Synthesis and Spectral Studies of Schiff Base Receptor for Fluorescence Detection of Hg(II)

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In this study, a fluorescent film probe with a structure centered on a Schiff base *viz*. ($N_{1'}$,$N_{2'}$)-N_1,N_2-*bis*(2-amino-3,5-dibromobenzylidene)-1,2-diamine (DAB) was synthesized. The probe was used as a fluorescence chemosensor for transition metal ion detection in an aqueous medium. Fluorescence was measured through fluorescence spectroscopy, and the emission maximum of the proposed sensor was 552 nm. Furthermore, the proposed film sensor exhibited a high sensitivity and selectivity toward Hg^{2+} ions. The limit of detection (LOD) of chemosensor, which was calculated using the fluorescence titration method, found to be 2.11 µM at 552 nm. The fluorescence spectroscopic data evidenced the potential of the proposed sensor for application in the detection and determination of Hg^{2+} ions in deionized water without the interference from other metal ions.

Keywords: Schiff base, Chemosensor, Hg^{2+} ion, Fluorescent sensor, pH effect.

INTRODUCTION

Schiff bases are compounds containing azomethine group benzylidene (-HC=N-), which are synthesized by a condensation reaction between a primary amine and an active carbonyl compound. Generally, condensation reactions occur under acid or base catalysis or by heating the reaction mixture [1]. Schiff bases are useful as chelators and widely used because of their simple synthetic methods, wide variety of structures, denticities and their response to subtle steric and electronic changes in their structural framework [2]. The nitrogen atom and other donors are responsible for the activity of Schiff bases as well their stability and applications in many fields [3]. They are considered "privileged ligands" and most widely used due to their versatile synthesis and relatively high solubility in common solvents [4]. In benzylidene derivatives, the C=N linkage is essential for biological activity. The nitrogen atom in benzylidene may be involved in the formation of biological constituents and may interfere in normal cell processes. Schiff bases are highly crucial reagents for inorganic chemists because these compounds are widely used in medicinal inorganic chemistry owing to their diverse biological and pharmacological activities and antitumor activity. Biomimetic modeling applications extensively use Schiff bases. Schiff bases are also used in designing

molecular magnet molecules and in the liquid crystal aspect [5]. Heterocyclic scaffolds containing an azole ring system and phenol derivatives have been reported to possess a wide range of biological activities, such as antifungal [6], antioxidant [7], antibacterial [8], antitumor [9], anti-inflammatory [10] and antipyretic activities [11]. Generally, Schiff bases exhibit excellent chelating properties. Schiff bases are also used as catalysts, intermediates in organic synthesis, dyes [12], pigments, polymer stabilizers and corrosion inhibitors [13],

Recently, many traditionally used techniques such as inductively coupled plasma-atomic emission spectroscopy [14,15], atomic absorption spectroscopy [16], electrochemical methods [4], HPLC [5] and fluorescence spectroscopy [17,18] have been refined. These techniques are also used for determination of transition metal such as Hg^{2+}, Cu^{2+}, Fe^{3+} and Co^{2+} in water, biological, medical, industrial and environmental samples. In the current scenario, fluorescence spectroscopy has advantages, such as rapid response, real-time monitoring, low cost, high sensitivity and ease of operation over other techniques [19].

Among the plethora environmental contaminants, mercury is highly toxic to humans because it can easily pass through the skin, respiratory and gastrointestinal tissues and can damage DNA as well as the liver, kidney, immune system and nervous system [20]. Furthermore, it is a persistent pollutant in the

environment and can bioaccumulate through the food chain. Mercury contamination in soft metals also has some natural and anthropogenic causes, including oceanic and volcanic emission, gold mining, solid waste incineration and combustion of fossil fuels [21]. The U.S. Environmental Protection Agency (USEPA) standard for the maximum allowable level of inorganic mercury in drinking water is 2 ppb [22]. Therefore, the development of selective and sensitive methods for the determination of trace amounts of Hg^{2+} is extremely crucial for both environmental safety and preservation of human health [23]. Although several techniques are currently available for Hg^{2+} detection, they require expensive instruments and well-controlled experimental conditions; furthermore, the samples often require complicated pretreatment procedures [24]. Among the various techniques available, fluorescence signaling is one of the first choices because it is simple and sensitive. Most importantly, most fluorescent sensors are also useful as cellular imaging agents; therefore, the fluorescence approach is superior to that of other analytical methods [25]. Recently, some fluorogenic chemosensors for Hg^{2+} have been identified, but many signaling units often exhibit non-specific fluorescence quenching on binding with metal ions [26-29]. Metal-induced reactions represent an excellent approach to overcome non-specific fluorescence because they form fluorescent or coloured products only when a specific chemical reaction occurs between the dosimeter molecule and target species [30-34]. Although various chemodosimeters for Hg^{2+}, which are based on mercury-promoted desulfurization, hydration and hydrolysis are currently available, a majority of the chemodosimeter related methods exhibit poor biocompatibility and are liable to interference from mercapto-based chemicals in the organisms [35-37]. Present research work involves the development of chemosensors for soft metal ions, inorganic anions and the evaluation of their switching behaviour [38-46].The proposed fluorescent sensor, with a structure based on Schiff base *viz.* (N₁′,N₂′)-N₁,N₂-*bis*(2-amino-3,5-dibromobenzylidene)-1,2-diamine (DAB) has low detection limits and high selectivity toward Hg^{2+} ion.

EXPERIMENTAL

All the reagents and solvents in this study were obtained commercially and used without further purification. A selectivity study of a probe compound (N₁′,N₂′)-N₁,N₂-*bis*(2-amino-3,5-dibromobenzylidene)-1,2-diamine (DAB) toward different metal ions was conducted using the chloride or nitrate salts of metal ions. All the reactions were monitored through TLC. The melting point was determined using a melting point apparatus by the open capillary method. ¹H and ¹³C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were recorded by using deuterated DMSO-d_6 as a solvent at 25 °C. All fluorescence measurements were carried out using a Perkin-Elmer LS 55 fluorescence spectrometer. Fluorescence spectra were measured using an excitation wavelength of 400 nm with a high-energy pulsed xenon source and a 5 nm width. The UV-visible absorption spectra of DAB fluorescent film probe were recorded using a Perkin-Elmer Lambda 25 UV-visible spectrophotometer at different concentrations of Hg^{2+} ions at room temperature.

Synthesis of N₁′,N₂′)-N₁,N₂-*bis*(2-amino-3,5-dibromobenzylidene)-1,2-diamine (DAB): A mixture of 4-substituted benzene-1,2-diamine and 2-amino-3,5-dibromo benzaldehyde (0.2 M) was refluxed in the presence of ethanol. The reaction mixture was allowed to reflux for 8 h under an air atmosphere. After 8 h the reaction mixture, solvents were evaporated under vacuum (**Scheme-I**).
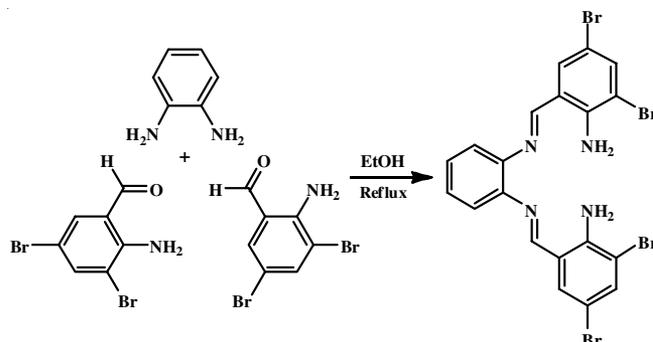
Scheme-I: Schematic representation of synthesis of DAB

UV-visible absorption and fluorescence titration: Stock solutions (1.0 mM) of metal cations such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+} and Zn^{2+} were prepared using deionized water their nitrate, chloride or acetate salts. These prepared stock solutions were also used in all measurements.

Preparation of buffer solution: The Britton-Robinson buffer solution was used for pH measurements. In these measurements, this buffer solution was prepared by mixing 40 mM acetic acid, 40 mM boric acid and 40 mM phosphoric acid. Furthermore, this buffer solution was used to adjust to the desired pH with 20 mM or 0.20 mM of NaOH or HCl, respectively. The desired pH value of fluorescent sensor is pH 7-9. For UV-visible and fluorescence titration, the stock solution of DAB (3.0×10^{-3} M) was prepared in ethanol:H_2O (4:1, v/v). The solution of the receptor then diluted to 1×10^{-5} M with the ethanol:H_2O solution (ethanol:H_2O = 4:1, v/v, 10 μM HEPES buffer, pH = 7.0). In each titration experiment, the solution of the ligand (1×10^{-5} M) taken in a quartz optical cell of 10 mm optical path length and then the ion stock solution was added into the cell gradually using a micropipette. The solutions of the guest cation containing different metal ions were performed using the chloride or nitrate salts in the order of 1×10^{-4} M prepared in deionized water at pH = 7.0. Solutions of various concentrations of the proposed compound and increasing concentration of the cation prepared separately. The spectra of these solutions were recorded using the UV-visible and fluorescence spectroscopy.

RESULTS AND DISCUSSION

The synthesized substituted hydraoznes were characterized by their elemental analysis and FT-IR, NMR spectral data. The physical constants, analytical and elemental analyses data of the ligand DAB are shown in Table-1.

FT-IR analysis: The key IR bands of compound (N₁′,N₂′)-N₁,N₂-*bis*(2-amino-3,5-dibromobenzylidene)-1,2-diamine (DAB) are given in Table-2. The N-H stretching vibration appeared as a strong and broad band in the region 3500-3100 cm⁻¹, synthe-

TABLE-1
PHYSICAL CONSTANTS, YIELDS AND ANALYTICAL DATA OF COMPOUND DAB

Entry	m.f.	m.w.	Yield (%)	m.p. (°C)	Elemental analysis (%): Found (calcd.)		
					C	H	N
DAB	$C_{20}H_{14}Br_4N_4$	629.97	84	210-212	38.07 (38.13)	2.20 (2.24)	8.81 (8.89)

TABLE-2
FT-IR SPECTRAL DATA (cm^{-1}) OF COMPOUND DAB

Assignments	DAB
ν(N-H)	3419.21
ν(ArC-H)	3055.63
	2971.81
ν(AliC-H)	
ν(C=N)	1627.42
ν(C=C)	1598.00
	1509.71
	1456.19
	1384.21
β(C-H)	1267.68
	1239.91
	1207.48
Γ(C-H)	1171.95-714.40

sized oxazine amines derivatives and reported assigned N-H stretching in the region 3559-3532 cm^{-1}. The strong bands in the region 3422.60-3399.44 cm^{-1} are assigned to N-H stretching. Generally, an aromatic compound commonly exhibits multiple weak bands in the region 3150-2930 cm^{-1}, this is also proved in this case as the IR bands in the region 3054.69-2929.21 cm^{-1} are obtained. The C-H stretching in alkanes occurs at lower frequencies than those of aromatic ring. The CH$_3$ stretching is expected at 2980-2870 cm^{-1} and usually the bands are weak. In this case, the carbonyl C=N stretching appeared in the region 1627.42-1582.08 cm^{-1}. The appearance of C=N band is the preliminary evidence for the formation of Schiff bases. The FT-IR band identified in the region 1598.00-1365.80 cm^{-1} are due to C=C stretching. Similarly, the band ascribed at 1385.69-1207.48 cm^{-1} had been designated to C-H in-plane bending vibrations. The bands in the range 1171.95-662.08 cm^{-1} are due to the aromatic C-H out-of-plane bending vibrations.

NMR analysis: The chemical shift values of Schiff bases are given in Table-3. The aromatic protons in compound DAB appeared in the interval 6.96-7.98 ppm. The upfield signal in the region 4.07-4.73 ppm is assigned to N-H proton present in compound DAB.

The ^{13}C chemical shifts values of compound DAB are also shown in Table-3. In ^{13}C NMR spectrum of DAB, the weak signal in the region 159.62-164.73 ppm is due to C=N of Schiff bases. The aromatic carbons could be easily distinguished by their characteristic absorption around 111.32-148.96 ppm. The *ipso* carbons should absorb at a higher frequency compared to other aromatic carbons. The *ipso* carbons signal appeared in the interval 145.69-149.08 ppm.

Fluorescence properties of DAB: The ligand DAB in deionized water was used for determining the excitation and emission spectra through fluorescence spectroscopy at room temperature (Fig. 1). The Schiff base exhibited two excitation bands at 374 nm. Similarly, the Schiff base also exhibited two emission bands at 552 and 400 nm, when excited. Moreover, the emission intensity of DAB was 305 a.u. at 552 nm. Stoke shift (ΔST) is defined as the difference between the maximum

TABLE-3
CHEMICAL SHIFTS OF NMR (δ ppm) SPECTRAL VALUES OF SCHIFF BASE DAB

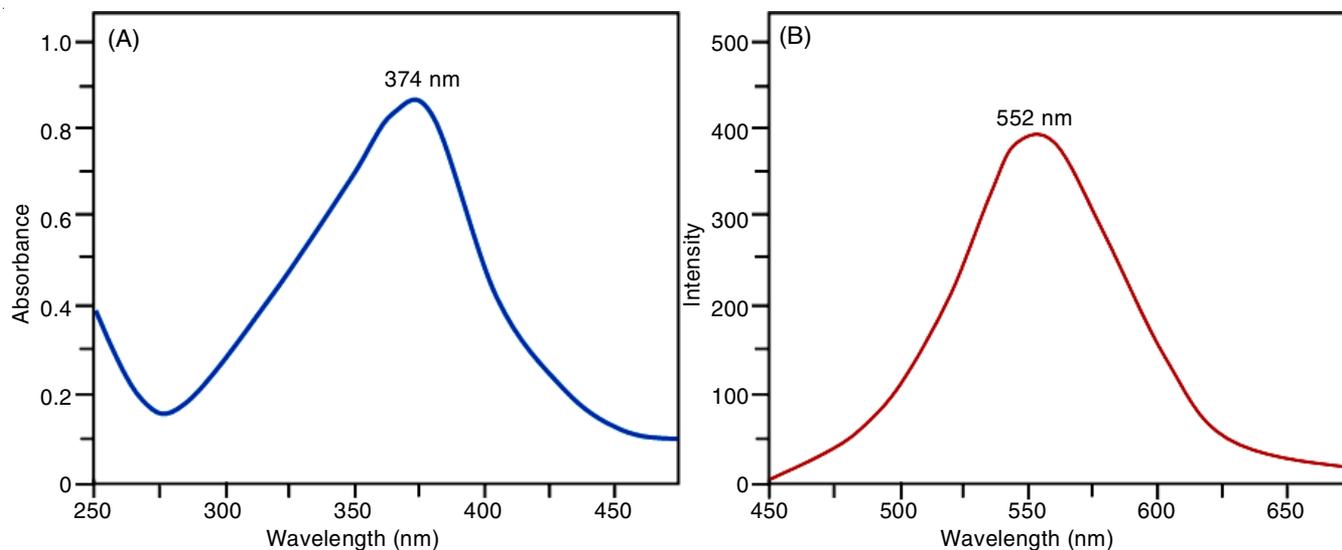| Entry	^1H NMR			^{13}C NMR		
	N-H	Ar-H	N=CH	C=N	C*ipso*	Ar-C
DAB	4.73	6.96-7.98	8.63	163.63	149.08	113.89-142.24

Fig. 1. (A) Excitation and (B) emission spectra of DAB in deionized water

wavelengths between the excitation and emission spectra. According to the results, the proposed sensor exhibited a relatively large ΔST value due to dual excitation and emission maxima. To calculate the quantum yield of DAB fluorescence sensor, fluorescein solution in ethanol was used as a reference ($\Phi 0f = 92$ %) and quantum yield of Schiff base probe calculated as 3.24 %.

Metal ions sensing properties: The proposed film probe's ability to sense metal cations was evaluated in the presence of a series of metal cations such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+} and Zn^{2+} (Fig. 2). The metal cations concentration was fixed at 1.0 mM. When 3 mL of cation metal solutions (1 mM) was added to the fluorescence probe, the emission intensity of DAB reduced in the presence of Hg^{2+} cation; however, the emission intensity of DAB increased in the presence of other metal cations at 552 nm. From these results (Table-1), it is concluded that DAB fluorescent probe was suitable for the detection of Hg^{2+} in aqueous solutions at these wavelengths.
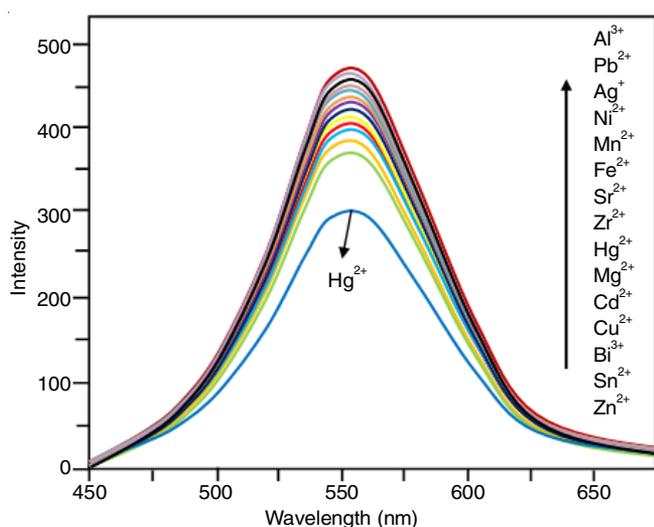

Fig. 3. Emission spectra of DAB in the presence of different Hg^{2+} ion concentration

Fig. 2. Emission spectra of DAB probe in the presence of different metal ions

Effect of Hg^{2+} concentration on DAB: To determine the effect of Hg^{2+} concentration on DAB film probe, the photoluminescence (PL) spectra of film probe were measured in the presence of different Hg^{2+} cation concentrations 62.5-1000 μM (Fig. 3). These photoluminescence spectra showed that the emission intensity of DAB fluorescent probe continuously decreased 552 nm with an increase in Hg^{2+} concentration.

UV-visible spectra of DAB fluorescent probe: The UV-visible absorption spectra of DAB were recorded in the presence of different Hg^{2+} concentrations (Fig. 4). The absorbance of DAB probe increased as Hg^{2+} concentration decreased from 1.0 to 0.00156 μM (Fig. 4).

Determination of limit of detection (LOD): To determine LOD value of DAB film probe, plots of ΔF, which is the difference between the emission intensities of the tested metal cation (F) and metal-free DAB (F_o), *versus* wavelength of spectra were obtained using fluorescence measurements (Fig. 5). According to the results, a satisfactory linearity response was obtained, and the regression coefficient was $R_2 = 0.951$ at 552 nm. Accor-
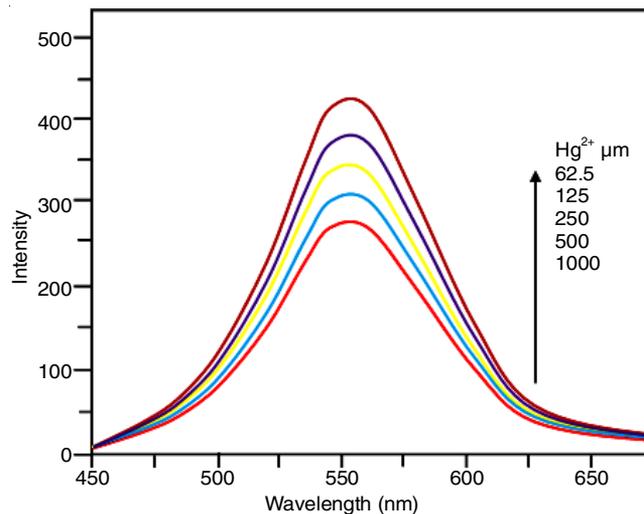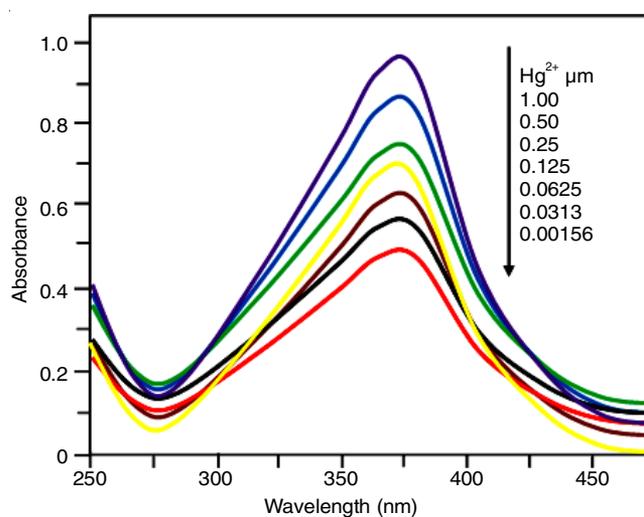

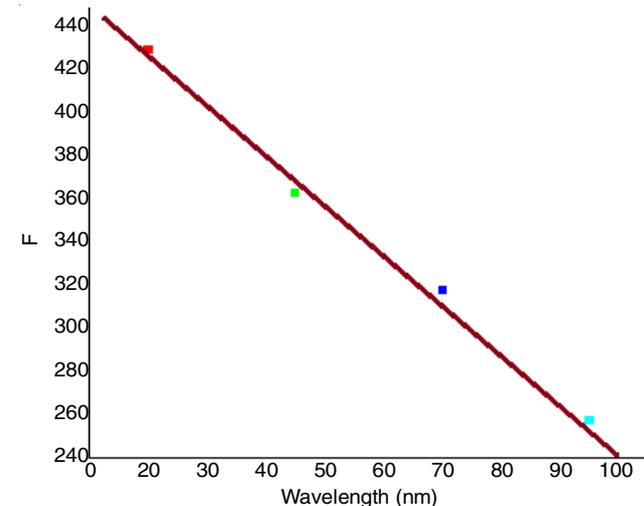Fig. 4. UV-visible spectra of DAB in the presence of different molarity Hg^{2+}

Fig. 5. Calibration curves for determination of Hg^{2+} ions by the proposed fluorescent probe at 552 nm

ding to these results, the proposed fluorescent sensor exhibited potential as a selective detector for Hg^{2+} in an aqueous medium.

Moreover, the LOD value of DAB chemosensor was calculated using the fluorescence titration method as mentioned in the literature. First, the standard deviation (σbi) of DAB probe without metal cations measured 10 times in deionized water was determined (0.221 at 552 nm). The slope was obtained from Fig. 5 and the LOD values of DAB probe was found to be 2.11 µM at the mentioned wavelength.

Effect of pH on DAB fluorescent film: pH is a crucial parameter affecting the functionality of the sensor. The effect of pH on DAB fluorescent film sensor was evaluated by measuring the emission spectra of DAB-Hg^{2+} complex at different pH. The effect of pH on the fluorescent sensor was studied using the Britton-Robinson buffer solution between pH 2 to 12. The pH of the solutions was adjusted to the desired value by using HCl or NaOH solutions. Furthermore, Hg^{2+} concentration was adjusted to 1.0 mM (Fig. 6). From Fig. 6, the emission intensities of DAB-Hg^{2+} cation complex did not change significantly with changes in pH and the proposed sensor was relatively stable toward pH changes. Furthermore, Schiff base fluorescent sensor was actually pH-independent in the range pH 5-9 at 552 nm. These results indicated that fluorescent chemosensor could work over a broad pH range.
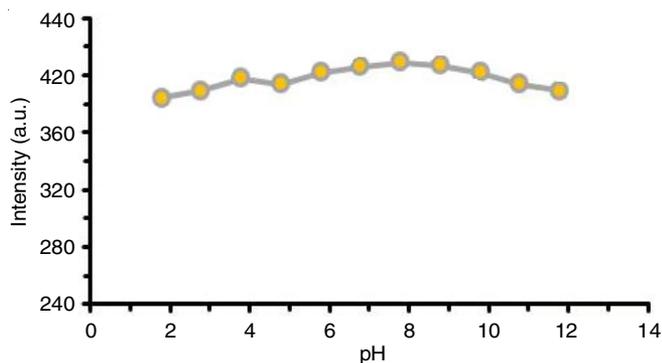

Fig. 6. pH effect on DAB fluorescent film probe in the presence of Hg^{2+} ion

Response mechanism: The Huckel calculation method was used to model the binding between DAB film probe and Hg^{2+}. The structure of DAB contains imine nitrogen (-N=CH) as a chromophore group. The Huckel charges on -N=CH group was calculated as -0.094. According to these results, the possible binding between DAB and Hg^{2+} could be mainly on account of imine nitrogen.

Conclusion

In this study, photoluminescence spectrophotometers were used to study the fluorescence properties of a proposed sensor. Schiff base viz., (N$_{1'}$,N$_{2'}$)-N$_1$,N$_2$-bis(2-amino-3,5-dibromobenzylidene)-1,2-diamine (DAB) exhibits two emission bands at 552 nm. The metal-ion-sensing property of fluorescent film probe was evaluated in the presence of a series of metal cations at 552 nm. The photoluminescence data showed that the proposed sensor was satisfactorily sensitive and selective toward Hg^{2+}. The values of Stoke shift (ΔST) and LOD of fluorescent sensor were calculated at 2.11 µM at the mentioned wavelength. The effect of interference and quenching ions on the proposed sensor were also investigated. From the results, the tested metal cations caused only a slight change in the emission intensity of DAB-Hg^{2+} complex. Consequently, the fluorescence data indicated that the proposed sensor has potential application in the detection and quantification of Hg^{2+} cation in deionized water without any interference from other metal ions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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