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Detection of trace amounts of Hg^{2+} in different real samples based on immobilization of novel unsymmetrical tetradentate Schiff base within PVC membrane

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ABSTRACT

A novel fluorescence optical sensor for sensitive and selective determination of Hg^{2+} ions in aqueous solution has been prepared. The sensing system is made of a novel unsymmetrical tetradentate Schiff base namely N-(2-hydroxyphenyl)-N′-(2-mercaptophenyl)-o-phthalylidene (HMP), as a neutral Hg^{2+}-selective fluoroionophore immobilized in a plasticized PVC membrane containing potassium tetrakis-(4-chlorophenyl) borate (KTpClPB) as a lipophilic anionic additive. The response of the optode is based on the strong fluorescence enhancement of HMP upon exposure to Hg^{2+} ions. Under the optimum conditions, the proposed sensor displays a linear response in concentration range of 2.27×10^{-11} to 1.13×10^{-3} mol/L, with a detection limit of 9.57×10^{-12} mol/L. Furthermore, the proposed optode displays a good selectivity toward Hg^{2+} ions in comparison with common coexisting cations. The sensor was applied successfully for determination of mercury ions in different real samples.

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1. Introduction

The determination of trace amounts of heavy metal ions is of interest in several fields including environmental analysis, process control, biology and medicine. Environmental contamination of Hg^{2+}, a widely known toxic heavy metal can result in death or severe damage to the brain [1–4]. Hg^{2+} is a highly stable inorganic form of mercury and according to WHO guidelines, its concentrations must be <0.002 mg/L in drinking water [5]. Recently, considerable progress has been made in analytical methodology for mercury detection, including atomic absorption spectrometry [6], inductively coupled plasma-mass spectroscopy [7], X-ray fluorescence spectrometry [8], neutron activation analysis [9], cold vapor atomic absorption spectrometry [10], electrothermal atomic absorption spectrometry [11], anodic stripping voltammetry [12], high-performance liquid chromatography [13], atomic fluorescence spectrometry [14], potentiometric ion-selective electrodes [15] and spectrophotometry [16,17]. However, many of those methods suffer from many problems such as poor reproducibility, limited sample adaptability, high cost, well-controlled experimental conditions, multi-step sample pretreatments, some inherent interference and time consuming.

The design of sensitive and discriminating optical sensors remains as an emerging frontier in analytical chemistry and has gained scientific interest, mainly due to the need for fast, easy and economical monitoring of our environmental samples especially for heavy metal ions in real time. Optical sensors have the advantages of size, cost effectiveness, simplicity, no necessity of the reference solution, and fieldwork applicability [18–22].

In construction of optical sensors Schiff's base ligands have been frequently used as ionophores in construction of membrane sensors because of their ability to form stable complexes with transition metal ions. Moreover, they produce remarkable selectivity, sensitivity and stability for a specific ion [23–26].

Metal-selective fluorescent chemosensors are served as useful tools for detection of metal ions due to their intrinsic sensitivity and selectivity [27,28]. Recently, some selective fluorescent chemosensors for Hg^{2+} based on fluorescence enhancement or fluorescence quenching has been reported [29–31]. However, most of

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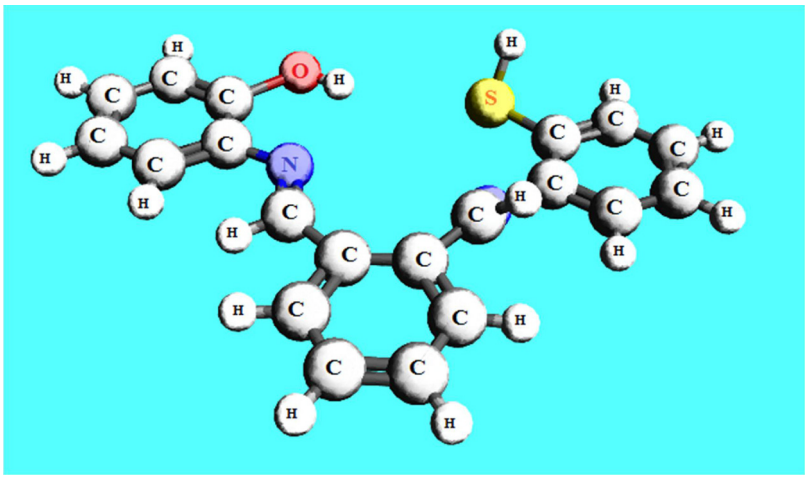

Fig. 1. Optimal structure of the chemosensor (HMP).

them have disadvantage in practical use, such as low water solubility, interference from other metal ions, strict reaction condition or complicated synthetic route. Therefore, development of simple fluorescent chemosensor that can selectively sense Hg^{2+} in aqueous media is significant.

In this work we introduce a novel optode for sensitive and selective determination of Hg^{2+}, based on a recently synthesized unsymmetrical tetradentate Schiff base namely: N-(2-hydroxyphenyl)-N′-(2-mercaptophenyl)-o-phthalylidene (HMP), as the sensing reagent immobilized in PVC membrane. The proposed optical sensor shows a significant fluorescence signal change on exposure to an aqueous solution containing Hg^{2+} ion, which accommodate the theoretically expected fluorescence response to Hg^{2+} ion concentration. The selectivity, response time, reproducibility, reversibility, and lifetime of the optode membrane were studied and the binding mode was elucidated via ^{1}H NMR and TOF-MS spectroscopy. Moreover, the applicability of the proposed chemosensor was assessed by detection of trace amounts of Hg^{2+} in various real samples.

2. Experimental

2.1. Materials and instrumentation

2-Aminothiophenol, 2-aminophenol, benzene-1,2-dicarboxaldehyde (o-phthaldehyde) and the lipophilic anionic additive reagent potassium tetrakis-(4-chlorophenyl) borate (KTpClPB) were supplied from Aldrich. The polymer membrane components, polyvinyl chloride (PVC) (high molecular weight) and the plasticizers, bis-(2-ethylhexyl) phthalate (DOP), bis(2-ethylhexyl)sebecate (DOS), bis-(2-ethylhexyl) adipate (DAO) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Absolute ethanol (EtOH), tetrahydrofuran (THF), and dicholormethane (DCM) were purchased from Merck. All solvents were of analytical grade and they were used as received. A stock solution of 1.0×10^{-2} M was prepared by dissolving 0.3606 g of $Hg(NO_3)_2{\cdot}2H_2O$ in exactly 100 mL of deionized water and standardized with the EDTA solution [32]. The stock solution was serially diluted to achieve the desired concentrations.

All fluorescence measurements were carried out on a on a Jenway 6270 Fluorimeter. The excitation source was a Pulsed Xenon Lamp. The UV–vis spectra were recorded on a Shimadzu UV 1800 Spectrophotometer. pH measurements were performed by Jenway pH meter model 3510 equipped with Glass bodied combination pH electrode (924005) and calibrated with Meck pH standards of pH 4.00, 7.00, and 10.00. All of the experiments were carried out at room temperature 25 ± 1 °C. FT-IR spectrum of the ionophore was obtained in KBr discs on a Unicam-Mattson 1000 FT-IR. ^{1}H NMR spectra were measured at room temperature on a Bruker AM300 NMR spectrometer using DMSO as a solvent. Mass spectra (TOF-MS) were recorded on Waters (USA) KC-455 model with ES^+ mode in DMSO.

2.2. Synthesis of the fluoroionophore (HMP)

An ethanolic solution of 2-amiothiophenol (5 mmol) and 2-aminophenol (5 mmol) were mixed with a hot ethanolic solution of o-phthaldehyde (5 mmol), 2 drops of acetic acid and magnetically stirred in a round bottom flask. The reaction mixture was then refluxed for 3 h at 60 °C in water bath and kept overnight. The resulting solution was then poured into crushed ice water. The precipitate formed was filtered and recrystallized from hot methanol and dried in a desiccator over anhydrous $CaCl_2$ under vacuum to get chromatographically (TLC) pure compound. Characteristics of HMP were as follows ($C_{20}H_{16}N_2OS$): M.Wt: 332.426 Yield: 65%. Color: Orange. Elemental analysis Calc. (%): C, 72.26; H, 4.85; N, 8.42 Found: C, 72.32; H, 4.79; N, 8.37. IR (KBr pellet. cm^{-1}): 3405 (ν_{OH}); 2548 (ν_{SH}); 1617 ($\nu_{C=N}$); 1278 (ν_{C-O}); 791 (ν_{C-S}). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.38 (s, 1H; OH); δ 4.38 (s, 1H; SH); 7.88 (s, 2H; HC=N); 6.50–7.25 (m, 12H; aromatic). TOF-MS (*m*/*z*): 333.4 $[HMP+H]^+$. UV–vis: 237 nm (π–π^* transition); 351 (n–π^* transition). The optimal structure of the chemosensor (HMP) is shown in Fig. 1 by using Avogadro program Version 1.0.1.

2.3. Membrane preparation

Membrane solutions were prepared by dissolving 30 mg of PVC, 65 mg of plasticizer (NPOE), 2.0 mg of KTpClPB and 3.0 mg the fluoroionophore in 2.0 mL THF. The solution was stirred with a magnetic stirrer to obtain a homogeneous mixture. Glass slides for bulk measurements were cut from microscope slides into 12 mm × 16 mm dimensions to fit precisely into its diagonal width of standard quartz cell. To improve the adhesion of the membrane, the glass slides were cleaned with THF, sulfuric acid and sodium hydroxide solutions, respectively, then thoroughly rinsed with deionized water and finally dried in an oven at 110 °C. Membranes were cast by placing 35 μL of the membrane solution onto the glass slide of ~10 μm thickness and spread evenly using a capillary glass tube [33,34]. The thickness of the films was in the order of 3–4 μm (as evaluated from the volume employed for spreading). After 2 min the coated slides were transferred to a Petri dish with a filter paper cover and then stored away from light for 12 h before

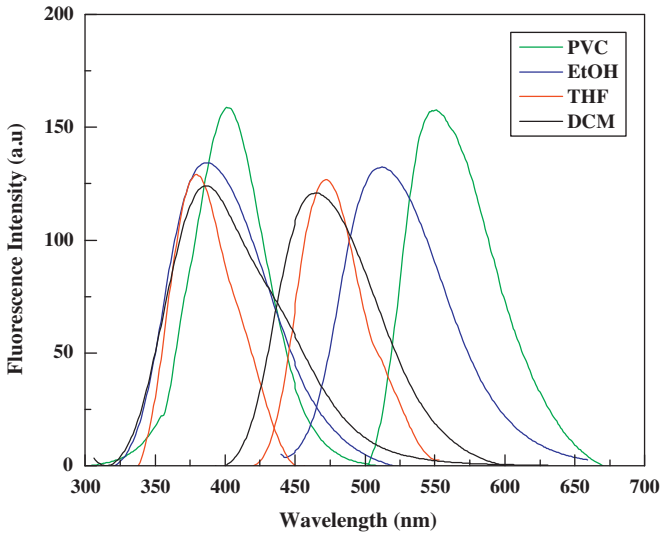

Fig. 2. Emission and excitation spectra of HMP in (a) DCM, (b) THF, (c) EtOH and (d) PVC.

use. Blank (reference) membranes were prepared in a similar way excluding HMP from the membrane solution. Fluorescence emission spectra of PVC membranes were recorded in quartz cells which were filled with sample solution. The polymer films were placed in diagonal position in the quartz cell. All of the experiments were operated at room temperature (25 ± 1 °C). The membranes were not conditioned before use.

2.4. Measurement procedure

The prepared membrane was placed in a buffer solution at pH 5.0 for 120 s to reach equilibrium. Then the sensing membrane was diagonally placed inside the sample cuvette of the instrument containing 2 mL of phthalate buffer solution (pH 5.0) and a blank membrane (without HMP) was put in the reference cuvette containing the buffer solution. The fluorescence intensity at an excitation wavelength of 401 nm was measured at 551 nm. The sample was then titrated with a standard Hg^{2+} ion solution using a pre-calibrated micropipette and the fluorescence intensity of the system was measured after ~120 s (required to reach equilibrium).

2.5. Preparation of real samples

2.5.1. Hair samples

Scalp hair sample was first soaked in deionized water for 10 min. This was followed by soaking in 1% triton X-100 solution for 20 min [35]. The hair sample was then rinsed five times with deionized water and air-dried. 0.250 g of dried hair sample was digested with 5.0 mL 0.1 M HNO_3 for 2 h at ~120 ◦C. Finally 3.0 mL of H_2O_2 was added to the sample and digested. The residue was diluted with deionized water to 50.0 mL volumetric flask.

2.5.2. Urine samples

24-h urine samples were obtained from dentists who had several months of steady exposure, at the end of a working week in 2.5 L polypropylene sampling vessels followed by the addition of concentrated HNO_3 to yield a final acid concentration of 1–3% (*v*/*v*) and the samples were stored at −20 °C prior to analysis.

2.5.3. Preparation of well water samples

Before the analysis, water samples were filtered through a Whatman No. 41 filter paper. The organic content of the water samples were oxidized in the presence of 1% H_2O_2 and addition of concentrated nitric acid, then the pH of water samples was adjusted to 5.0.

3. Results and discussion

3.1. Fluorescence quantum yield calculations

Fluorescence quantum yield values (Φ_F) of the HMP chemosensor in EtOH and PVC matrix were calculated employing the comparative William's method which involves the use of well-characterized standards with known (Φ_F) values [36]. Quinine sulphate was used as reference quantum yield standard (λ_{ex} = 410 nm, quantum yield = 0.54 in 0.1 M H_2SO_4) [37]. For this purpose, the UV–vis absorption and emission spectra of six different concentrations of reference standard and HMP were recorded. The integrated fluorescence intensities were plotted versus absorbance for the reference standard and HMP. The gradients of the plots are proportional to the quantity of the quantum yield of the studied molecules. The equations of the plots are $y = 17.80x$; $R^2 = 0.9984$ for reference standard, $y = 39.907x$; $R^2 = 0.9946$ for HMP in PVC and $y = 35.458x$; $R^2 = 0.9966$ for HMP in EtOH. The data obtained and quantum yield (Φ_F) values calculated according to Eq.:

$$\Phi_S = \Phi_R \left(\frac{Grad_S}{Grad_R}\right)\left(\frac{\eta_S^2}{\eta_R^2}\right)$$

where R and S denote standard and sample, respectively, Grad is the gradient from the plot and η is the refractive index of the solvent or polymer matrix material. The data obtained are shown in Table 1.

3.2. Fluorescence spectral responses of HMP

In order to perform the fluorescence characterization of the HMP, the emission and excitation spectra of HMP were recorded in solvents of different polarities and PVC matrix. The gathered excitation-emission spectra are shown in Fig. 2. The Stokes shift values, $\Delta\lambda_{ST}$ (the difference between excitation and emission maxima) were extracted from spectral data which are given in Table 1. Since larger Stokes shifts are obtained in polar solvents [38], the highest Stokes shift for HMP was observed in EtOH, which confers to the advantage of better spectral resolution in emission based studies. Moreover, HMP exhibited higher fluorescence intensity in PVC matrix compared to that in the solvents. The immobilization of HMP molecules in solid matrix may reduce intramolecular motions and rearrangements, thus leading to enhanced fluorescence capability.

As shown in Fig. 3, fluorescence spectra of HMP immobilized in PVC membrane (5 μM) showed a very weak fluorescence when excited at 401 nm in the absence of metal ions. When 10 equiv. metal ions of K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Mn^{2+}, Fe^{3+} and Cr^{3+} were added, no obvious changes on fluorescence intensity could be observed (Fig. 3). However, under the same condition of Hg^{2+} (10 equiv.) resulted in a remarkably enhancement of fluorescence at 551 nm.

3.3. Optimization of the membrane composition

It is well known that the composition of the PVC membranes can naturally affect their characteristics [39], hence, some different compositions of the Hg^{2+}-selective membrane were optimized and the results are summarized in Table 2.

$$L_{(org)} + K^+ + TpClPB^- + Hg^{2+}_{(aq)} \rightleftharpoons LHg_{(org)} + TpClPB^-_{(org)} + K^+_{(aq)}$$

Scheme 1. Response mechanism of immobilized HMP on PVC membrane toward Hg^{2+}.

Table 1
Emission and excitation spectral data of HMP in various solvents and PVC membrane.

Solvent	Polarity index (*P*)	Wavelength (nm)		$\Delta\lambda_{ST}$ (Stock's shift, nm)	Refractive index	Quantum yield
		λ_{ex}	λ_{em}		η	Φ_F
DCM	3.1	387	465	78	1.42	–
THF	4	380	473	93	1.40	–
EtOH	5.2	388	511	123	1.36	0.008
PVC	–	401	551	150	1.52	0.097

A comparative study on the effect of different plasticizers and matrix materials on the performance of sensor has been made. Several optode membranes were prepared using different plasticizers such as DOP, DOS, DAO, NPOE, and the fluorescence measurements were made for different concentrations of Hg^{2+}. The widest working concentration range was obtained with NPOE; therefore, this plasticizer was used in the following studies. Lipophilic borate salts are frequently used as anionic additives in potentiometric and optical cation-selective sensors based on solvent polymeric membranes [40]. The amount of anionic sites in the membranes has effects on the linear range and selectivity of optodes [41]. The composition of the optode membrane with respect to KTpClPB was optimized by preparing several membranes with different amounts of KTpClPB. From the results shown in Table 2, one can see that the response concentration range of the optode membrane becomes wider and response time shorter as the amount of KTpClPB in the optode membrane increases from 1% to 2%. Therefore, 2% KTpClPB provided the best response for Hg^{2+} and was chosen for further studies.

As is seen in Table 2, the presence of 3 wt.% of HMP in the PVC membrane resulted in an improved lower limit of the working range. Further addition of the ionophore, however, was found to decrease the optode response which could have been due to the phenomenon of saturation of the membrane with the ionophore at amounts higher than 3 wt.%.

3.4. Effects of pH

The pH of the sample solution influences on the sensor selectivity and the linear dynamic range [42]. The influence of pH of the test solution on the fluorescence response of the proposed Hg^{2+} sensor was studied and the fluorescence intensity versus pH plot for the HMP optode was obtained by changing the solution pH with different buffer solutions and fixing the Hg^{2+} concentration at 1×10^{-8} mol/L (Fig. 4). The response of the optode is based on the Hg^{2+}–H^+ exchange between the membrane and the solution phases.

The pH of solution was adjusted by CH_3COOH/CH_3COONa buffer, potassium hydrogen phthalate buffer, Tris–HCl buffer and NH_4Cl/NH_3 buffers. As it is seen, the response of the sensor is independent of the pH of the test solution in a range of 4.0–7.0. At pH < 4.0 the fluorescence response of the sensor membrane decreased with decreasing pH value due to proton binding by imine nitrogen [43] and on the other hand, the diminished fluorescence response at pH > 7.0 could be attributed to the formation of Hg^{2+} ion hydroxides, as well as a possible slight swelling of the polymeric film under alkaline conditions. Hence, in the subsequent experiments, the pH values of all solutions were adjusted to 5.0 for further studies.

3.5. Response mechanism, binding mode and measuring range

When HMP (H_2L) was doped in plasticized PVC together with the anionic additive KTpClPB at pH 5.0, the system becomes a selective Hg^{2+} sensor and the fluorescence intensities of the optode membrane gradually increased with increasing Hg^{2+} concentrations. The lipophilic anionic sites, i.e. $TpClPB^-$ provide the optode membrane with the necessary ion-exchange properties because the flouroionophore acts as a neutral ligand and hence cannot function as an ion exchanger. The overall equilibrium between the

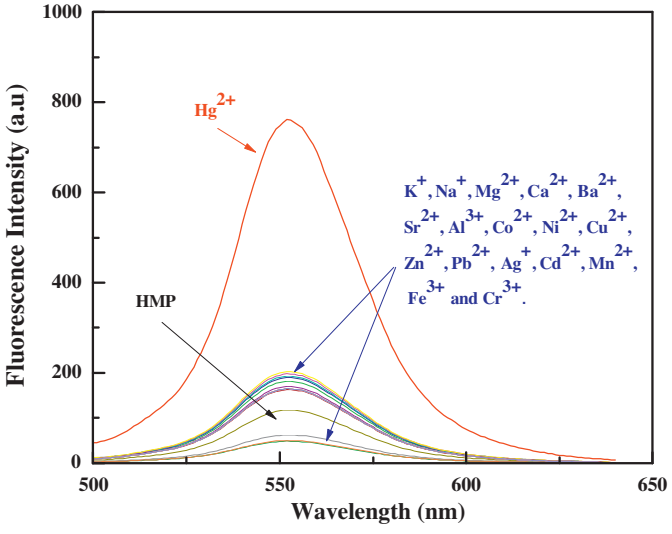

Fig. 3. Emission spectra of HMP sensing membrane after exposure to 1.0 μM different metal ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+},$Al^{3+}$and Hg^{2+}).

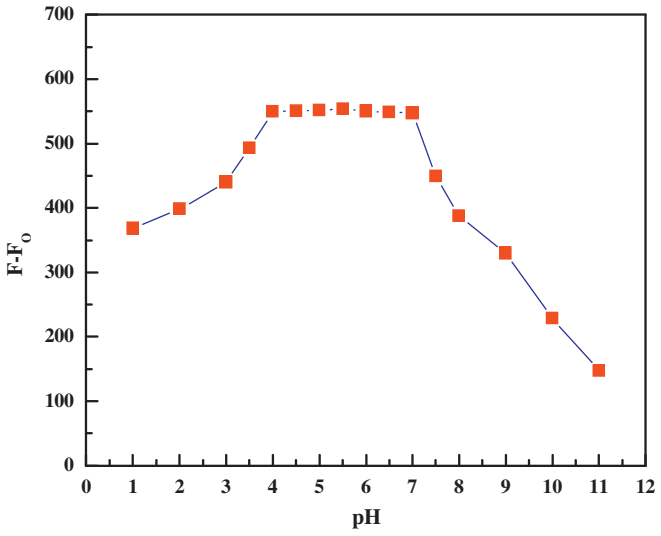

Fig. 4. Effect of pH on the response of the HMP optode in the presence of 1.0 μM Hg^{2+} at 551 nm (λ_{ex} = 401 nm).

Table 2
The effect of membrane ingredients on the response behavior of optodes ($n = 5$).

Optode no.	PVC (mg)	Plasticizer (mg)	KTpClPB (mg)	ATBD (mg)	Working concentration range (mol L^{-1})	Response time (s)
1	30	DOP (67)	0	3	5.0×10^{-6} to 1.0×10^{-4}	135
2	30	DOS (67)	0	3	1.0×10^{-6} to 5.0×10^{-3}	170
3	30	DOA (67)	0	3	5.0×10^{-7} to 3.0×10^{-4}	210
4	30	NPOE (67)	0	3	1.0×10^{-9} to 3.0×10^{-4}	110
6	30	NPOE (66)	1	3	1.0×10^{-10} to 1.0×10^{-3}	100
7	30	NPOE (65)	2	3	2.27×10^{-11} to 1.13×10^{-3}	75
8	30	NPOE (64)	3	3	6.4×10^{-7} to 4.0×10^{-5}	90
9	30	NPOE (64)	4	2	8.0×10^{-7} to 3.0×10^{-3}	95
10	30	NPOE (64)	5	1	2.0×10^{-6} to 3.0×10^{-4}	115

aqueous sample solution (aq) and the organic membrane phase (org) is represented in Scheme 1.

Schiff bases containing nitrogen, oxygen and sulphur chelating groups in their structures have received much attention because of their complexing behavior toward heavy metals [44,45].

The enhancement of the fluorescence of Hg^{2+} complex compared to the parent ligand may be due to CHEF (chelation enhancement of fluorescence emission) [46]. Factors like a simple binding of the ligand to the metal ions [47], an increase in rigidity in structure [48] seem to be responsible for fluorescence enhancement.

In order to elucidate the complexation behavior of HMP with Hg^{2+}, ^1H NMR experiments were carried out in DMSO-d_6. Fig. 5 displays the chemical shifts of receptor HMP upon the addition of

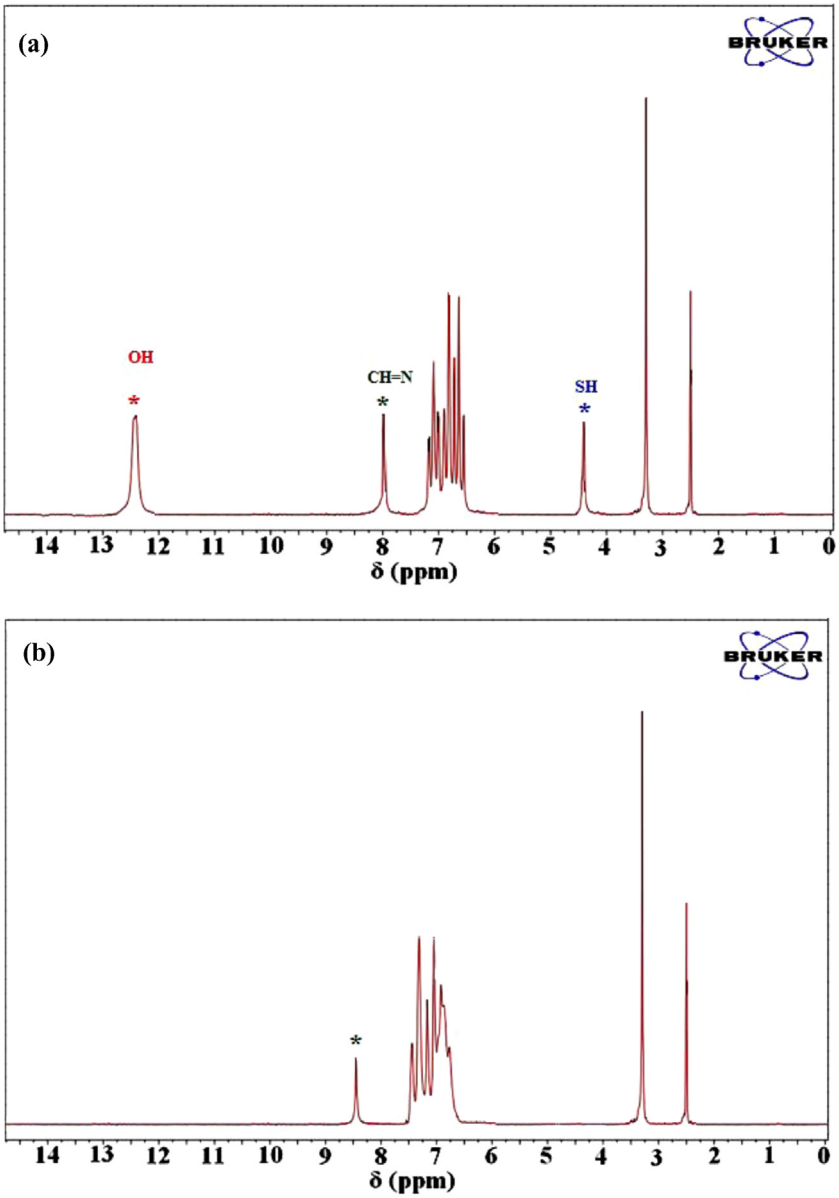

Fig. 5. ^1H NMR spectra of sensor HMP (1.0 μM) in absence (a) and in presence of 1.0 equiv. Hg^{2+} (b).

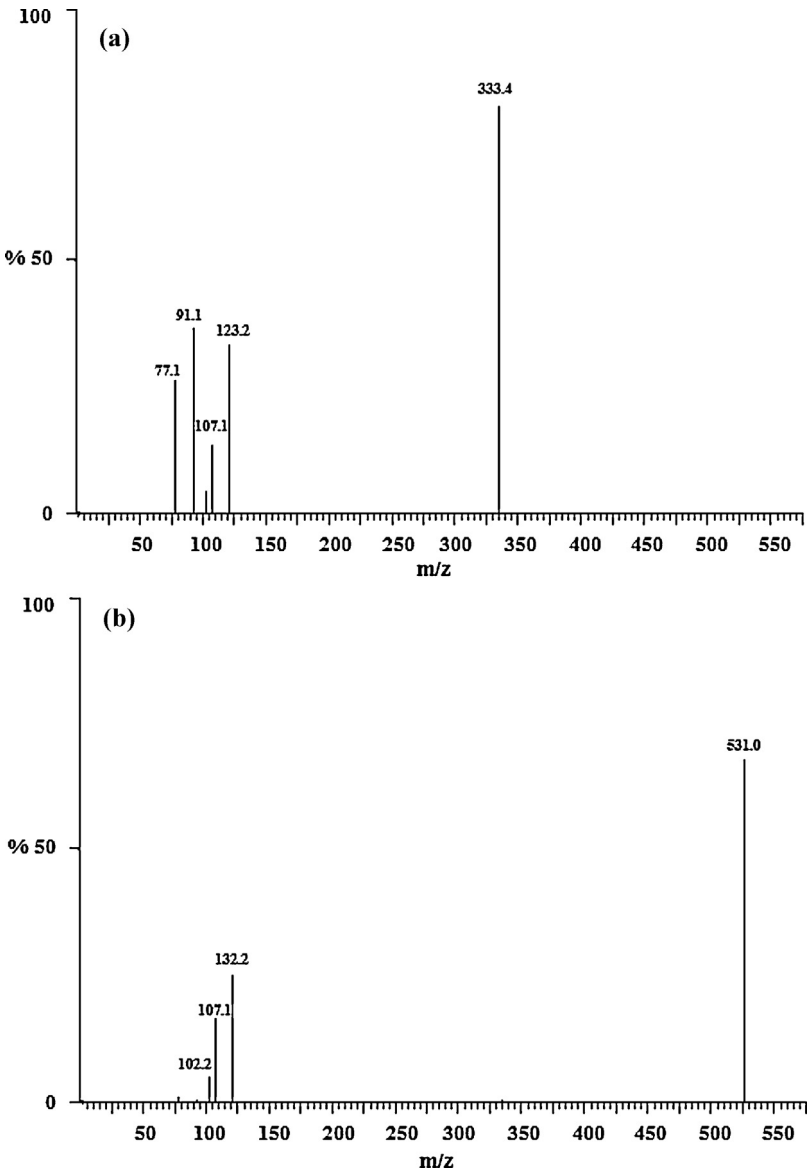

Fig. 6. TOF-MS spectra of sensor HMP (1.0 μM), (a) in absence and (b) in presence of 1.0 equiv. Hg^{2+}.

Hg^{2+} ion. A shown in Fig. 5, in the presence of 1.0 equiv. of Hg^{2+}, the singlet signals of the protons at δ 12.38 and 4.38 ppm disappeared, which suggested that Hg^{2+} bound to both oxygen and sulphur atoms of HMP backbone via deprotonation of both OH and SH groups. Furthermore, the resonance signal at δ 7.88 ppm in the parent HMP which was attributed to the azomethine (—CH=N—) protons displayed a down filed shift (δ 8.31) upon the addition of Hg^{2+} which originated from the coordination of the azomethine nitrogen to Hg^{2+}. In good agreement with this finding, the recognition mechanism of the sensor HMP with Hg^{2+} was also investigated by TOF-MS spectroscopy (Fig. 6). The positive-ion mass spectrum of HMP (H_2L) showed an obvious peak at m/z 333.4 assignable $[HMP+H]^+$ and upon addition of Hg^{2+} (1 equiv.), an intense peak at m/z = 531.0 assignable [HgL], corroborating 1:1 binding stoichiometry of HMP with Hg^{2+}.

Fig. 7 shows the fluorescence emission spectra of the sensing membrane exposed to the solutions containing different concentrations of Hg^{2+} (λ_{em} = 551 nm). The linearity was determined by plotting the fluorescence enhancement value ΔF ($\Delta F = F - F_0$, where F_0 and F were the fluorescence emission intensities before and after addition of Hg^{2+}) against the logarithm of Hg^{2+} concentration, obtaining a linear equation of $\Delta F = 1363.83 + 102.45 \log [Hg^{2+}]$ ($R^2 = 0.9998$) in the concentration range of 2.27×10^{-11} to 1.13×10^{-3} mol/L (Fig. 8). The limit of detection (LOD) based on 3σ of the blank was 9.57×10^{-12} mol/L.

3.6. Response time, repeatability, reproducibility, short-term stability, lifetime and regeneration

The dynamic response time of the present optode is controlled by the time required for the analyte to diffuse from the bulk of the solution toward the membrane interface to associate with the ligand. Fig. 9 shows the optical response of the proposed Hg^{2+}-selective fluorescence sensor at different mercury ion concentrations (1.0×10^{-12} to 1.0×10^{-2} mol/L), obtained under optimal membrane ingredients at pH 5.0. As shown in Fig. 9, the response of the membrane was found to be about 120 s to reach equilibrium over the entire calibration concentration of the Hg^{2+} ion.

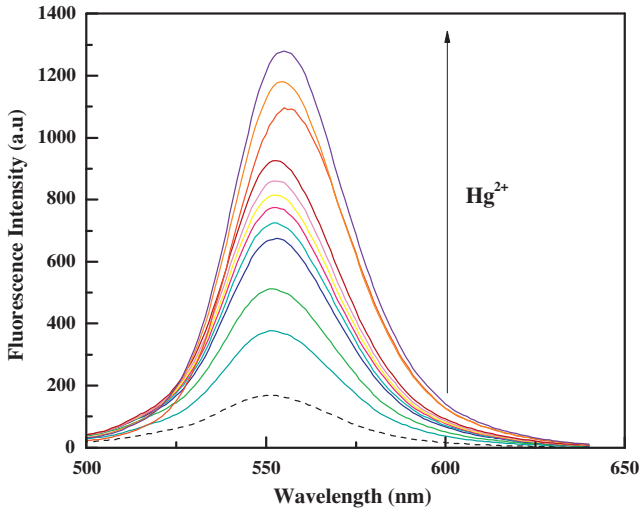

Fig. 7. Emission spectra of HMP sensing membrane after exposure to different Hg^{2+} concentrations (1.0×10^{-12} to 1.0×10^{-2} mol/L) at pH = 5.0. Dashed curve represent blank solution and arrows show the changes in fluorescence intensity with respect to an increase of Hg^{2+} concentration (λ_{ex} = 401 nm and λ_{em} = 551 nm).

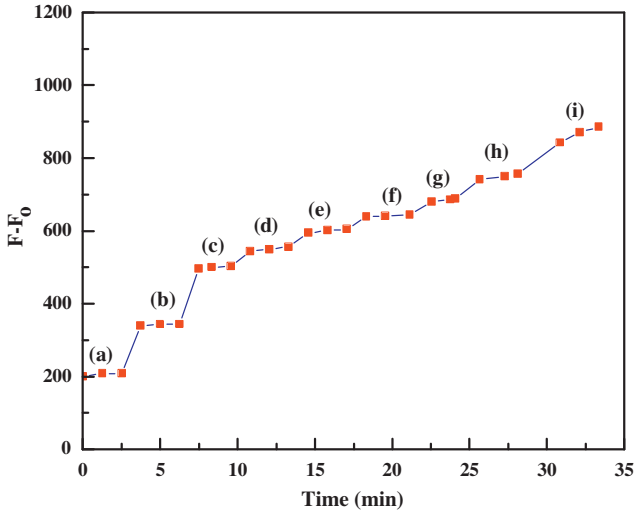

Fig. 9. Dynamic response time of the optical sensor at pH 5.0 for Hg^{2+} ion at (a) 1.0×10^{-11}, (b) 1.0×10^{-10}, (c) 1.0×10^{-9}, (d) 1.0×10^{-8}, (e) 1.0×10^{-7}, (f) 1.0×10^{-6}, (g) 1.0×10^{-5}, (h) 1.0×10^{-4}, (i) 1.0×10^{-3} mol/L.

The repeatability of the proposed optode was evaluated by repetitive exposing the optode into 1.0×10^{-8} mol/L Hg^{2+} solution. The relative standard deviation of the measured absorbance values (λ_{em} = 551 nm) in Hg^{2+} solution was ~1.94% for eight measurements.

The difference in the response of individual sensors was evaluated by preparing eight membranes and the reproducibility of the response of different sensors was obtained for determination of 1.0×10^{-8} mol/L Hg^{2+} ion. The relative standard deviation of the measured fluorescence values (λ_{em} = 551 nm) in Hg^{2+} solution was ~3.5%. The results show that the reproducibility of the proposed sensor is satisfactory.

To study the short-term stability of the optode membrane, the fluorescence intensity of the membrane in contact with 1.0×10^{-8} mol/L Hg^{2+} at pH 5.0 over a period of 5 h with an interval of 30 min (n = 10). From the fluorescence measurements, the membrane exhibited good stability with a relative standard

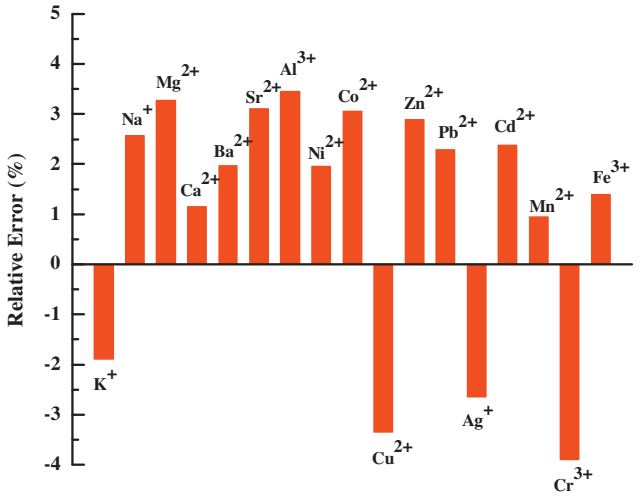

Fig. 10. Interferences of different metal ions (1.0×10^{-2} mol/L) onto the fluorescence determination of Hg^{2+} ion (1.0×10^{-8} mol/L) using the proposed membrane sensor at pH 5.0.

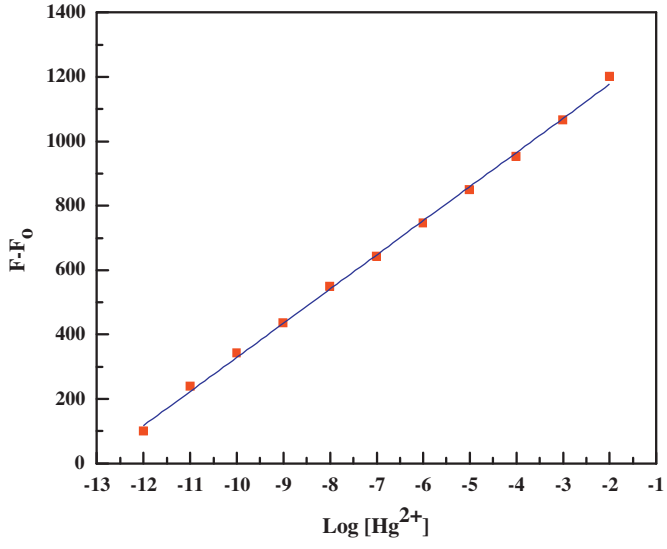

Fig. 8. Calibration plot of the sensor in the concentration range of 1.0×10^{-12} to 1.0×10^{-2} mol L^{-1} at pH = 5.0 (λ_{ex} = 401 nm).

Table 3
Determination of Hg^{2+} in real samples of six replicate measurements.

Sample	Amount of mercury[a]		Relative error (%)
	CVAAS	Proposed sensor	
Hair samples[c]			
1	172.90[a] ± 0.90[b]	174.05[a] ± 0.80[b]	−0.66
2	279.50[a] ± 4.40[b]	280.32 ± 1.40[b]	−0.29
3	197.50[a] ± 2.40[b]	195.93 ± 1.25[b]	0.79
Urine samples[d]			
1	3.47[a] ± 0.05[b]	3.45[a] ± 0.05[b]	0.57
2	3.80[a] ± 0.08[b]	3.75 ± 0.08[b]	1.31
3	3.65[a] ± 0.02[b]	3.59[a] ± 0.02[b]	1.64
Well water samples[d]			
1	1.72[a] ± 0.03[b]	1.74[a] ± 0.02[b]	−1.16
2	1.10[a] ± 0.07[b]	1.08[a] ± 0.06[b]	1.81
3	1.45[a] ± 0.05[b]	1.48[a] ± 0.07[b]	−2.06

[a] Mean values of three determinations.
[b] Standard deviation.
[c] Reported value: μg/kg.
[d] Reported value: μg/L.

Table 4
Comparison between the proposed optode for determination of Hg^{2+} and recent literatures.

Reagent	Membrane	Working range (mol L^{-1})	Limit of detection (mol L^{-1})	Response time (s)	Signal	Reference
4-(2-Pyridylazo)-resorcinol	Triacetylcellulose	5.0×10^{-6} to 3.4×10^{-3}	1.5×10^{-6}	1200	Fluorescence	[49]
Tetra(p-dimethylaminophenyl) porphyrin	PVC	4.0×10^{-8} to 4.0×10^{-6}	8.0×10^{-9}	300	Fluorescence	[50]
4-Ethyl-5-hydroxy-5,6-di-pyridin-2-yl-4,5-dihydro-2H-[1,2,4]triazine-3-thione Hexathiacyclooctadecane	PVC	5.0×10^{-10} to 5.0×10^{-5}	1.8×10^{-10}	360	Fluorescence	[51]
(1Z,2Z)-N_1,N_2-dihydroxy-N1,N2-dipyridin-2-ylethanediimidamide	PVC	5.78×10^{-9} to 1.05×10^{-3}	1.71×10^{-9}	<120	Fluorescence	[52]
Rhodamine B derivative	PVC	1.0×10^{-9} to 2.0×10^{-3}	8.1×10^{-10}	180 –900	Fluorescence	[53]
N,N/bis(2-aminothiophenol)benzene-1,2-dicarboxaldehyde	PVC	1.0×10^{-10} to 1.0×10^{-2}	7.23×10^{-11}	45	Fluorescence	[54]
N-(2-hydroxyphenyl)-N′-(2-mercaptophenyl)-o-phthalideneimine	PVC	2.27×10^{-11} to 1.13×10^{-3}	9.57×10^{-12}	120	Fluorescence	Current method

derivation of less than 2.0 after 5 h monitoring. In addition, it was found that the membrane sensor could be stored in wet conditions without any measurable change in its fluorescent intensity for at least 2 months, which implies that the fluoroionophore HMP is quite stable in a membrane contacting with water. Thus, the sensor was immersed in phthalate buffer (pH 5.0) when not in use.

It is necessary that the membrane sensor be regenerated by a suitable solution, and get ready for the following measurements. The reversibility of the optode was checked by washing the used optodes with thiocyanate, iodate, EDTA, HNO_3 and HCl, all 0.1 mol/L in concentration. The optical sensor was put in a mercury solution (1.0×10^{-8} mol/L) to reach the equilibrium. Then, the result membrane was put in the regenerating solution until the fluorescence of the membrane got stabilized. The results showed that, the optodes could be regenerated in 0.10 mol/L HNO_3 solution within 420 s. Therefore, each optode can be used several times for Hg^{2+} analysis.

3.7. Sensor selectivity

The selectivity behavior which is the relative optode response for the primary ion over other ions present in solution is one of the most important characteristics of any ion-selective optical sensor. To investigate the selectivity of the proposed membrane sensor, the interference of foreign ions with the determination of Hg^{2+} (1.0×10^{-8} mol/L) was examined under the experimental conditions. The tolerance limit was taken as the maximum concentration of the foreign substances which caused an approximately ±5% relative error in the determination of Hg^{2+}.

The resulting relative error was defined as is defined as RE (%) = $[(F - F_0)/F_0] \times 100$ where F_0 and F are the fluorescence intensity before after addition of some potentially interfering ions. The experimental results (Fig. 10) revealed that most alkali, alkaline earth, and many transition metal cations do not show significant interference on the Hg^{2+} assay, where the observed relative error is considered as tolerable.

3.8. Analytical applications

To investigate the potential use of the new sensor, an attempt was made to determine Hg^{2+} ions in different real samples including human hair samples, urine samples and well water samples. The water samples were collected from three different places in Tabuk (Saudi Arabia). For evaluating the accuracy of the method, a comparison between results obtained by proposed method and cold vapor atomic absorption spectrometry (CVAAS) was performed. As can be seen in Table 3, the results obtained for both methods have good agreements.

3.9. Comparison of the proposed optode with previously reported methods

The present proposed sensor was compared to recently Hg^{2+} sensing methods based on fluorescence signal measurements (Table 4) [49–54]. As can be seen, the proposed sensor shows better selectivity and lower limit of detection (9.57×10^{-12} mol/L) relative to other reported methods.

4. Conclusion

The results obtained from the present study show that, a novel simple, sensitive and time saving method for routine environmental analysis of with good sensitivity and precision without the need of a pre-concentration step. The novel method based on synthesis of a highly sensitive tetradentate Schiff base receptor namely: N-(2-hydroxyphenyl)-N′-(2-mercaptophenyl)-o-phthalylidene (HMP) immobilized within a plasticized PVC membrane. The optode is fully reversible and can be regenerated readily with dilute nitric acid solution. The proposed optode has a wide response range, high reproducibility, and relatively short response time. The proposed fluorescence optode was successfully applicable for field analysis and the determination of the Hg^{2+} ions different real samples.

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