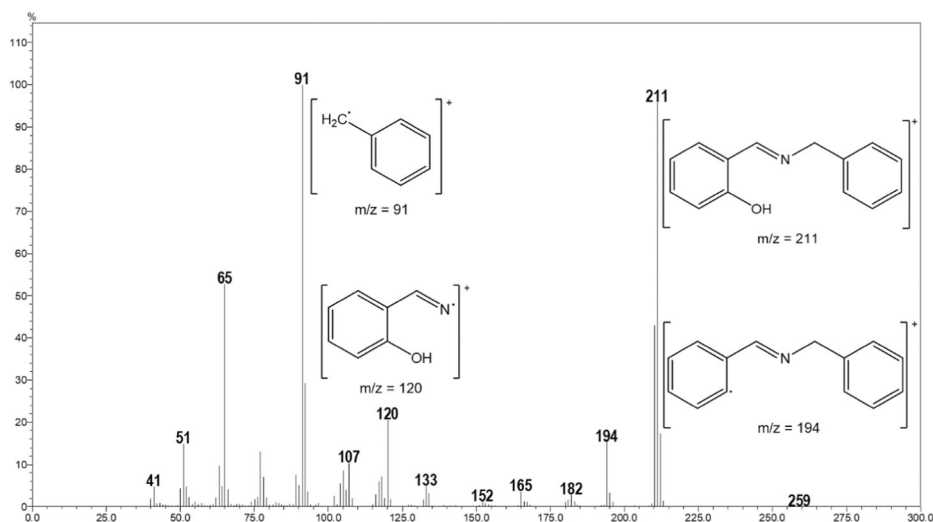
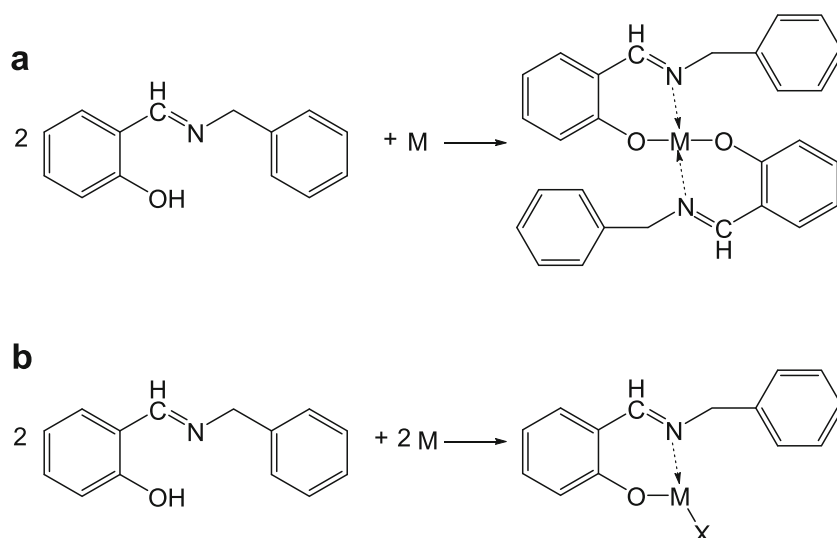


Fig. 3 Synthesis of HL-metal complexes a. M: Zn^{2+} and Hg^{2+} , b. M: Cd^{2+} , X: Cl^-



concentration of the sensor and metal ion solutions. A series of a solution containing HL (3.0×10^{-4} M in ethanol) and Zn^{2+} , Cd^{2+} , Hg^{2+} (3.0×10^{-4} M in double-distilled water) were prepared, in which the total volume of HL and metal ion solution was kept constant at 4 mL. The molar fraction at maximum emission intensity gives the binding stoichiometry. Maximum emission intensity was observed at 0.675 for Zn^{2+} , 0.428 for Cd^{2+} and 0.667 for Hg^{2+} (Fig. 6). This result shows that chemosensor HL forms 2:1 complex with Zn^{2+} and Hg^{2+} and forms 1:1 complex with Cd^{2+} .

Optimization Studies

pH Effect

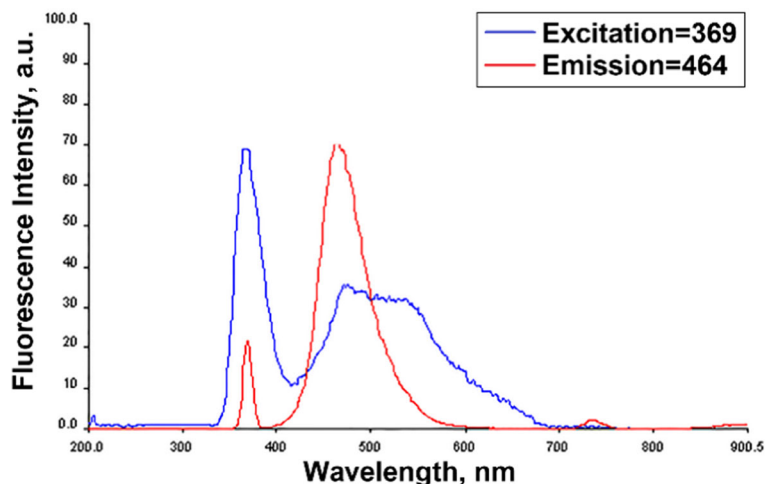
In order to determine the optimum pH in the determination of zinc, cadmium and mercury(II) ions with the chemosensor HL, pH scan was performed. After mixing the HL solution

(3.0×10^{-4} M in ethanol) with the same concentration of metal ion solutions (3.0×10^{-4} M in double-distilled water) the pH was adjusted between 5 and 9 with Britton-Robinson buffer. Fluorescence spectra were recorded after 40 minutes at 452 nm for Zn^{2+} , at 474 nm for Cd^{2+} and at 491 nm for Hg^{2+} (Fig. 7). Fluorescence is very weak in the acidic media due to the protonation of the nitrogen in the imine bond of HL. This situation was interpreted as the ligand coordination with metal ions becomes difficult due to protonation [27]. Since metal hydroxides precipitated at pH above 9, higher values of pH scanning were not performed. Fluorescence emission was found to be quite high at pH 8 to 9. Since the pH values of the HL-metal complexes are between 8.0 and 8.5, there is no need to adjust the pH.

Solvent Effect

Since most of the Schiff bases are insoluble in water, different solvents should be used. Therefore, the experiments were

Fig. 4 Excitation and emission spectra of HL (3.0×10^{-3} M in ethanol)



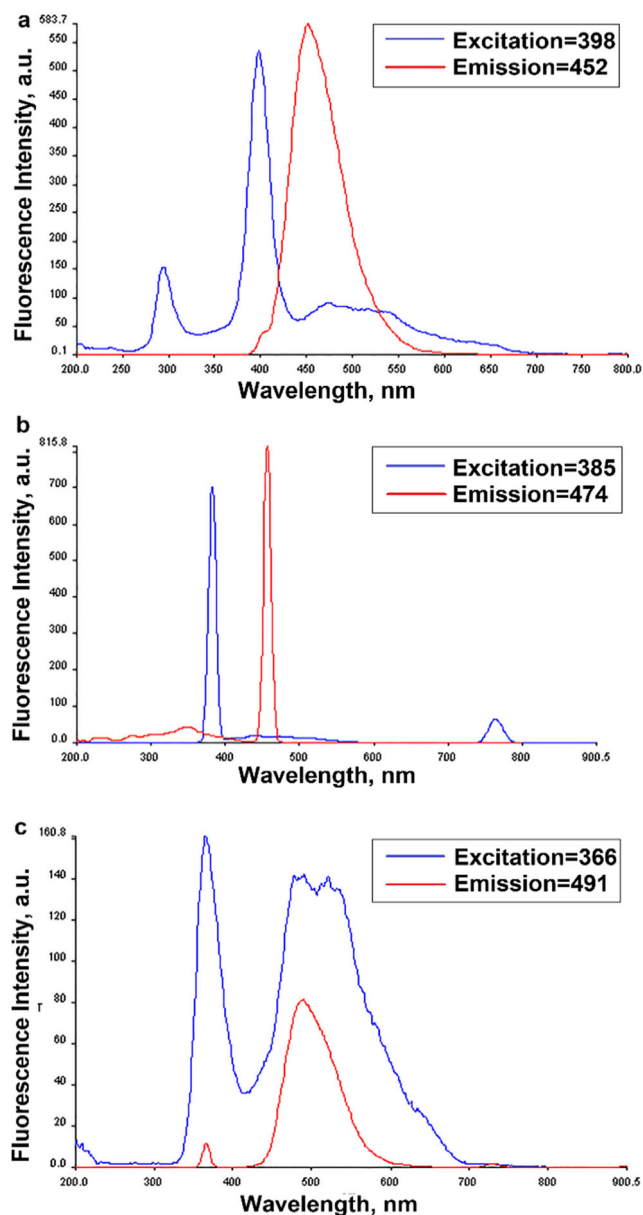


Fig. 5 Excitation and emission spectra of HL-M complexes ($[HL]=3.0 \times 10^{-4}$ M, $[M]=3.0 \times 10^{-3}$ M) a. M: Zn^{2+} , b. Cd^{2+} , c. Hg^{2+}

carried out using organic solvents that can be mixed with water because the purpose of the study was to determine zinc, cadmium and mercury(II) ions in aqueous solutions. The ligand was dissolved in ethanol, methanol, acetone, acetonitrile and N,N-dimethylformamide (3.0×10^{-5} M) to determine the fluorescent emission behavior of HL-M (M: Zn^{2+} , Cd^{2+} and Hg^{2+}) complexes in different solvents. Ethanol, methanol, acetone, acetonitrile and dimethylformamide showed strengthening and attenuating effects on fluorescence intensity (Fig. 8). It is thought that fluorescence intensity significantly increases due to the fact that the molecules become more stable, especially when dimethylformamide is coordinated to

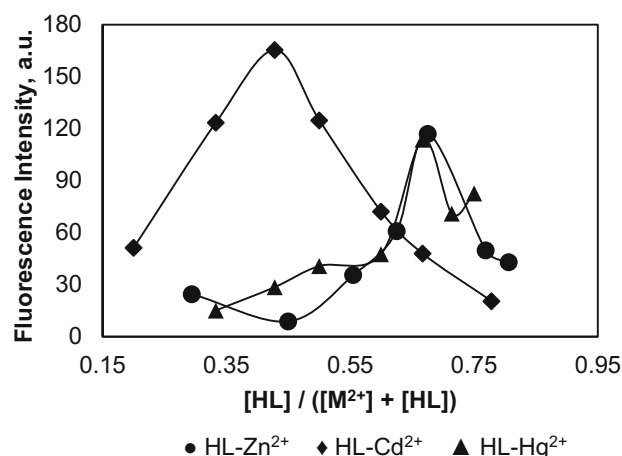


Fig. 6 Job plots for determination of binding stoichiometry of HL-M (M: Zn^{2+} , Cd^{2+} and Hg^{2+}) complexes

the structure of complexes. However, due to its practical use, ligand dissolved in ethanol was used in the experiments.

Ligand Concentration

There is an equilibrium between HL and metal ion in free form and HL-metal complex (Fig. 3). The increase in the amount of ligand shifts the equilibrium reaction to the right in favor of the complex, resulting in an enhancement in the intensity of fluorescence. In order to determine optimum ligand concentration, HL solutions were prepared in ethanol at 3.0×10^{-3} M, 3.0×10^{-4} M and 3.0×10^{-5} M, respectively. After adding metal ion solutions (3.0×10^{-3} M) to each chemosensor solution (1:2 for Zn^{2+} and Hg^{2+} , 1:1 for Cd^{2+}), fluorescence spectra were recorded at 452 nm for Zn^{2+} , at 474 nm for Cd^{2+} and at 491 for Hg^{2+} . It was observed that 3.0×10^{-3} M metal ion solution with 3.0×10^{-4} M HL solution caused much more fluorescence intensity compared to the signals obtained from other HL concentrations (Fig. 9). Subsequent experiments were performed with a 3.0×10^{-4} M HL solution.

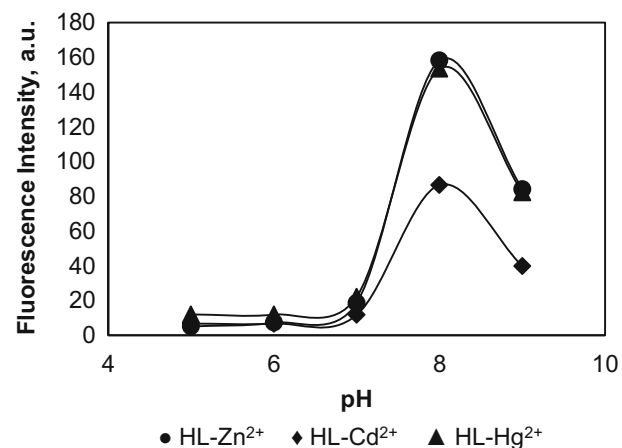


Fig. 7 The effect of pH on the fluorescence emission of HL-metal complexes

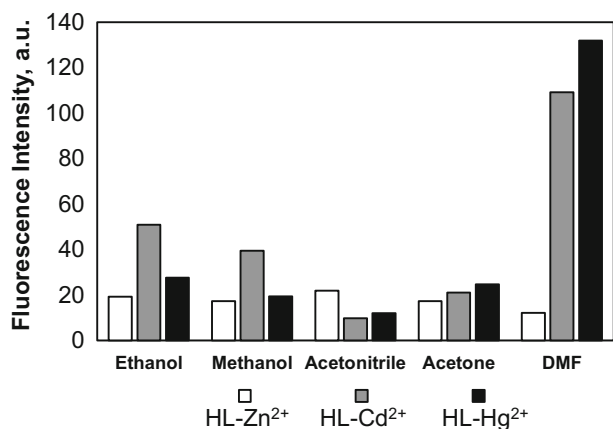


Fig. 8 Fluorescence intensity of HL-metal complexes in different solvents

Interference Effect

The high selectivity of a fluorescent sensor for detecting analytes in the presence of other ions is one of the most important characterization parameters [28]. The selectivity of HL for Zn²⁺, Cd²⁺ and Hg²⁺ over other metal ions such as Ni²⁺, Cu²⁺, Co²⁺ and Fe³⁺ was investigated. Equivalent volume of each metal ion solution (3.0×10^{-3} M) was added separately to Zn²⁺, Cd²⁺, Hg²⁺ solutions (3.0×10^{-4} M) and then the solutions were mixed with HL (3.0×10^{-4} M). Fluorescence spectra were recorded at 452 nm for Zn²⁺, at 474 nm for Cd²⁺ and at 491 nm for Hg²⁺ after 40 minutes (Fig. 10). In the presence of Fe³⁺ and Cu²⁺, the intensity of HL-M (M: Zn²⁺, Cd²⁺ and Hg²⁺) decreases considerably. Co²⁺ and Ni²⁺ also have a negative effect on the selectivity of HL for Zn²⁺ and Cd²⁺. This effect can be explicated by the fact that Cu²⁺ and Fe³⁺ have more affinity in the ligand than Zn²⁺, Cd²⁺ and Hg²⁺.

Calibration Studies

After the optimum conditions were determined, calibration curves were established for the quantitative determination of

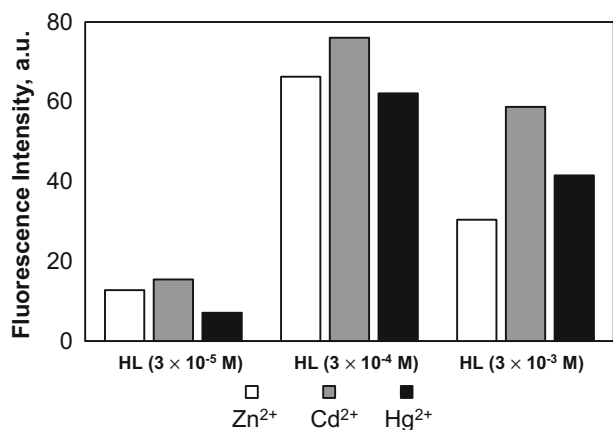


Fig. 9 Fluorescence intensity of HL-M complexes prepared with different concentrations of HL (M: Zn²⁺, Cd²⁺ and Hg²⁺; [M]= 3.0×10^{-3} M)

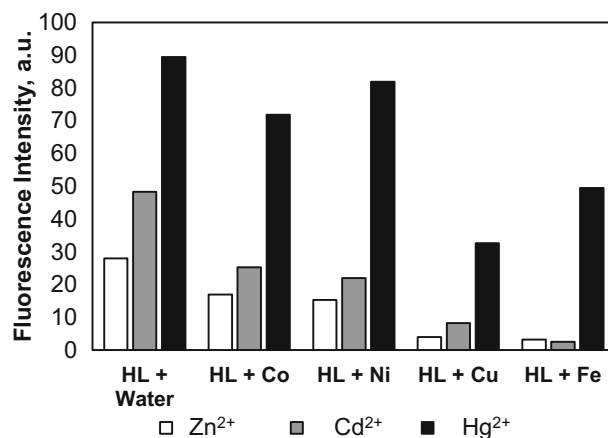


Fig. 10 Effects of interfering ions on the selectivity of HL for Zn²⁺, Cd²⁺ and Hg²⁺

zinc, cadmium and mercury. As shown in Table 1, HL gave a linear response for Zn²⁺, Cd²⁺ and Hg²⁺ in the range of $0.6 - 9.0 \times 10^{-5}$ M, $0.3 - 3.0 \times 10^{-5}$ M, $0.6 - 7.8 \times 10^{-5}$ M with a correlation coefficient of $R^2 = 0.9932$, 0.9952 and 0.9938 ($n=5$), respectively. Limit of detection (LOD) were determined by using the equation $LOD = 3 S_b/m$. In this equation, m refers to the slope of the calibration graph and S_b refers to the standard deviation of 10 different fluorescence intensity recorded for the lowest metal ion concentration in the calibration graph. LOD was found to be $2.7 (\pm 0.2) \times 10^{-7}$ M, $6.0 (\pm 0.5) \times 10^{-7}$ M and $7.5 (\pm 0.4) \times 10^{-7}$ M, respectively (Table 1). Errors were calculated by dividing the standard deviation by the square root of number of measurements.

A comparison of limit of detection and working range with the previously reported sensors for Zn²⁺, Cd²⁺ and Hg²⁺ is presented in Table 2. The proposed method displays comparable detection limits with the reported sensors.

According to EPA standards, the maximum contaminant level (MCL) for inorganic chemical contamination in ground water and drinking water is 0.005 mg L^{-1} for Cd²⁺ and 0.002 mg L^{-1} for Hg²⁺. Using available organoleptic data,

Table 1 Calibration parameters of fluorescent sensors prepared

	HL-Zn ²⁺	HL-Cd ²⁺	HL-Hg ²⁺
Wavelength, nm	$\lambda_{\text{exc}}=398$ $\lambda_{\text{ems}}=452$	$\lambda_{\text{exc}}=385$ $\lambda_{\text{ems}}=474$	$\lambda_{\text{exc}}=366$ $\lambda_{\text{ems}}=491$
Linear working range, M	$0.6 - 9.0 \times 10^{-5}$	$0.3 - 3.0 \times 10^{-5}$	$0.6 - 7.8 \times 10^{-5}$
Slope	7.7×10^6	7.6×10^6	5.2×10^6
Intercept	97.47	80.49	121.77
Limit of detection, M	2.7×10^{-7}	6.0×10^{-7}	7.5×10^{-7}
Limit of quantification, M	9.1×10^{-7}	2.0×10^{-6}	2.5×10^{-6}
Correlation coefficient	0.9932	0.9952	0.9938

Table 2 Comparison of the proposed HL sensor with the previously reported sensors

Metal Ion	Synthesized Fluorescent Sensor (L)	Working Range	Limit of Detection	Ref.
Hg ²⁺	2-(4-(diphenylamine)benzylidene) thiosemicarbazide	0.45 – 3.6 μ M	0.17 μ M	[64]
Hg ²⁺	Condensation of benzophenone and 2-aminobenzenethiol	0.05 – 2×10^{-6} M	2.268×10^{-8} M	[62]
Zn ²⁺	7-methoxychromone-3-carbaldehyde-(30-hydroxy-20-naphthaleneformyl) hydrazone	0 – 1.5 equiv. of L (50 μ M)	1.73×10^{-7} M	[58]
Zn ²⁺	Condensation of 8-hydroxyjulolidine-9-carboxaldehyde and 1-(3-Aminopropyl) imidazole	0.1 – 1.0 equiv. of L (40 μ M)	15.6 μ M	[55]
Zn ²⁺	Condensation of salicylaldehyde and 3-amino-2-hydroxyacetophenone	0 – 1.0 equiv. of L (10 μ M)	1.44×10^{-7} M	[53]
Zn ²⁺	2,4-di-tert-butyl-6-[(1-hydroxycyclohexyl)methylimino]methylphenol	0 – 8 μ M	7.25×10^{-7} M	[52]
Zn ²⁺	2-[(1-hydroxycyclohexyl)methylimino]methylphenol	0 – 12 μ M	3.08×10^{-7} M	[46]
Zn ²⁺ , Cd ²⁺	N,N'-bis(salicylidene)-1,2-phenylenediamine	0 – 45 μ M		[44]
	N'-bis-(N,N-di-(2-pyridyl)methyl)-ethane-1,2-diamine)-perylene-3,4,9,10-tetracarboxylic-diimide	0.1 – 4.0 μ M	32 nM	[44]
Zn ²⁺	N,N',N''-tris(salicylidene)(2-aminoethyl) amine	0.1 – 5.0 μ M	48 nM	[43]
Zn ²⁺	2-hydroxynaphthalene-1-carboxaldehyde with tris(2-aminoethyl) amine	1 – 12 μ M	1.1 μ M	[41]
Cd ²⁺	Condensation of semicarbazide and salicylaldehyde	0 – 10 equiv. of L (25 μ M)	4.89×10^{-8} M	[40]
Zn ²⁺ , Cd ²⁺ , Hg ²⁺	N,N'-((5,5'-(Quinoxaline-2,3-diyl)bis(1H-pyrrole-5,2-diyl))bis(methanylylidene))bis(4-methoxyaniline)	0 – 2×10^{-5} M		[38]
	N,N'-((5,5'-(quinoxaline-2,3-diyl)-bis(1H-pyrrole-5,2-diyl))bis(methanylylidene))dianiline	0 – 3×10^{-5} M		
		0 – 4×10^{-5} M		
Zn ²⁺	Bis-N,N'-(salicylidene)-1,3-propanediamine	0.8 – 6.0×10^{-5} M	0.5×10^{-6} M	[27]
Zn ²⁺	Bis-N,N'-(salicylidene)-2,2'-dimethyl-1,3-propanediamine	0.3 – 5.0×10^{-5} M	0.1×10^{-6} M	[25]
Zn ²⁺ , Cd ²⁺	Tris(3-(2-hydroxyacetophenone)propyl)amine	1.6×10^{-7} – 5.0×10^{-5} M	8.8×10^{-8} M	[24]
	Quinoline based fluorescent probe	0 – 1.0 equiv. of L (5 μ M)		
		0 – 1.0 equiv. of L (5 μ M)		
		0 – 12 equiv. of L (5 μ M)		
Zn ²⁺	Tris(2-pyridinecarboxaldehyde)triaminoguanidinium chloride	(5 $\times 10^{-5}$ M)	2.5×10^{-6} M	[22]
		0 – 40 μ M		
Zn ²⁺	Benzene-1,2-dicarbaldehyde bis-benzoyl hydrazide	0.6 – 9.0×10^{-5} M	2.7×10^{-7} M	[20]
Zn ²⁺ , Cd ²⁺ , Hg ²⁺	(E)-2-((benzylimino)methyl)phenol	0.3 – 3.0×10^{-5} M	6.0×10^{-7} M	Proposed sensor
		0.6 – 7.8×10^{-5} M	7.5×10^{-7} M	

Table 3 Comparison of the results obtained by proposed HL fluorescent sensor and AAS

Sample	Zn ²⁺ (mg L ⁻¹)		Cd ²⁺ (mg L ⁻¹)	
Synthetic sample	Proposed sensor ^a	AAS ^b	Proposed sensor ^a	AAS ^b
	0.655 ± 0.015	0.639 ± 0.069	1.748 ± 0.031	1.596 ± 0.002

^a The mean of five measurements, ^b The mean of three measurements

for controlling taste and odor quality of water, the estimated level of Zn²⁺ is 5 mg L⁻¹ [67, 68].

In order to examine the applicability of HL as a fluorescent sensor, Zn²⁺, Cd²⁺ and Hg²⁺ were determined in synthetic aqueous samples that contain known amounts of metal ions. Fluorescence spectra were recorded 40 minutes after mixing 5.0 mL of the aqueous sample with 10.0 mL. The results were compared with those obtained with AAS method and presented in Table 3. As can be seen, the results of zinc and cadmium selective fluorescent sensors and AAS are in agreement. The accuracy was tested by *t*-test. The *t*_{experimental} was found as 1.18 for HL-Zn²⁺ and 1.03 for HL-Cd²⁺ at 95% confidence level (*t*_{critic} = 2.45). The *t*-test shows that there is no significant difference between the results of the two methods.

In order to test the accuracy of the method based on HL proposed as a chemosensor, recovery experiments were performed. For this purpose, known amounts of Zn²⁺, Cd²⁺ and Hg²⁺ solutions were added to the synthetic aqueous sample. Fluorescence intensities were measured 40 minutes after mixing 5.0 mL of the synthetic sample with 10.0 mL of 3 × 10⁻⁴ M HL solution. The recoveries of Zn²⁺, Cd²⁺ and Hg²⁺ from the spiked sample are given in Table 4. The recovery values are in the range from 101 to 108% for zinc, 103 to 104% for cadmium and 101 to 105% for mercury. The results show that the accuracy of the HL chemosensor is quite good.

Table 4 Recoveries of Zn²⁺, Cd²⁺ and Hg²⁺ from spiked sample

	Zn ²⁺ (mg L ⁻¹)	
Calculated	Found ^a	Recovery ^a
1.24	1.32	105.99 ± 0.02
1.44	1.45	100.94 ± 0.02
2.22	2.41	107.92 ± 0.02
	Cd ²⁺ (mg L ⁻¹)	
Calculated	Found ^a	Recovery ^a
2.70	2.79	103.4 ± 1.1
3.02	3.13	103.8 ± 1.4
4.29	4.45	103.8 ± 1.5
	Hg ²⁺ (mg L ⁻¹)	
Calculated	Found ^a	Recovery ^a
1.60	1.64	104.5 ± 2.3
2.09	2.12	101.3 ± 3.0
4.19	4.31	103.1 ± 1.9

^a The mean of five measurements

Conclusions

In this study, an ON type Schiff base, (E)-2-((benzylimino)methyl)phenol, was synthesized and its fluorescence properties against zinc, cadmium and mercury(II) ions were investigated. This ligand was found to have good selectivity to zinc, cadmium and mercury(II) ions. Optimization studies were carried out to improve sensitivity and selectivity. It was observed that some ions have decreasing effects on the fluorescence sensitivity of these ions investigated. Zn²⁺, Cd²⁺ and Hg²⁺ can be determined quantitatively in neutral aqueous samples. For samples containing a known amount of metal ions, the results obtained with the fluorescence spectrometer are compatible with the results obtained with AAS, indicating that the accuracy of the method based on HL chemosensor is very good. The method based on HL exhibits a wide linear range, good accuracy and low detection limits. Emission of HL-M (M: Zn²⁺, Cd²⁺ and Hg²⁺) complexes at different wavelengths also made it possible to determine these ions simultaneously. As a result, it was concluded that the HL ligand can be used as a chemosensor in determining zinc, cadmium and mercury ions in aqueous samples.

Authors' Contributions Not applicable

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Availability of Data and Material Available

Compliance with Ethical Standards

Conflicts of Interest The author declares that there is no conflict of interest.

Code Availability ChemBioDraw Ultra 14.0
Adobe Photoshop CC (64 Bit)

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