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ORIGINAL PAPER

Development of an Optode for Detection of Trace Amounts of Hg^{2+} in Different Real Samples Based on Immobilization of Novel Tetradentate Schiff Bases Bearing Two Thiol Groups in PVC Membrane

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Abstract A very sensitive and reversible optical chemical sensor based on a novel tetradentate Schiff base namely N.N′bis(2-aminothiophenol)benzene-1,2-dicarboxaldehyde (ATBD) immobilized within a plasticized PVC film for Hg^{2+} determination is described. At optimum conditions (i.e. pH 6.0), the proposed sensor displayed a linear response to Hg^{2+} over 1.0×10^{-10} – 1.0×10^{-2} mol L^{-1} with a limit of detection of 7.23×10^{-11} mol L^{-1} (0.0145 μgL^{-1}). Moreover, the results revealed that, under batch condition, the sensor is fully reversible within a response time~35 s. In addition to its high stability and reproducibility, the sensor showed good selectivity towards Hg^{2+} ion with respect to common metal cations. The sensor was successfully applied for determination of Hg^{2+} ion in some real samples, including hair, urine and well water samples. The results were in good correlation with the data obtained using cold vapor atomic absorption spectrometry.

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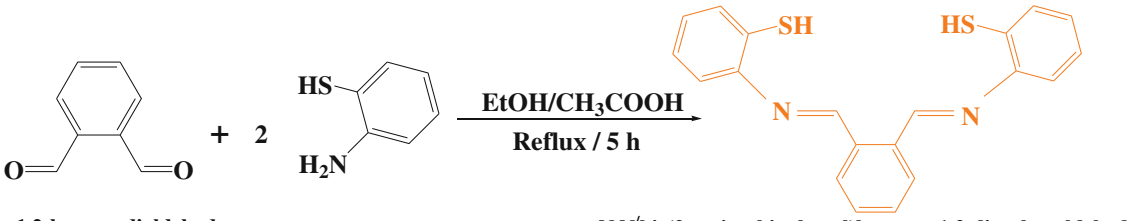
Introduction

Development of sensitive chemosensors have been receiving much attention in recent years because of their potential applications in clinical biochemistry and environment. Metal-selective fluorescent chemosensors are served as useful tools for detection of metal ions due to their intrinsic sensitivity and selectivity [1, 2].

Chemical optical sensors (optodes) offer several advantages such as simple preparation procedure, relatively fast response, wide response range, reasonable selectivity and high sensitivity [3, 4]. The immobilization of various sensing reagents of optode membranes have been developed for many analytically relevant ions, especially heavy metal ions. Immobilization of dyes into or onto a solid support is a key issue for their application in optical sensing [5]. The reagent is normally physically entrapped by adsorption, electrostatic attraction or chemical bonding to the solid support. Generally, sol–gel glasses [6, 7] or polymer matrices [8, 9] are used for the preparation of the optodes. Poly(vinyl chloride) (PVC) has been used for the preparation of membrane optodes due to its relatively low cost, good mechanical properties and amenability to plasticization [10].

Mercury ion is one of the most prevalent toxic heavy metal ions causing environmental and health problems because of its wide distribution and severe immunotoxic, genotoxic, and neurotoxic effects [11–13]. Hg^{2+} is a highly stable inorganic form of mercury, which, according EPA and WHO guidelines, must be in concentrations<0.002 mgL^{-1} in well water [14].



1,2-benzenedialdehyde 2-aminothiophenol N.N/bis(2-aminothiophenol)benzene-1,2-dicarboxaldehyde

ATBD

Scheme 1 Synthetic route of ATBD

Many current techniques for mercury screenings were assigned such as atomic absorption spectrometry [15–18], inductively coupled plasma-mass spectroscopy [19–21], X-ray fluorescence spectrometry [22, 23], neutron activation analysis [24, 25], cold vapor atomic absorption spectrometry [26], electrothermal atomic absorption spectrometry [27–29], anodic stripping voltammetry [30–33], high-performance liquid chromatography [34–36], atomic fluorescence spectrometry [37], potentiometric ion-selective electrodes [38–40] and spectrophotometry [41–50].

Most of these methods suffer from some problems such as poor reproducibility, limited sample adaptability, high cost, well-controlled experimental conditions, multi-step sample pre-treatments, some inherent interference, time consuming procedures and too expensive involving the use of sophisticated instrumentation, the wide utilization of these methods is largely limited. So, for simplicity, convenience, no necessity of the reference solution, low cost, and fieldwork applicability the easily prepared optical sensors are highly demanding.

Recently, some selective fluorescent chemosensors for Hg^{2+} based on fluorescence enhancement or fluorescence quenching has been reported [51–67]. However, most of 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 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. They produce remarkable selectivity, sensitivity and stability for a specific ion [68–71].

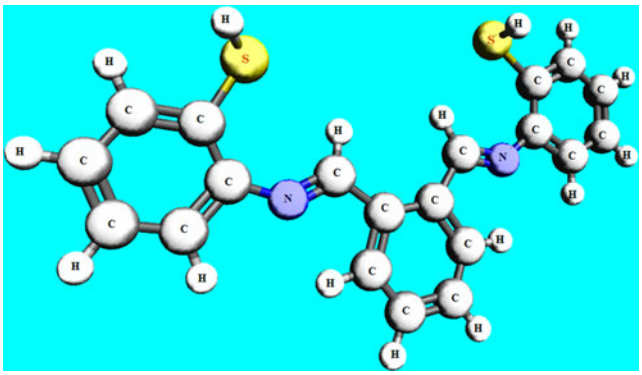


Fig. 1 Optimal structure of the chemosensor (ATBD)

Keeping these facts in mind, in this work, we develop an optode for sensitive and selective determination of Hg^{2+}. This optode is prepared by immobilizing a novel tetradentate Schiff base bearing two thiol groups as the sensing reagent in PVC membrane according to a simple method. The membrane sensitivity, selectivity, reproducibility, short-term stability, lifetime and regeneration under optimum conditions were fully studied. Moreover, the response mechanism and binding mode were investigated by ^{1}H NMR and TOF-MS. Finally, the novel sensor was applied for determination of Hg^{2+} ion in some different real samples, including hair, urine and well water samples.

Experimental

Instruments

All fluorescence measurements were carried out 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 performed on a 300 MHz NMR spectrometer in DMSO-d_6 solvent and TMS was used as an internal reference. Mass spectra (TOF-MS) were recorded on Waters (USA) KC-455 model with ES^+ mode in DMSO.

Materials and Reagents

2-aminothiophenol, benzene-1,2-dicarboxaldehyde (o-phthaldhyde) and the lipophilic anionic additive reagent potassium tetrakis-(4-chlorophenyl) borate (KTpClPB) were supplied from Aldrich. The polymer membrane components, polyvinyl

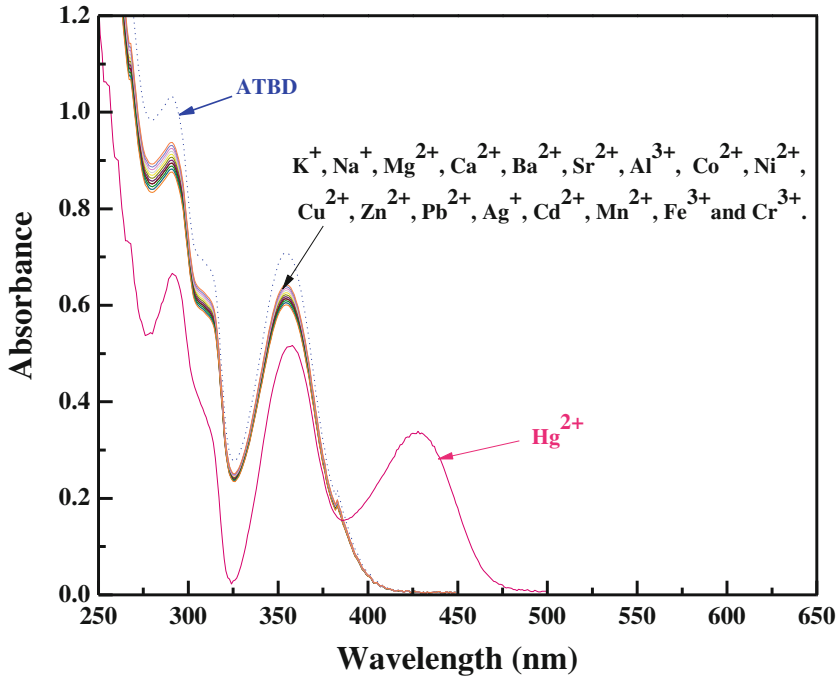


Fig. 2 UV–Vis absorption spectra of ATBD (2.0 μM) with 1 equivalent metal ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+} and Hg^{2+})

chloride (PVC) (high molecular weight) and the plasticizers, bis-(2-ethylhexyl) phtalate (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 [72]. The stock solution was serially diluted to achieve the desired concentrations.

Synthesis of N.N′bis(2-aminothiophenol) benzene-1,2-dicarboxaldehyde (ATBD)

An ethanolic solution of 2-amiothiophenol (10 mmol) was mixed with an ethanolic solution of o-phaldehyde (5 mmol), 2 drops of acetic acid and magnetically stirred in a round bottom flask. The reaction mixture was then refluxed for~5 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. Synthetic route of ATBD is shown in Scheme 1.

Characteristics of ATBD were as follows ($C_{20}H_{16}N_2S_2$): M.Wt: 348.494 Yield: 87 %. Color: Orange. Elemental analysis Calc. (%): C, 68.93; H, 4.62; N, 8.03 Found: C, 68.40; H, 4.39; N, 8.00. IR (KBr pellet. cm^{-1}): 2543 (ν_{SH}); 1612 ($\nu_{C=N}$); 798 (ν_{C-S}). ^1H NMR (DMSO-d_6, 300 MHz): δ 3.64 (s, 2H; SH); 8.23 (s, 2H; HC=N); 6.74−7.57 (m, 14H; aromatic). TOF-MS (m/z): 348 (M^+). The optimal structure of the chemosensor (ATBD) is shown in Fig. 1 by using Avogadro program Version 1.0.1.

Preparation of the Optode Membrane

Membrane solutions were prepared by dissolving 30 mg of PVC, 65 mg of plasticizer (DOS), 2.0 mg of KTpClPB and 3.0 mg ATBD 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

Fig. 3 The color change of the sensor upon complexation with Hg^{2+} ions (1 ATBD; 2 ATBD + Hg^{2+})

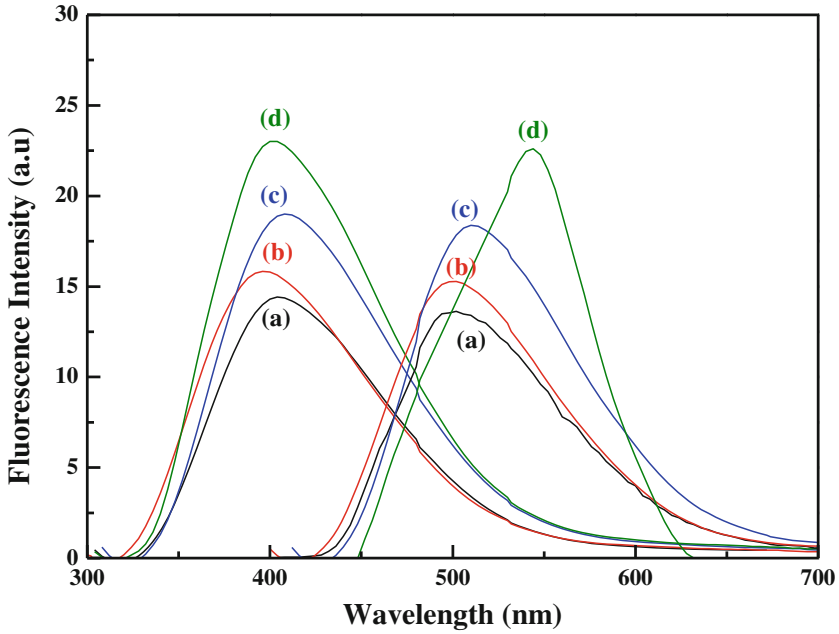


Fig. 4 Emission and excitation spectra of ATBD in (*a*) DCM, (*b*) THF, (*c*) EtOH and (*d*) PVC

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 [73, 74]. 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 use. Blank (reference) membranes were prepared in a similar way excluding ATBD from the membrane solution. Absorption and 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.

Measurement Procedure

The membranes were diagonally placed inside the sample cuvette of the instrument containing 2 ml buffer solution of pH 6.0 and a blank membrane (without ionophore) was put in the reference cuvett containing the buffer solution. The fluorescence intensity at an excitation wavelength of 403 nm was measured at 544 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 ~35 s (required to reach equilibrium).

Preparation of Real Samples

Hair Samples

Scalp hair samples as a suitable specimen for monitoring human exposure to mercury, were used in this study. The 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 [75]. 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.

Urine Samples

Most mercury present in the urine is in the form of inorganic mercury. The mercury concentration in the urine increases in relation to the level of inorganic mercury accumulated in the kidneys [76]. Accordingly, the total mercury value in the urine is an important biomarker for evaluating inorganic mercury/mercury vapor exposure. Dental clinics are known to be one of the largest users of inorganic and metalic mercury [77]. Mercury, which vaporizes at room temperature and easily enters the environment, is used in the preparation of amalgam alloy

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

Solvent	Polarity index (P)	Wavelength (nm)		Stokes shift	Refractive index
		λ_{ex}	λ_{em}	$\Delta\lambda_{ST}$ (nm)	η
DCM	3.1	406	502	96	1.42
THF	4	400	498	98	1.40
EtOH	5.2	408	510	102	1.36
PVC	–	403	544	141	1.52

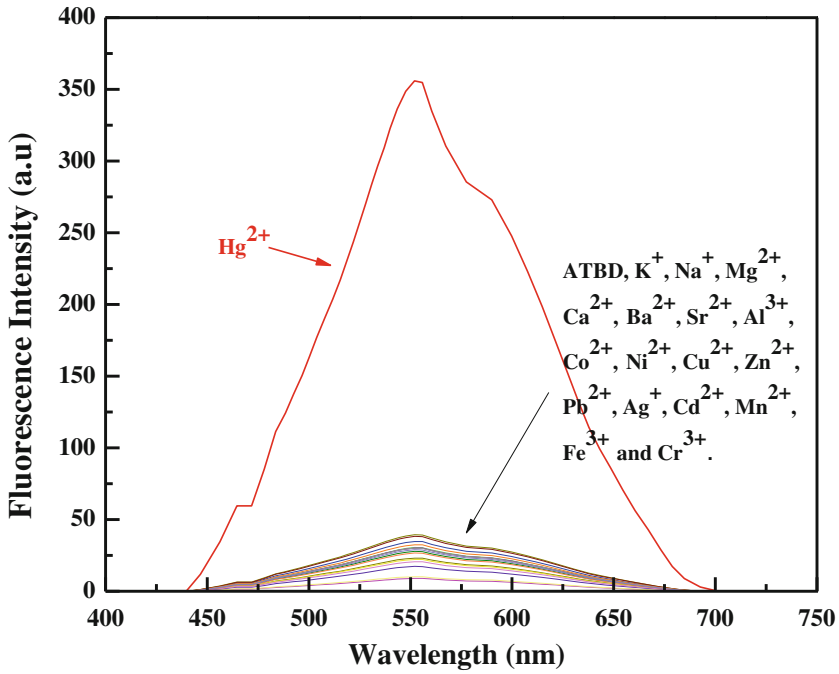


Fig. 5 Emission spectra of ATBD sensing membrane after exposure to 1.0 μM different metal ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+},$Al^{3+}$and Hg^{2+})

that consists chiefly of silver mixed with mercury and variable amounts of other metals and is used as a dental filling. It is well documented that dentists who work with amalgam are chronically exposed to mercury vapors, which can accumulate in their bodies to much more higher levels than for most non-occupationally exposed individuals. 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.

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 followed by addition of concentrated nitric acid, then the pH of water samples was adjusted to 6.0.

Results and Discussion

UV–Vis Spectral Responses of ATBD

It has been anticipated that, due to the presence of various donor sites in the form of N and S atoms, ATBD would behave as a potential ligand for complexation reaction with metal ions. To explore the properties of ATBD as an optically sensing material, various metal ions were tested in a preliminary experiment. The binding affinity of ATBD was monitored through absorption spectra of ATBD (2.0 μM) in

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 (sec)
1	30	NPOE (67)	0	3	6.4×10^{-7} to 2.0×10^{-5}	120
2	30	DOA (67)	0	3	2.6×10–6 to 1.0×10^{-5}	150
3	30	DOP (67)	0	3	5.0×10^{-7} to 3.0×10^{-4}	200
4	30	DOS (67)	0	3	1.0×10^{-8} to 3.0×10^{-4}	80
6	30	DOS (66)	1	3	1.3×10^{-9} to 2.0×10^{-3}	60
7	30	DOS (65)	2	3	1.0×10^{-10} to 1.0×10^{-2}	35
8	30	DOS (64)	3	3	6.4×10^{-7} to 4.0×10^{-5}	80
9	30	DOS(64)	4	2	8.0×10^{-7} to 3.0×10^{-3}	100
10	30	DOS (64)	5	1	2.0×10^{-6} to 3.0×10^{-3}	130

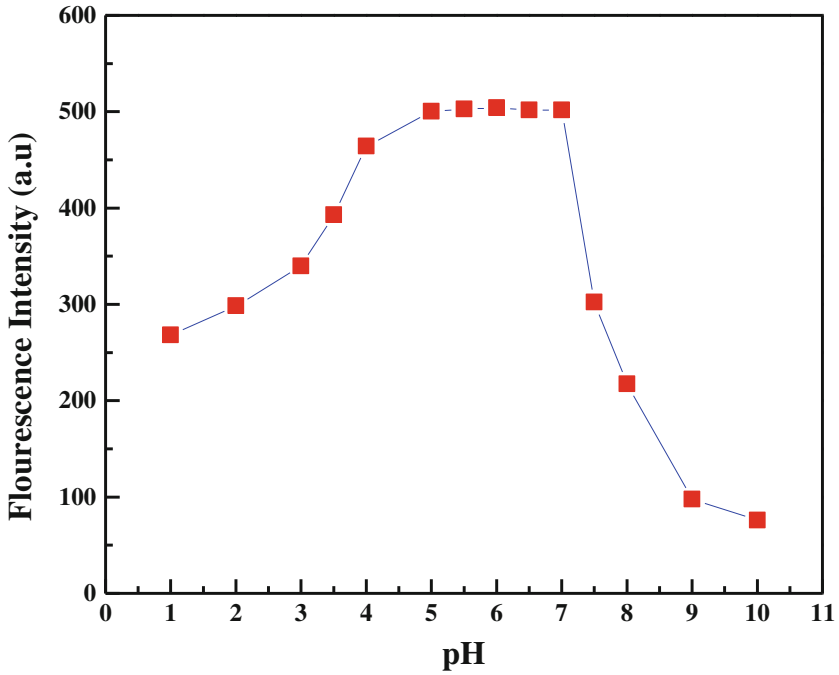


Fig. 6 Effect of pH on the response of the ATBD optode in the presence of 1.0 μM Hg^{2+} at 544 nm (λ_{ex} 403 nm)

absence and presence of 1 equivalent tested 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+} Cr^{3+} and Hg^{2+} (Fig. 2). As shown in Fig. 2, ATBD shows two absorption bands, the first at 293 which can be assigned to π-π* transitions from the benzene ring and the double bond of the azomethine group and the second at 356 nm due to n-π* transition of non-bonding electrons present on the nitrogen of the azomethine group. Upon addition of addition of Hg^{2+}, the color of ATBD solution concomitantly, changes from yellow-orange to a pink (Fig. 3), inducing a bathochromic shift of ATBD bands and a new band was originated at 428 nm, which may assigned to charge transfer. In contrast, addition of other metal ions showed insignificant changes. The results demonstrated that ATBD is characteristic of high selectivity toward Hg^{2+} over other competitive metal ions.

Fluorescence Spectral Responses of ATBD

In order to perform the fluorescence characterization of the ATBD, the emission and excitation spectra of ATBD were recorded in solvents of different polarities and PVC matrix. The gathered excitation-emission spectra are shown in Fig. 4. 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 [78], the highest Stokes shift for the ATBD was observed in EtOH. Moreover, ATBD exhibited higher fluorescence intensity in PVC matrix compared to that in the solvents. The immobilization of ATBD molecules in solid matrix may reduce intramolecular motions and rearrangements, thus leading to enhanced fluorescence capability.

In order to explore the selective sensing of ATBD towards Hg^{2+}, fluorescence spectra of ATBD immobilized on PVC membrane were measured in EtOH with respective metal ions including 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+} and Hg^{2+} (Fig. 5). As in shown in Fig. 5, ATBD exhibit weak fluorescence emission when excited at 403 nm and when Hg^{2+} (1.0 μM) was added, a prominent fluorescent enhancement was observed at 544 nm and it was found that the other studied ions didn't induce any apparent fluorescent enhancement.

Optimization of Composition of the Membrane Components

The response characteristics and working concentration range of optical membrane sensors are known to be largely affected by changes in the membrane composition [9, 79]. 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

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

Scheme 2 Response mechanism of immobilized ATBD on PVC membrane towards Hg^{2+}

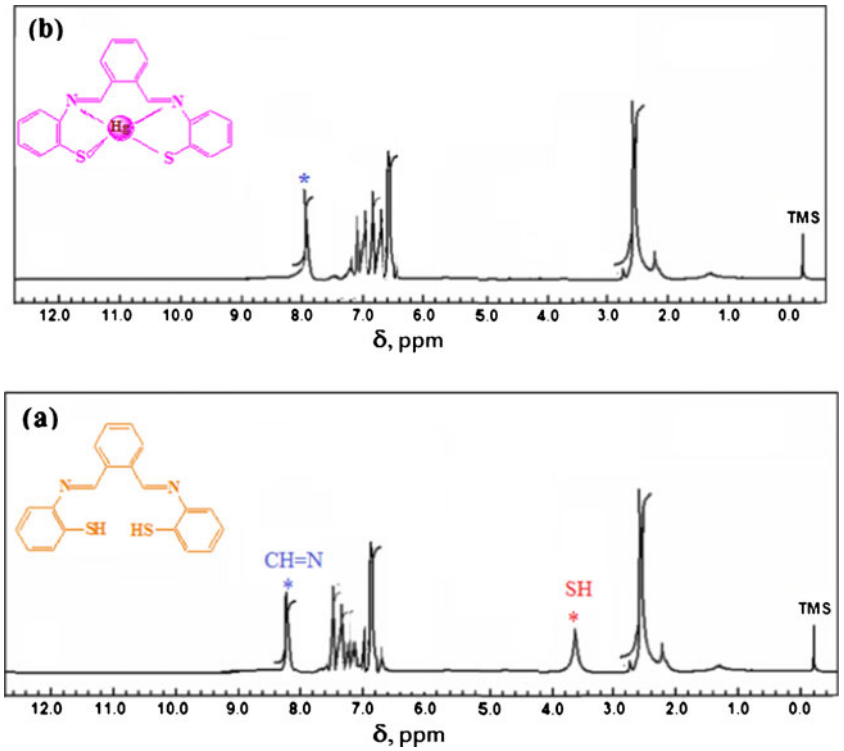


Fig. 7 ^{1}H NMR spectra of sensor ATBD (1.0 μM) with Hg^{2+} in d_6-DMSO: (**a**) ATBD and (**b**) ATBD + Hg^{2+} (1.0 eq.)

Hg^{2+}. The results are shown in Table 2. The widest working concentration range was obtained with DOS; therefore, this plasticizer was used for further studies. Lipophilic borate salts are frequently used as anionic additives in potentiometric and optical cation-selective sensors based on solvent polymeric membranes [80]. The amount of anionic sites in the membranes has effects on the linear range and selectivity of optodes [8]. The composition of the optode membrane with respect to KTpClPB was optimized by preparing several membranes with different amounts of KTpClPB. The response behavior of these optode membranes are shown in Table 2. From the results it can be seen that the response concentration range of the optode membrane becomes wider with shorter response time as the amount of KTpClPB in the optode membrane increases from 1 % to 2 %, which might be attributed to the increasing of hydrophilicity upon addition of KTpClPB. However, the response concentration range of the optode membrane becomes narrower when the content of KTpClPB is larger than 2 %. Therefore, 2 % KTpClPB provided the best response for Hg^{2+} and was chosen for further studies.

The data given in Table 2 give an indcation of the pronounced influence of the amount of the ionophore on the working range of the proposed optical sensor. As it can be seen, an increase in the amount of ATBD from 1 % to 3 % resulted in an improved lower limit of the working range, emphasizing the expected increase in the sensitivity of the optical sensor in the presence of increased amount of the ionophore in the membrane phase.

Effects of pH

The effect of the pH of the solution, in which the sensor is applied is a critical factor that must be considered definitely. To study the effect of pH on the optode response to Hg^{2+}, the fluorescence intensity versus pH plot was obtained by changing the solution pH with different buffer solutions and fixing the Hg^{2+} concentration at 1.0 μM (Fig. 6). The pH of solution was adjusted by buffers of $CH_3COOH/NaCH_3COONa$ Tris–HCl buffer and NH_4Cl/NH_3. As it is seen, the response of the sensor increased with increasing pH value of solution and reached a plateau between pH 5.0 and 7.0. At pH<5.0 the fluorescence response of the sensor membrane decreased with decreasing pH value due to proton binding by imine nitrogen [81] and on the other hand, the diminished fluorescence response at pH>7.0 could be attributed to the formation of Hg^{2+} ion hydroxides [82], 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 6.0 for further studies.

Response Mechanism, Binding Mode and Measuring Range

Among the various detection systems used in mercury optodes, those based on sulfur-containing ligands. Generally, these systems have shown better selectivity and sensitivity [82]. Hg^{2+} displays great affinity for soft coordination centers like sulfur [83, 84], therefore, ligand ATBD with sulfur-containing sites was investigated as an active ionophore for

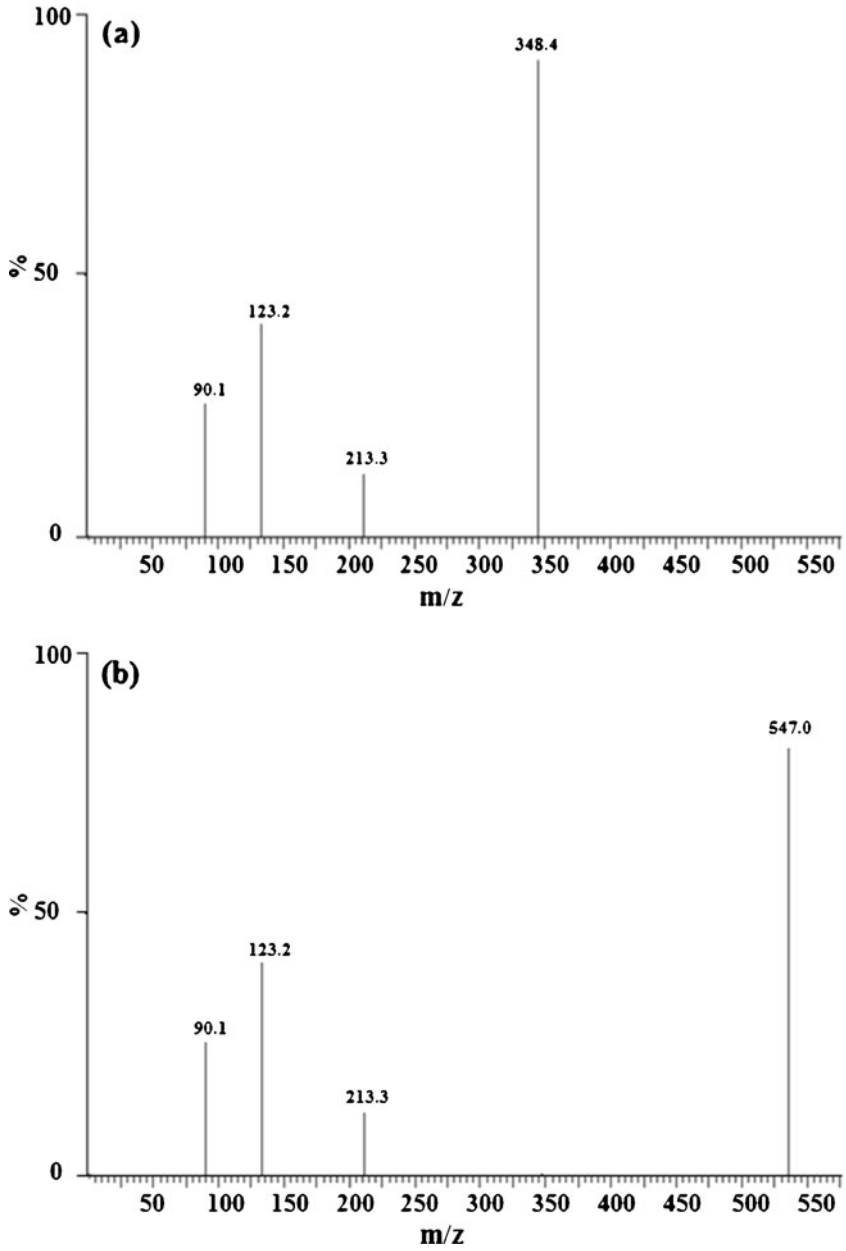
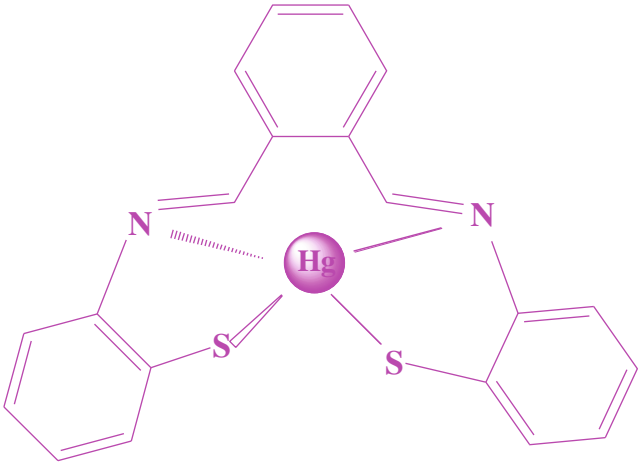


Fig. 8 TOF-MS spectra of sensor ATBD (1.0 μM) with Hg^{2+} in d_6-DMSO: (**a**) ATBD and (**b**) ATBD + Hg^{2+} (1.0 eq.)

highly selective and sensitive determination of mercury ion. Hg^{2+} bonding takes place with NSSN donor sites of the azomethine –N and thiophenolate -S [85]. When ATBD (LH_2) was doped in plasticized PVC together with the anionic additive KTpClPB at pH 6.0, the system becomes a selective Hg^{2+} sensor. Furthermore, the fluorescence intensities of the optode membrane gradually increased with increasing Hg^{2+} concentrations, which constitutes the basis for the determination of Hg^{2+} with the proposed sensor proposed in this work. 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 can't function as an ion exchanger. The overall equilibrium between the aqueous sample solution (aq) and the organic membrane phase (org) is represented in Scheme 2.

The enhancement of the fluorescence of Hg^{2+} complex compared to the parent ligand may be due to CHEF (chelation enhancement of fluorescence emission) [86]. Factors like a simple binding of the ligand to the metal ions [87], an increase in rigidity in structure [88], a restriction in the photo induced electron transfer (PFT) [89, 90] etc. are assigned to the appearance and enhancement of the photoluminescence (PL). In the present case, the first two factors seem to be responsible for the enhancement PL.

For elucidation the binding mode, the ^1H NMR-titration experiments were carried out. As shown in Fig. 7, the ^1H



Scheme 3 Plausible interaction mode of ATBD/Hg^{2+}

NMR spectrum of ATBD showed a singlet signal at δ 3.64 ppm which was attributed to thiol -SH protons. Upon addition of Hg^{2+}, the SH signal disappeared, which suggested that a Hg^{2+} bound to the two sulphur atoms of the ATBD backbone via deprotonation of SH groups. The singlet signal at δ 8.23 ppm in the parent ATBD which was attributed to the azomethine (-CH=N-) protons displayed an upper filed shift (δ 7.94) upon the addition of Hg^{2+} which originated from the coordination of the azomethine nitrogen to Hg^{2+}. Moreover, the binding mode of ATBD (LH_2) with Hg^{2+} was also examined by TOF-MS spectra (Fig. 8). The positive-ion mass spectrum of ATBD upon addition of Hg^{2+} (1 equiv) exhibited one intense peak at m/z=547, corresponding to the ion [HgL], corroborating the 1:1 binding stoichiometry of LH_2 (ATBD) with Hg^{2+}. Taken together, the above results indicated a plausible interaction mode of ATBD/Hg^{2+} as proposed in Scheme 3, in which Hg^{2+} ion was coordinated with two "N" and two "S" atoms of ATBD.

Figure 9 shows the fluorescence emission spectra of the sensing membrane exposed to the solutions containing different concentrations of Hg^{2+} (λ_{ex} 403 nm). The linearity was determined by plotting the fluorescence enhancement value ΔF (ΔF=F - F_0, where F_0 and F were the fluorescence emission intensities before and after addition of Hg^{2+}) against the negative logarithm of Hg^{2+} concentration, obtaining a linear equation of ΔF=995.99+84.689 log [Hg^{2+}] (R=0.9948) in the concentration range of 1.0×10^{-10} to 1.0×10^{-2} mol L^{-1} (Fig. 10). The limit of detection (LOD) based on 3σ of the blank was 7.23×10^{-11}.

Response Time, Reproducibility, Short-Term Stability, Lifetime and Regeneration

The dynamic response time, is an important analytical feature of any optode. The response time was tested by recording the fluorescence intensity change from a buffered solution at pH= 6 to a buffered Hg^{2+} solution over a wide concentration range (1.0×10^{-10} to 1.0×10^{-2} mol L^{-1}). The resulting intensity–time curve (Fig. 11) revealed that, the fluorescence intensity of the corresponding signal reached its equilibrium response in a relatively short time of less than 35 s. It was obvious that the response time is lower in concentrated solutions than dilute solutions.

The repeatability and reproducibility of optical sensors are two of their important characteristic features both of which

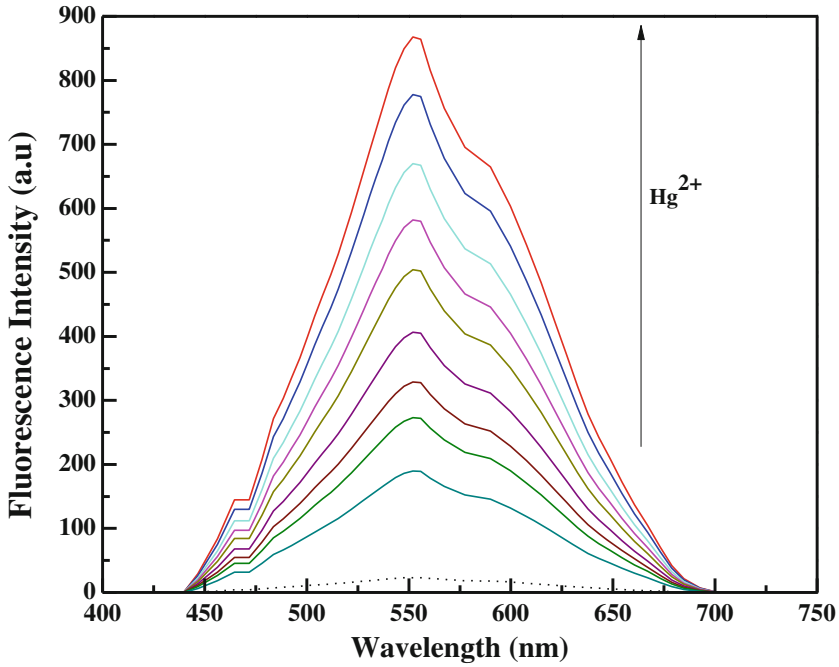


Fig. 9 Emission spectra of ATBD sensing membrane after exposure to different Hg^{2+} concentrations (1.0×10^{-10}–1.0×10^{-2} mol L^{-1}) at pH=6.0. *Dashed curve* represent blank solution and arrows show the changes in fluorescence intensity with respect to an increase of Hg^{2+} concentration (λ_{ex} 403 nm and λ_{em} 544 nm)

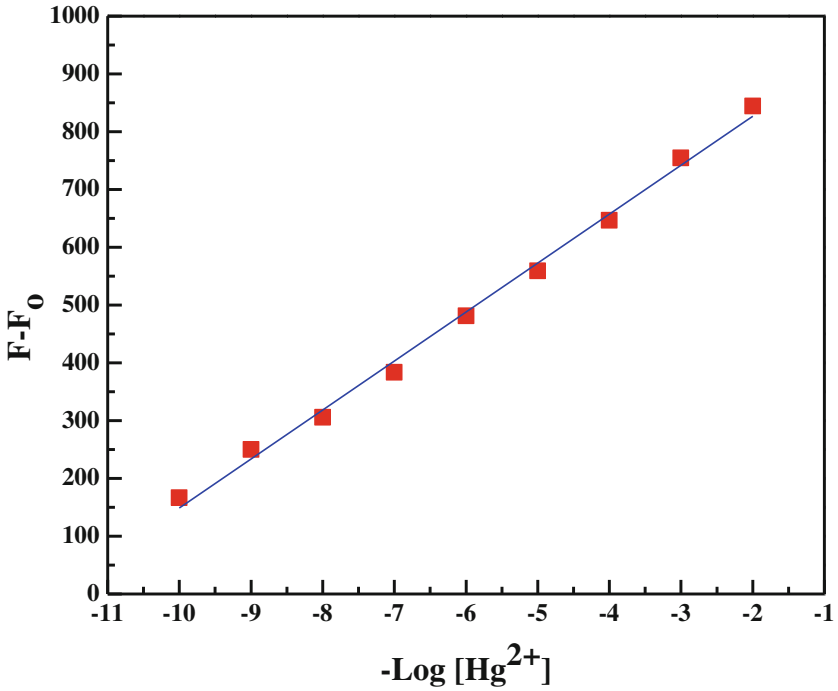


Fig. 10 Calibration plot of the sensor in the concentration range of 1.0×10^{-10} – 1.0×10^{-2} mol L^{-1} at pH=6.0 in EtOH (λ_{ex}=403 nm)

were studied in this work. The reproducibility was examined by preparing 8 different membranes from the same mixture and measuring the fluorescence of each membrane at 544 nm using 1.0 μM Hg^{2+} (three repeated determinations) in the buffer solutions at pH 6.0. The resulting coefficient of variation was found to be±1.7 %. The short-term stability of the optical sensor was studied by measuring its fluorescence intensity in contact with 1.0 μM Hg^{2+} at pH 6.0 over a period of 10 h. From the fluorescence measurements, after every 60 min (n=10), it was found that the response was almost complete with only 2.5 % change in the fluorescence after 10 h monitoring. In addition, it was found that the membrane sensor could be stored in wet conditions without any measurable changes in its fluorescence for at least 15 weeks, which implies that the ionophore is quite stable in the membrane. Thus, the membrane sensor was immersed in the buffer solution of pH 6.0 when not in use.

The reversibility of the optode was checked by washing the used optodes with 0.2 mol L^{-1} thiocyanate and/or iodate

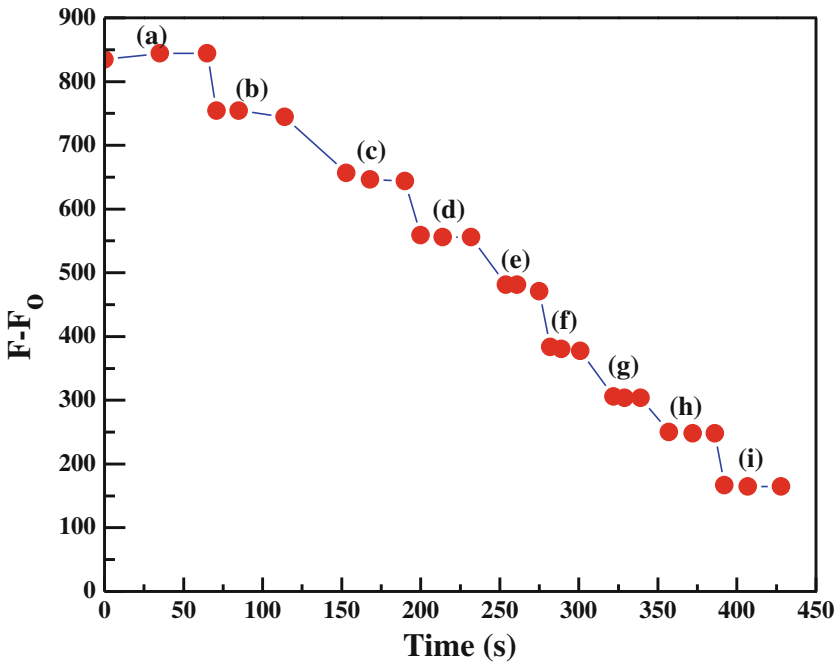


Fig. 11 Dynamic response of the proposed fluorescence membrane sensor for step change in concentration of Hg^{2+} ion at pH= 6.0): (*a*) 1.0×10^{-2}, (*b*) 1.0×10^{-3}, (*c*) 1.0×10^{-4}, (*d*) 1.0×10^{-5}, (*e*) 1.0×10^{-6}, (*f*) 1.0×10^{-7}, (*g*) 1.0×10^{-8}, (*h*) 1.0×10^{-9}, (*i*) $1.0\times-^{10}$

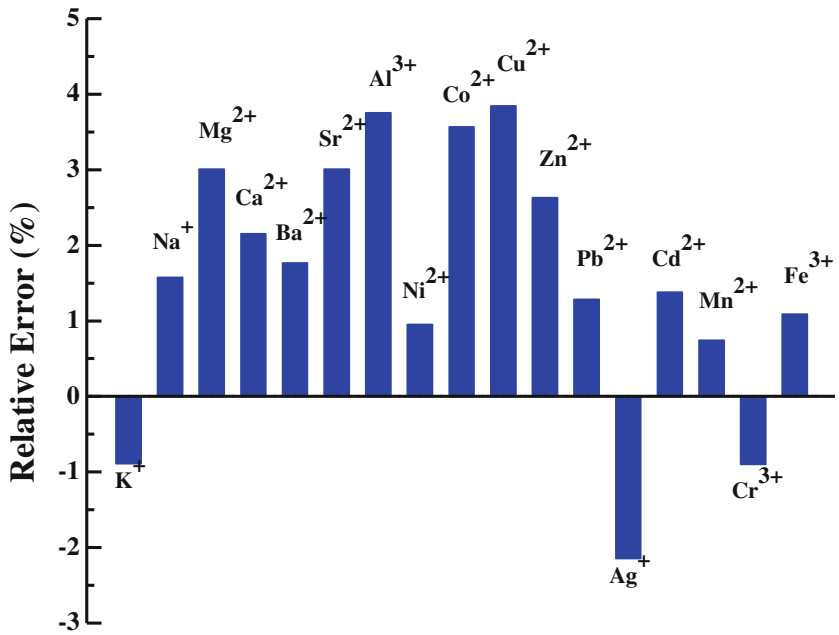


Fig. 12 Interferences of different metal ions (1.0×10^{-2} mol L^{-1}) onto the fluorescence determination of Hg^{2+} ion (1.0×10^{-10} mol L^{-1}) using the proposed membrane sensor at pH 6.0

solutions. The results showed that the optodes were not regenerated to use one more time for Hg^{2+} determination. In addition, HCl and/or HNO_3 were also checked for the regeneration of the used optode by immersion of the used optode to the acids solution (0.01, 0.05, and 0.10 mol L^{-1}) for 180 s. The results showed that the optodes could be regenerated in 0.10 mol L^{-1} HNO_3 solution. Therefore, each optode can be used several times for Hg^{2+} analysis.

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 fluorescence intensity of a fixed concentration of Hg^{2+} (1.0×10^{-10} mol L^{-1}) in a solution of pH 6.0 was measured before (F_0) and after addition (F) of some potentially interfering ions such as 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+} at concentrations up to 1.0×10^{-2} mol L^{-1}. The resulting relative error is defined as RE (%)=$[(F-F_o)/F_o]\times100$. The experimental results (Fig. 12) revealed that most alkali, alkaline earth, and many transition metal cations don't show significant interference on the Hg^{2+} assay, where the observed relative error was less than±5 % relative error, which is considered as tolerable.

Analytical Applications

To assess the applicability of the proposed chemosensor to real samples, we further conducted Hg^{2+} detection in different human hair samples, urine samples, collected from dentists 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.

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]	173.64 [a]±0.80[b]	−0.43
2	279.50[a]±4.40[b]	277.43±1.40[b]	0.74
3	197.50[a]±2.40[b]	1.96.43±1.25[b]	0.56
Urine samples[d]			
1	3.47[a]±0.05[b]	3.45[a]±0.05[b]	0.58
2	3.80[a]±0.08[b]	3.83[a]±0.08[b]	−0.78
3	3.65[a]±0.02[b]	3.62[a]±0.02[b]	0.82
Well water samples[d]			
1	1.72[a]±0.03[b]	1.71[a]±0.02[b]	0.58
2	1.10[a]±0.07[b]	1.12[a]±0.06[b]	−1.82
3	1.45[a]±0.05[b]	1.43[a]±0.07[b]	1.38

[a] Mean values of three determinations

[b] Standard deviation

[c] Reported value: μgKg^{-1}

[c] Reported value: μgL^{-1}

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 (Sec.)	Signal	Reference
2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide	Sol–gel thin film of (PVF/SiO_2),	$5.0\times10^{-3}-5.0\times10^{-4}$	5.0×10^{-5}	600	Absorbance	[91]
1-(2-Pyridylazo)-2-naphthol (PAN)	PVC	$1.0\times10^{-5}-1.0\times10^{-3}$	5.5×10^{-7}	NR[a]	Absorbance	[92]
Dithizone	Triacetylcellulose	$7.5\times10^{-7}-9.7\times10^{-6}$	1.0×10^{-7}	180−540	Absorbance	[93]
1-(dansylamidopropyl)-1-aza-4,10-dithia-7-oxacyclododecane	PVC	$1.0\times10^{-4}-5.0\times10^{-12}$	8.0×10^{-13}	60	Fluorescence	[82]
Trityl-picolinamide (T-Pico)	PVC	$5.0\times10^{-7}-5.0\times10^{-4}$	5.0×10^{-7}	300−600	Absorbance	[94]
4-(2-Pyridylazo)-resorcinol	Triacetylcellulose	$5.0\times10^{-6}-3.4\times10^{-3}$	1.5×10^{-6}	1200	Fluorescence	[95]
4-hydroxy salophen	Triacetylcellulose	$1.0\times10^{-6}-1.0\times10^{-2}$	1.3×10^{-7}	300−360	Absorbance	[96]
2-mercaptopyrimidine (2-MP)	PVC	$2.0\times10^{-9}-2.0\times10^{-5}$	4.0×10^{-10}	≤45 s	Absorbance	[73]
2-mercapto-2-thiazoline (MTZ)	PVC	$2.0\times10^{-10}-1.5\times10^{-5}$	5.0×10^{-11} M	150 s	Absorbance	[97]
4-(2-Pyridylazo)resorcinol (PAR)	Tri-(2-ethylhexyl) phosphate plasticized cellulose triacetate	$\times10^{-6}-6.6\times10^{-6}$	1.1×10^{-6}	300	Absorbance	[98]
1,3-Di(2-methoxyphenyl)triazene	PVC	$2.1\times10^{-7}-1.2\times10^{-4}$	2.0×10^{-7}	300	Absorbance	[99]
4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1, 4, 7]trioxononin-9-yl)pyrylium perchlorate	PVC	$2.95\times10^{-10}-3.20\times10^{-3}$	1.01×10^{-10}	120	Absorbance	[100]
Tetra(p-dimethylaminophenyl) porphyrin	PVC	$4.0\times10^{-8}-4.0\times10^{-6}$	8.0×10^{-9}	300	Fluorescence	[101]
4phenyl2,6bis(2,3,5,6tetrahydrobenzo[b][1, 4, 7]trioxononin9yl) pyrylium perchlorate	So-gel	$1.52\times10^{-9}-1.70\times10^{-2}$	1.11×10^{-9}	180	Absorbance	[102]
4-Ethyl-5-hydroxy-5,6-di-pyridin-2-yl-4,5-dihydro-2H-[1, 2, 4]triazine-3-thione Hexathiacyclooctadecane	PVC	$5.0\times10^{-10}-5.0\times10^{-5}$	1.8×10^{-10}	360	Fluorescence	[63]
2-[(2-sulfanylphenyl)ethanimidoyl]phenol	Sol–gel	$1.0\times10^{-2}-1.0\times10^{-5}$	1.0×10^{-6}	180	Absorbance	[68]
(1Z,2Z)-N_1,N_2-dihydroxy-N1,N2-dipyridin-2-ylethanediimidamide	PVC	$5.78\times10^{-9}-1.05\times10^{-3}$	1.71×10^{-9}	< 120	Fluorescence	[103]
Tetrathia-12-crown-4	PVC	$1.0\times10^{-9}-9.5\times10^{-5}$	8.1×10^{-10}	100 s	Absorbance	[45]
Indigo carmine; N-cetyl pyridinium chloride (IC-N-CPC)	Triacetylcellulose	$2.4\times10^{-5}-4.7\times10^{-4}$	7.2×10^{-6}	480−600	Absorbance	[104]
Rhodamine B derivative (RND)	PVC	$1.0\times10^{-9}-2.0\times10^{-3}$ M	8.1×10^{-10}	180−900	Fluorescence.	[105]
1,15-diaza-3,4,12,13-dibenzo-8-oxa-16,18-pyridin-5,1-dithiacyclo octadecane-2,14-dione	PVC	$1.0\times10^{-12}-8.6\times10^{-4}$	5.3×10^{-13}	49.8	Absorbance	[54]
N.N′bis(2-aminothiophenol)benzene-1, 2-dicarboxaldehyde (ATBD)	PVC	$1.0\times10^{-10}-8.6\times10^{-2}$	7.23×10^{-11}	< 35		Current method

[a] *NR* not reported

Comparison of the Proposed Optode with Previously Reported Methods

The present proposed sensor was compared to recently Hg^{2+} sensing methods based on S-containing, Schiff bases or immobilized ionphore (Table 4) [45, 54, 63, 68, 73, 82, 91–105]. Each of the reported method has its own merits, but each method also offers some problems such as poor reproducibility, limited sample adaptability, high cost, well-controlled experimental conditions, complicated sample-pretreatment, some inherent interference and time consuming procedures. As can be seen, the proposed sensor shows better selectivity, better LOD (7.23×10^{-11} mol L^{-1}) and short response time (35 s) relative to other reported methods.

Conclusion

In conclusion, an efficient, easy, low-cost and high selective fluoroionophore is developed and potentially utilized for selective and sensitive determination of Hg^{2+} based on a novel dithiol Schiff base namely: N.N′bis(2-aminothiophenol)benzene-1,2-dicarboxaldehyde (ATBD) immobilized within a plasticized PVC membrane, with good optical and mechanical properties. The sensor showed short response time (35 s), appropriate linear dynamic range (1.0×10^{-10} − 1.0×10^{-2} mol L^{-1}) and low detection limit (7.23×10^{-11} mol L^{-1}). The proposed fluorescence optode was successfully applied to the determination of Hg^{2+} ions in hair, urine and well water samples.

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