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ORIGINAL ARTICLE

A Novel Fluorescent Optode for Recognition of Zn^{2+} ion Based on N,N$^{'}$-bis-(1-Hydroxypheylimine) 2,5-Thiophenedicarobxaldehyde (HPTD) Schiff Base

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Abstract A novel fluorescent sensing film has been proposed for sensitive determination of Zn^{2+} ion in EtOH-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0). The novel sensor based on incorporating a novel qaudridentate Schiff base N,N$^{'}$-bis-(1-hydroxypheylimine)2, 5-thiophenedicarobxaldehyde (HPTD) as ionophore in the plasticized PVC membrane containing bis(2-ethylhexyl)sebecate (DOS) as plasticizer. The novel optode membrane works on the basis of a cation-exchange mechanism and shows a significant fluorescent emission enhancement on exposure to HEPES buffer solution of pH 7.0 containing Zn^{2+} ion. Under optimal conditions, the proposed sensing film displays a linear range of 1.0×10^{-12} to 8.6×10^{-4} M with a limit of detection 5.3×10^{-13} M. The response characteristics of the sensor including reversibility, reproducibility, response time and lifetime are discussed in detail. The optode membrane has been applied to determine Zn^{2+} in various real water samples.

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Introduction

The development of selective and sensitive fluorescent chemosensors for transition and post-transition metal ions, based on ion-induced changes in fluorescence, are particularly attractive because of their simplicity, high sensitivity, and instantaneous response [1–3]. Zinc is one of the most abundant transition metals in human body. It plays an important role in various biological systems such as gene expression, protein–protein interaction and neurotransmission [4, 5]. In addition, zinc is also a contributing factor in many severe neurological diseases such as Alzheimer's disease, epilepsy, cerebral ischemia and neurodegenerative disease [5]. The total concentration of zinc lies over a very broad range (in the order of nanomolar to millimolar) [6]. Though zinc is a relatively non-toxic element, it can be toxic if consumed in large enough quantities. For example, zinc is a metal pollutant of environment, significant concentrations of which may reduce the soil microbial activity causing phytotoxic effect [7, 8] and which is also a common contaminant in agricultural and food wastes [9]. Thus, the determination of trace amounts of zinc is currently of great interest in many scientific fields, including medicine analyses and environmental monitoring [10].

From a structural point of view, Schiff bases are well known for the formation of stable complexes with transition metal ions, and their behavior as ion carriers. The structure of Schiff bases render geometric and cavity control of host–guest complexation and produce remarkable selectivity, sensitivity and stability for a specific ion. Consequently, Schiff base complexes have attracted increasing attention in the area of ionic binding. Schiff bases with proper placement of additional N or O as donor atoms are well known to form strong complexes with transition metal ions and have been used as the ionophore in optical sensor for determining various cations [11–13]. Several publications have demonstrated the use of

purposefully designed Schiff base ligands for optical sensing of metal ions [14–19].

In this paper, we develop a simple, facile and reliable new fluorescent probe for Zn^{2+} ions with mixed nitrogen, oxygen donor sites based on a novel tetradentate Schiff base obtained by condensation of 2,5-thiophenedicarboxaldehyde and 2-aminophenol (Scheme 1). The new ionophore was supported on a plasticized PVC membrane and the resulting optode was used for sensing of traces of Zn^{2+} ions in real samples.

Experimental

Instruments

Fluorescence measurements were carried out on a Jenway 6270 Fluorimeter. The excitation source was a Pulsed Xenon Lamp. Measurements of pH were performed with a Jenway pH meter model 3510 equipped with Glass bodied combination pH electrode (924 005) 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. Elemental analyses were carried out on an Elemental Vario EL analyzer. FT-IR spectra in KBr Pellets (4000–400 cm^{-1}) were carried out on a Unicam-Mattson 1000 FT-IR. ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker Avance Drx 300-MHz spectrometer with TMS as an internal standard. Mass spectra were recorded on a JEOL JMS-600 mass spectrometer. PerkinElmer ELAN® ICP-MS was used for the determination of zinc at water research center, king Abdulllah University of Science and Technology.

Materials and Reagents

2,5-thiophenedicarboxaldehyde and HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) 1 M in H_2O and the lipophilic anionic additive reagent Potassium tetrakis(4-chlorophenyl)borate (KTpClPB) were supplied from Sigma-Aldrich. 2-Aminophenol was obtained from Merck and was used without further purification. The polymer membrane components, polyvinyl chloride (PVC) (high molecular weight) and the plasticizers, dibutyl phthalate (DBP), bis-(2-ethylhexyl) phthalate (DOP), bis(2-ethylhexyl)sebecate

(DOS), 2-nitrophenyl octyl ether (NPOE) and bis-(2-ethylhexyl) adipate (DAO) were obtained from Fluka.

The photoluminescence quantum efficiencies of HPTD (H_2L) was calculated by using quinine sulphate as reference quantum yield standard ($\lambda_{ex} = 410$ nm, quantum yield =0.54 in 0.1 M H_2SO_4). All solvents were of analytical grade and they were used as received. A stock solution of Zn^{2+} (1.0×10^{-2} M) was prepared by dissolving 0.2974 g $Zn(NO_3)_2{\cdot}6H_2O$ in exactly 100 ml of deionized water and standardized with EDTA [20].

Synthesis of N,N′-bis-(1-Hydroxypheylimine) 2,5-Thiophenedicarobxaldehyde (HPTD)

The Schiff base ligand was synthesized by conventional method according to the following procedure: A hot methanolic solution (10 mL) of 2,5-thiophenedicarboxaldehyde (5.0 mmol) was added drop wise to a another hot methanolic solution (10 mL) of 2-aminophenol (10.0 mmol). After completion of addition, the resulting reaction mixture was refluxed on a water bath for 2 h and then allowed to cool overnight. The colored crystalline solid of the obtained Schiff base was filtered, washed with cold methanol and hot petroleum ether 40–60 for several times and dried in air at room temperature and finally preserved under reduced pressure in a desiccator. Characteristics of the ligand were as follows: HPTD ($C_{18}H_{14}N_2O_2S$): F.W:322.387 Yield: 95 %. Color: Golden yellow. Elemental analysis Calc. (%):C, 67.06; H, 4.37; N, 8.68; S, 9.94. Found (%): C, 66.89; H, 4.17; N, 8.53; S, 9.89. FT-IR (KBr pellet. cm^{-1}): 3357 (ν_{OH}); 1613($\nu_{C=N}$); 1297 (ν_{C-O}). ^{1}H NMR (DMSO-d_6, δ ppm): 9.15 (s, 2 H; OH), 8.91 (s, 2 H; Thiophene H); 7.71 (s, 2 H CH = N); 6.82–7.21 (m 8 Aromatic H). ^{13}C NMR (300 MHz, DMSO, ppm): δ 116.22; 119.48; 120,58; 127.56; 132.99; 137.21; 146.11; 150.97; 152.92. FT-IR, ^{1}H NMR ^{13}C NMR and mass spectra of HPTD are represented in figs. S1, S2, S3 and S4, respectively.

Preparation of the Optode Membrane

The optimized optode membranes were prepared by mixing 61 mg of plasticizer DOS, 35 mg powdered PVC, 3 mg of fluorogenic Schiff base ligand HPTD (H_2L) and 1 mg of additive KTpClPB, which totally were dissolved in exactly 3 mL THF. 0.2 ml of the THF cocktail was pipetted and and spread

Scheme 1 Synthesis of N,N′-bis-(1-hydroxypheylimine) 2,5-thiophenedicarobxaldehyde (HPTD) ionophore

N,N'-bis-(1-hydroxypheylimine)2,5-thiophenedicarobxaldehyde (HPTD)
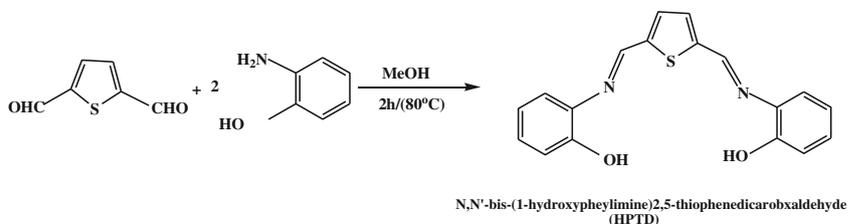
onto a 7 mm × 50 mm quartz plate located in a THF-saturated desiccators. Prior to coating, all glass plates were cleaned with pure THF and HNO_3 to remove organic impurities and dust. The optimal membrane had a thickness of approximately 3 μm. In all studies, the blank membrane had the same composition as the proposed membranes except that the ligand HPTD was absent.

Fluorescence Measurements

The film was first soaked for more than 20 min in HEPES buffer solution of pH 7.0 until the membrane had a stable fluorescence value before the first Zn^{2+} measurement was made. During its use the membranes were placed diagonally inside the sample cuvette of the instrument containing 2 mL EtOH-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0). The fluorescence intensity, at an excitation wavelength of 387 nm was measured at 520 nm. Then the sample was titrated with standardized Zn^{2+} ion solutions and the fluorescence intensity of the system were measured within <50 s, required to reach the equilibrium.

Water Samples Collection and Treatment Before Analysis

Samples of tap water (Cairo City), underground water (Western Sahara), sea water (Alexandria City) and waste water (New Cairo Waste water Treatment Plant) are collected according to ISO 5667. Volume of the taken sample should be not less than 250 mL. For transportation and storage of the samples, PE or PTFE containers were used. To conserve the samples, contecentrated HNO_3 is added in proportion of 3 mL for one liter of the sample. The conserved sample can be stored for 3 days. A non conserved sample should be analyzed within 4 h after collection. If the sample was not conserved, it has to be acidified prior to the analysis by 0.7 % HNO_3 in the proportion of 3 mL for one liter of the sample.

Results and Discussion

Fluorescence Spectral Responses of HPTD (H_2L)

In order to evaluate whether HPTD (H_2L) could be used as a suitable fluorescent chemosensor for Zn^{2+} ion, in this work we studied the optical response of HPTD to the presence of a larger number of different metal ions in EtOH-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0) at 25.0 ± 0.1 °C. A 1.0×10^{-6} M solution of HPTD in ethanol was titrated with microliter amounts of 1.0×10^{-9} M solutions of metal ions spectrofluorometrically (Fig. 1). As It is seen from Fig. 1, the shape and position of the fluorescence excitation ($\lambda_{ex} = 388$ nm) and emission ($\lambda_{em} = 513$ nm) bands almost does not change in the presence of Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+},
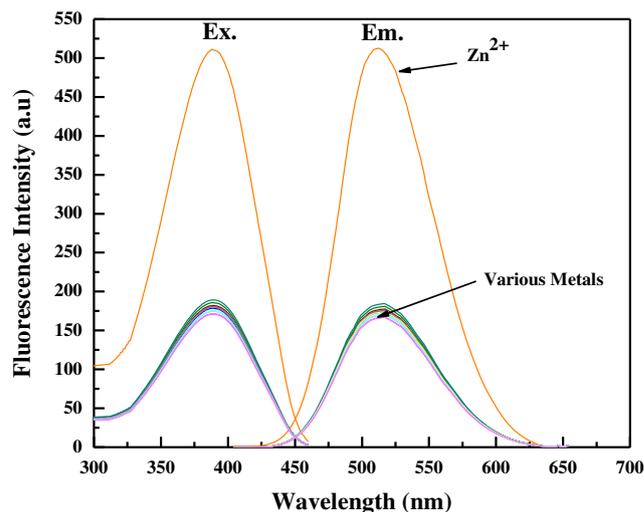
Fig. 1 Fluorescence excitation (left) and emission (right) spectra of HPTD (1.0×10^{-6} M) in EtOH in the presence of in the presence of different ions, such as Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Ba^{2+}, Cr^{3+}, Ag^+, Al^{3+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+} (1.0×10^{-9} M) in EtOH-HEPES buffer solution (20 mM HEPES, 50:50, v/v, pH 7.0, $\lambda_{ex} = 388$ nm, $\lambda_{em} = 513$ nm)

Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Ba^{2+}, Cr^{3+}, Ag^+, Al^{3+}, Fe^{3+}, Hg^{2+}, Mn^{2+} and Pb^{2+} compared to those of the free ligand, whereas the introduction of Zn^{2+} could induce remarkable enhancement of both the excitation and emission intensities. These studies clearly indicate that the chemosensor can be utilized for the selective detection of Zn^{2+} without interference from the other metal ions.

In order to gain an insight into the signaling properties of HPTD toward Zn^{2+}, fluorescence titration experiments were carried out in EtOH-HEPES buffer solution (20 mM, pH = 7.0, 50 % (v/v) H_2O/EtOH). A linear increasing of fluorescence intensity could be observed with increasing Zn^{2+} concentration in the range of 1.0×10^{-10} to 1.0×10^{-3} M (Fig. 2). Moreover, binding analysis using the method of continuous variations (Job's plot), which exhibited a maximum at a molar fraction 0.5, indicated that a 1:1 stoichiometry for the binding mode of HPTD and Zn^{2+} (Fig. 3).

In comparison to the solution phase, the PVC matrix provided high fluorescence intensity and satisfactory quantum yield in immobilized form due to the matrix rigidity. The emission and excitation spectra of Schiff base HPTD were recorded in the solvents of different polarities and PVC matrix. The gathered excitation-emission spectra of the HPTD are shown in Fig. 4. Upon increasing the solvent polarity, the quantum yields found decreased significantly, that is in accordance with the literature [21].

Fluorescence Quantum Yield Calculations

Determination of the relative quantum yield is generally accomplished by a comparison of the wavelength-integrated
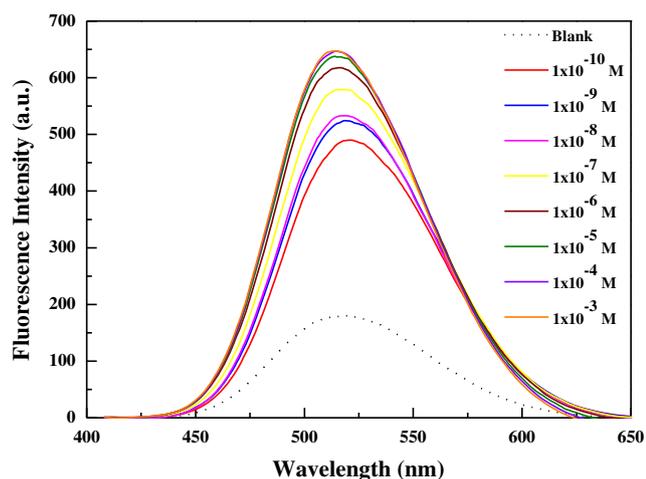
Fig. 2 Fluorescence spectra of HPTD (5.0×10^{-6} M, $\lambda_{ex} = 388$ nm) upon the titration of Zn^{2+} (1.0×10^{-10}–1.0×10^{-3} M) in EtOH-HEPES buffer solution (20 mM, pH = 7.0, 50 % (v/v) H₂O/EtOH)

intensity of the unknown sample with the standard. There are two main approaches for relative quantum yield measurements: The "one point" method, where the quantum yield is calculated, using only one emission value for the sample and one for the standard is fast, but not always reliable. The second approach is the comparative method described by Williams et al. [22]. It is more time consuming nevertheless providing greater accuracy by comparing the integrated fluorescence intensity and the absorption for sample and reference. Fluorescence quantum yield values (Φ_F) of the employed Schiff base HPTD were calculated by using the comparative William's method [22]. For this purpose, quinine sulphate was used as reference quantum yield standard ($\lambda_{ex} = 410$ nm, quantum yield =0.54 in 0.1 mol L^{-1} H₂SO₄). The integrated fluorescence intensities were plotted versus absorbance for the
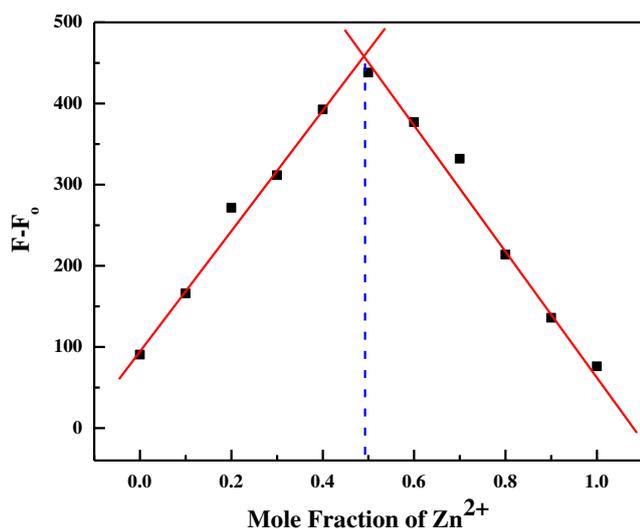
Fig. 3 Job's plot for Zn^{2+} sensor in EtOH-HEPES buffer solution (20 mM, pH = 7.0, 50 % (v/v) H₂O/EtOH). The total concentration of HPTD and Zn^{2+} is 1.0×10^{-6} M
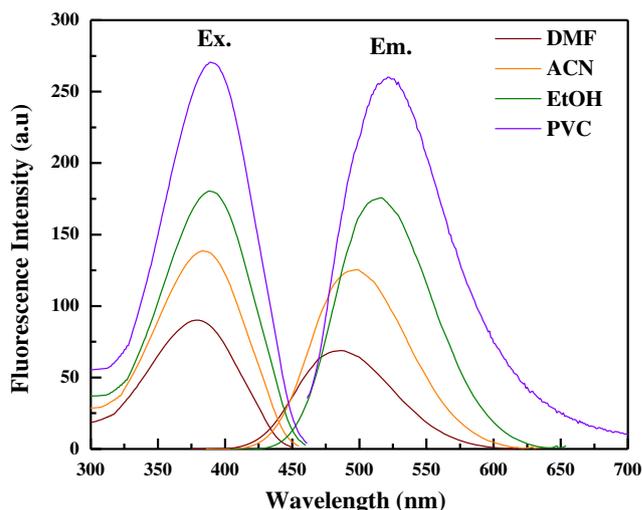
Fig. 4 Emission and excitation spectra of HPTD Schiff base in different solvents and PVC

reference standard and the Schiff base HPTD. Quantum yield (Φ_F) values calculated according to Eq. (1) are shown in Table 1.

$$\Phi_S = \Phi_R \left(\frac{(Grad)_S}{(Grad)_R} \right) \left(\frac{\eta^2_S}{\eta^2_R} \right) \qquad (1)$$

where R and S denote reference and sample, respectively, Grad is the gradient from the plot and η is the refractive index of the solvent or polymer matrix material.

Operation Principle

The fluorescent optode membrane proposed in this work is based on the incorporation of the ionophore HPTD (H₂L) in a plasticized PVC containing KTpClPB, as a lipophilic anionic additive. The ionophore possesses selective binding properties to Zn^{2+} ions and changes its fluorescence intensity as a result of the binding event. Since the ionophore is neutral and, therefore, cannot function as an ion-exchanger, the presence of a lipophilic anionic site is necessary to provide the optode membrane with the ion-exchange properties. Under the experimental conditions used and supposing the formation of a 1:1 metal-to-ligand complex between HPTD (H₂L) and Zn^{2+} ion in the organic phase, the response mechanism of this optical system can be described by the following ion-exchange mechanism (Scheme 2) [23–26]:

Effect of Membrane Composition

It is well documented that the membrane composition may largely influence the response characteristics and working concentration range of the optical sensors [27, 28]. Thus, in this work, eight PVC-membranes with plasticizer/PVC ratios in the range 1.7–2.1, but with varying nature and amount of

Table 1 The excitation-emission spectra related characteristics of HPTD in solutions of DMF, ACN, and EtOH and in solid matrices of PVC

Matrix	λ_{ex} (nm)	λ_{em} (nm)	Stokes' shift $\Delta\lambda_{ST}$ (nm)	Refractive index, n	Quantum yield (Φ_F)
DMF	377	489	112	1.4305	0.011
ACN	382	499	117	1.3441	0.020
EtOH	388	513	125	1.3614	0.024
PVC	387	520	133	1.5247	0.041

other ingredients were prepared (Table 2). It is known that the plasticized PVC-membranes used in ion sensors will usually result in the best response membrane characteristics at a plasticizer/PVC ratio of about 2 [29]. As is obvious from Scheme 2, since the bulk membrane optodes must be in thermodynamic equilibrium with the sample, the mass transfer of analyte into the membrane is required [30]. Thus, in the proposed zinc-selective optical sensor containing HPTD (H_2L) as a neutral ionophore, the presence of a lipophilic additive such as KTpClPB is necessary to facilitate the ion-exchange equilibrium. The absence of KTpClPB was found to affect not only the working concentration range of the sensor (Table 2), but also resulted in the prolonged response time and reduced selectivity of the sensor [31]. The presence of 61–63 % plasticizer in the PVC-membranes resulted in optimum physical properties, as well relatively high mobilities of their constituents [32, 33]. The nature of plasticizer also influences considerably the measuring range of the polymeric membrane sensors and their selectivity coefficients [34, 35]. As is obvious from Table 3, the use of DOS as plasticizer resulted in a large widening of measuring range of the proposed optical sensor over the membrane based on DOP and NPOE. As is seen from Table 2, the presence of 3 % fluoroionophore HPTD (H_2L) and 1 % of additive KTpClPB in the PVC-membrane resulted in the best optical response of the zinc-selective sensor. Thus, the membrane number 4 (Table 2) with an optimized PVC:DOS:KTpClPB:HPTD wt.% ratio of 35:61:1:3 was used for further studies.

Effect of pH

The effect of pH of the test solution on the optical response of Zn^{2+} ion-selective sensor was studied in the presence of 1.0×10^{-6} M solution of Zn^{2+} over the range of 2.0–9.0, and the results are illustrated in Fig. 5. The pH of solution was adjusted by either HNO_3 or NaOH. As it is obvious from Fig. 5, the response of the sensor is independent of the pH of the test solution in a range of 6.0–8.0. The decreased intensity at lower pH might be due to the extraction of H^+ from the aqueous sample solution into the PVC-membrane, via protonation of the azomethine nitrogen atoms of HPTD (H_2L)

molecule, which results in an expected change in the mobility of electrons of the system. On the other hand, the reduced optical response of the sensor at pH > 8.0 could be due to a possible slight swelling of the polymeric film under alkaline conditions, as well as the hydroxide formation of zinc ions, resulting in decreased concentration of free Zn^{2+} ions in sample solution. Thus, in subsequent experiments, a solution of pH 7.0 adjusted by a HEPES buffer solution was used for further studies.
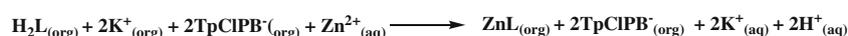
Measuring Range and Dynamic Response Time

Figure 6 displays the optical response of the proposed optode to various concentrations of Zn^{2+} ion under optimal experimental conditions. As is obvious, this curve can be suitably used as a calibration curve (Fig. 7) for the determination of Zn^{2+} ions in a concentration range of 1.0×10^{-12} to 8.6×10^{-4} M. The limit of detection (LOD) based on 3σ of the blank was 5.3×10^{-13} M.

The dynamic response time of the present optode, as an important characteristic for any membrane sensor [28], it is controlled by the time required for the analyte to diffuse from the bulk of the solution toward the membrane interface to associate with ligand. In the case of the proposed fluorescence membrane sensor, the membrane response found to be relatively fast so that the fluorescence intensity of the corresponding signal reached equilibrium within <50 s, over the entire calibration concentration of Zn^{2+} ion from 1.0×10^{-12} M to 1.0×10^{-4} M.

Reproducibility, Reversibility, Short-Term Stability and Life Time

The regeneration of the proposed membrane sensor was studied in by the use of different reagents including HCl, HNO_3, H_3PO_4, bis(aminoethyl)-glycoether-N,N,N,N-tetraacetic acid (EGTA), nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). It was found that, in presence of 0.001 M EDTA, the optode membrane will be regenerated completely within a short regeneration time period of 10–20 s. This is because of non-affinity of EDTA with polymeric support as well as its ability to form preferential complex with

$$H_2L_{(org)} + 2K^+_{(org)} + 2TpClPB^-_{(org)} + Zn^{2+}_{(aq)} \longrightarrow ZnL_{(org)} + 2TpClPB^-_{(org)} + 2K^+_{(aq)} + 2H^+_{(aq)}$$

Scheme 2 The proposed binding model for interaction between HPTD membrane and Zn^{2+}

Table 2 Optimization of membrane ingredients

Membrane no.	Composition (%)				Working range (M)
	PVC	Plasticizer	KTpClPB	HPTD (H_2L)	
M_1	35	62, DOS	0	3	2.0×10^{-3} to 5.0×10^{-7}
M_2	35	63, DOS	1	1	1.0×10^{-3} to 1.0×10^{-9}
M_3	35	62, DOS	1	2	5.0×10^{-3} to 5.0×10^{-10}
M_4[a]	35	61, DOS	1	3	8.6×10^{-4} to 1.0×10^{-12}
M_5	35	61, NOPE	1	3	5.0×10^{-5} to 1.0×10^{-9}
M_6	35	61, DBP	1	3	1.0×10^{-3} to 1.0×10^{-6}
M_7	35	61, DOP	1	3	1.0×10^{-3} to 1.0×10^{-7}
M_8	35	61, DAO	1	3	4.0×10^{-3} to 1.0×10^{-5}

[a] Optimum membrane composition

Zn^{2+} ions, which permit complete regeneration in an optimally reasonable conditioning time. After regeneration and for the next Zn^{2+} ion concentration measurement, the membrane should be kept in a buffer solution of pH 7.0.

The reproducibility and reversibility are two important characteristics in evaluating the suitability of an ion-selective optical sensor for selective determination of ion of interest. These characteristics were studied by fluorescence intensity measurements of the same membrane sensor when it was exposed to repeated concentration step changes between 1.0×10^{-7} and 1.0×10^{-6} M Zn^{2+} at pH 7.0. The coefficient of variation of 5 determinations for the 1.0×10^{-7} and 1.0×10^{-6} M were found to be ±1.5 and ±0.95, respectively.
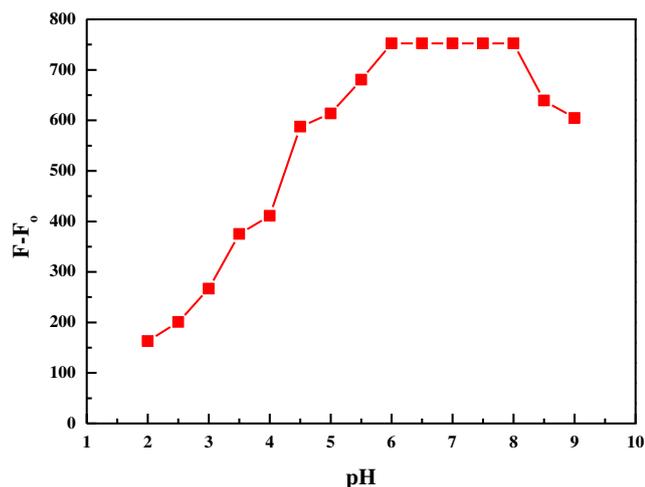
The results indicated that the proposed sensor possess good repeatability and reversibility.

The difference in the response of individual membrane was evaluated by preparing seven membranes from the same mixture and the reproducibility was obtained by determining the fluorescence signal of the membrane to 1.0×10^{-7} M solution of Zn^{2+}. The standard deviation of response between membranes was found to be ±0.90. The results show that the reproducibility is satisfactory. To study the short-term stability of the optode membrane, the fluorescence intensity of the membrane in contact with 1.0×10^{-7} M Zn^{2+} at pH 7.0 was recorded over a period of 5 h with an interval of 30 min. The membrane exhibited good stability with a relative standard derivation of

Table 3 Determination of Zn^{2+} in water samples at the optimum conditions ($n = 5$)

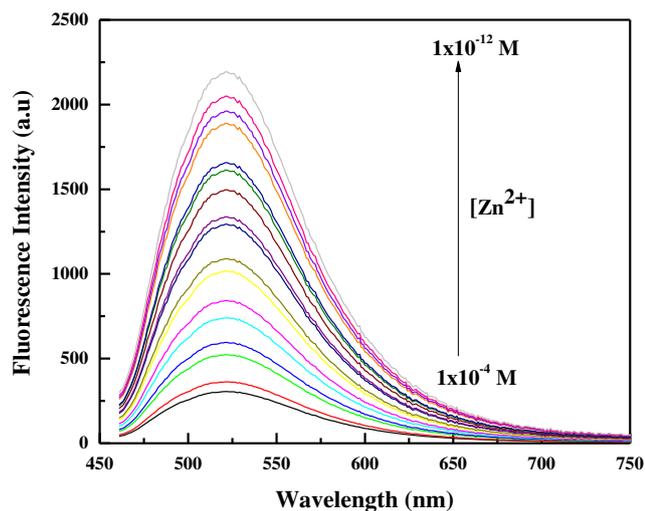| Sample	Zinc content[a]		Relative error (%)
	Proposed Optode	(ICP-MS)	
Tap water			
1	Not detected	–	–
2	$(1.09$[b] ± 0.04[c]$) \times 10^{-8}$	$(1.05$[b] ± 0.03[c]$) \times 10^{-8}$	−3.81
3	$(2.91$[b] ± 0.11[c]$) \times 10^{-8}$	$(2.87$[b] ± 0.07[c]$) \times 10^{-8}$	−1.39
Underground water			
1	$(2.67$[b] ± 0.11[c]$) \times 10^{-5}$	$(2.75$[b] ± 0.07[c]$) \times 10^{-5}$	2.90
2	$(7.23$[b] ± 0.23[c]$) \times 10^{-5}$	$(7.41$[b] ± 0.18[c]$) \times 10^{-5}$	2.43
3	$(4.45$[b] ± 0.19[c]$) \times 10^{-5}$	$(4.29$[b] ± 0.14[c]$) \times 10^{-5}$	−3.72
Sea water			
1	$(2.07$[b] ± 0.09[c]$) \times 10^{-7}$	$(2.00$[b] ± 0.04[c]$) \times 10^{-7}$	−3.50
2	$(1.94$[b] ± 0.08[c]$) \times 10^{-7}$	$(1.88$[b] ± 0.11[c]$) \times 10^{-7}$	−3.19
3	$(1.66$[b] ± 0.03[c]$) \times 10^{-7}$	$(1.70$[b] ± 0.05[c]$) \times 10^{-7}$	2.35
Waste water			
1	$(1.29$[b] ± 0.02[c]$) \times 10^{-7}$	$(1.27$[b] ± 0.02[c]$) \times 10^{-7}$	−1.57
2	$(1.66$[b] ± 0.07[c]$) \times 10^{-7}$	$(1.64$[b] ± 0.04[c]$) \times 10^{-7}$	−1.22
3	$(1.39$[b] ± 0.03[c]$) \times 10^{-7}$	$(1.41$[b] ± 0.07[c]$) \times 10^{-7}$	1.42

[a] mol/L

[b] Mean

[c] Standard deviation

Fig. 5 Effect of pH of the test solution on the optical response in the presence of 1.0×10^{-6} M Zn^{2+}

Fig. 7 Calibration curve for determination of Zn^{2+} ions by the proposed optode
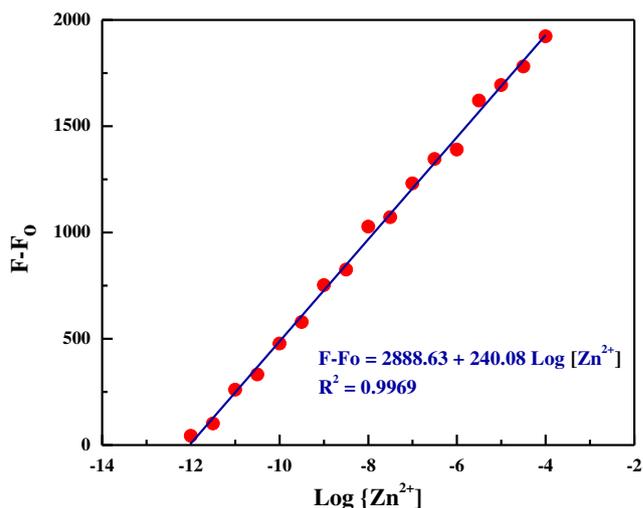
less than 2.0. In addition, it was found that the membrane sensor could be stored in wet conditions without any measurable change in its fluorescent intensity for at least 2 months, which implies that the ionophore HPTD (H_2L) is quite stable in a membrane contacting with water.

Selectivity Studies

The most important characteristic of ion-selective optode is its selectivity, which reflects the relative response of the optode for primary ion over divers ions present in solution. To study the selectivity of the sensor, the effect of various species including K^+, Li^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Ba^{2+},

Cr^{3+}, Ag^+, Al^{3+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Mn^{2+}, SO_4^{2-} (2×10^{-2} M), Na^+ (0.5 M), Mg^{2+} (0.6 M), Cl^- (0.05 M), and CO_3^{2-} (15×10^{-2} M) on the determination of Zn^{2+} ion was tested under optimum conditions. The experiments were carried out by fixing the concentration of Zn^{2+} at 1.0×10^{-9} M and then recording the change in the fluorescence intensity before (F_0) and after adding the interfering species level (F) into the zinc ion solution buffered at pH 7.0. The resulting relative error (RE) is defined as relative signal change, RE (%) = [(F-F_0)/F_0] × 100. The results of selectivity studies are summarized in Fig. 8. The data shown in Fig. 8 clearly indicate that, in the presence of all the interfering ions studied, the relative error is less than 5.0 %, which is recognized as tolerable. The results confirmed that the optode membrane exhibited good selectivity toward Zn^{2+} ion with respect to the other coexisting interfering ions.
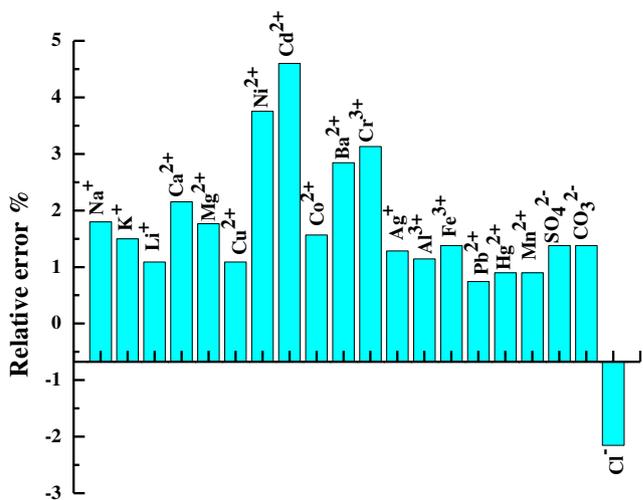

Fig. 6 The fluorescence emission spectra of the PVC sensing membrane exposed to the solutions containing different concentrations of Zn^{2+} at pH 7.0 (λ_{ex} = 387 nm, λ_{em} = 520 nm)

Fig. 8 Competitive selectivity of the propsed optode

Analytical Application

In order to test the practical application of the present sensor, the feasibility of the proposed method was explored using it for the determination of Zn^{2+} ion in various real water samples, including tap water, underground water, sea water and waste water. For evaluating the accuracy of the method, the results obtained by the developed sensor are compared with those obtained from ICP-MS (Table 3). As seen, the agreement is satisfactory, showing the applicability of the optode in the selective Zn^{2+} monitoring of real water samples.

Conclusion

In summary, fluorescent sensor for zinc ions based on the enhancement of the fluorescence emission of novel quadridentate Schiff base N,N'-bis-(1-hydroxypheylimine)2, 5-thiophenedicarobxaldehyde (HPTD) incorporated in plasticized PVC membrane containing bis(2-ethylhexyl)sebecate (DOS) as plasticizer. The sensor shows remarkable analytical characteristics including fast response and recovery time, sufficient reproducibility, high sensitivity and selectivity for the determination of Zn^{2+} ions. It has also been shown that the response of this sensor does not vary significantly in the pH range 6.0–8.0. No significant effect of common metal ions was observed on the sensor response. The developed optode was applied successfully for determination of Zn^{2+} in various real water samples with high accuracy.

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