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ORIGINAL ARTICLE

A Phenylamine-Oligothiophene-Based Fluorescent Chemosensor for Selective Detection of Hg(II)

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Abstract A phenylamine-oligothiophene-based fluorescent chemosensor I3TEA was reported. This sensor exhibited highly selective and fast detection of Hg^{2+} ion in $MeCN/H_2O$ (8/2, *v*/v) solution through fluorescence quenching. The detection was unaffected by the other competitive metal cations. The low detection limit was found to be 5.92×10^{-7} M. In addition, the recognition process is reversible and confirmed by EDTA experiment.

Keywords Fluorescence chemosensor · Mercury ion · Phenylamine-oligothiophene · Quenching

Introduction

The development of sensitive imaging instruments capable of detecting heavy and transition metal (HTM) ions has attracted much attention due to the wide use of these metal ions and their subsequent impact on the environmental and biological systems. Mercury is considered a great health threat because both elemental and ionic mercury can be converted into highly toxic organo-mercury compounds by bacteria in the environment, which subsequently bio-accumulates through the food chain [1, 2]. Mercury can cause many serious health issues since it can easily and quickly pass through the outer skin, respiratory and cell membranes, leading to DNA damage, mitosis impairment, and permanent damage to the central nervous system [3, 4]. Therefore, the development of more efficient chemosensors which can monitor Hg^{2+} ions is very important.

In recent years, fluorescent sensors are very useful tools to monitor HTM ions because of their superior sensitivity and selectivity, low cost, facile operation, non-destructive analysis, instant response, local observation and the wide spread availability of equipment for analysis [5–7]. To date, many fluorescent chemosensors for selective detection of Hg^{2+} and other HTM ions have been reported [8–28], but some practical applications are limited. Therefore, the development of more efficient fluorescent chemosensors for detecting HTM ions is still a challenge.

Our previous studies reported the synthesis, electrochemical and photophysical properties of a phenylamine-oligothiophene-based derivative I3TEA [29] (Scheme 1). Today, in order to further expand our interest to the fluorescent chemosensor for metal-ion screening studies, we continue to investigate its cation-sensing properties. In this paper, the experimental results demonstrated that I3TEA exhibited an obvious fluorescence turn-off response to Hg^{2+} with high selectivity and sensitivity over other metal cations such as Mn^{2+}, Cr^{6+}, Na^{+}, K^{+}, Ag^{+}, Ca^{2+}, Al^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+} and Cr^{3+} in $MeCN/H_2O$ (8/2, *v*/v) solution. In addition, this sensor showed low detection limit and rapid response time.

Highlights

- A phenylamine-oligothiophene-based fluorescent chemosensor I3TEA was reported.
- The sensor exhibited highly selective and sensitive detection of Hg^{2+}.
- This sensor could rapidly detect Hg^{2+} ion in real time.

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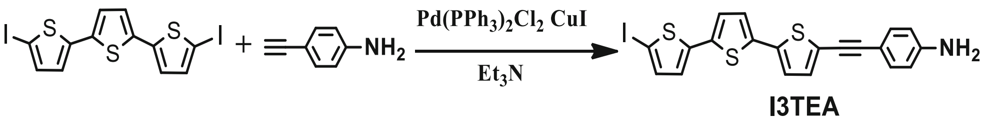
Scheme 1 The synthetic route for the sensor **I3TEA**



Experimental

Reagents

Unless otherwise stated, solvents and reagents were of analytical grade from commercial suppliers, and were used without further purification. Metal salts were purchased from Sigma–Aldrich and used as received. MeCN was spectrometric grade and purchased from Qingdao Yage Chemical Reagent Company. Water was deionized with a Milli-QSP reagent water system (Millipore) to a specific resistivity of 18.4 MΩcm. MeCN and deionized water were used in all of the experiments. All other reagents are analytical grade and also from Beijing Chemical works. The salts used in stock solutions of metal ions were $MnCl_2{\cdot}4H_2O$, $K_2Cr_2O_7$, $NaNO_3$, $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, $AgNO_3$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, KNO_3, $Hg(NO_3)_2{\cdot}H_2O$, $FeCl_2{\cdot}4H_2O$ and $CrCl_3{\cdot}6H_2O$. I3TEA was prepared as reported previously [29].

Apparatus

All UV-visible absorption spectra were recorded with a Shimadzu UV-2600 spectrophotometer at room temperature. All fluorescence measurements were carried out on a Hitachi F-4600 fluorescence spectrophotometer with a scan rate at 1200 nm/min. The excitation wavelength was set at 320 nm. The slits for excitation and emission were set at 5 nm/5 nm, respectively.

General Procedures for Spectral Determination

All tests described in this paper were carried out at room temperature. All the metal salts of Mn^{2+}, Cr^{6+}, Na^+, K^+, Ag^+, Ca^{2+}, Fe^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Fe^{2+} and Cr^{3+} were dissolved in water to prepare the stock solution with the concentration of 1.0×10^{-3} M. I3TEA was dissolved in MeCN to give the stock solution (5.0×10^{-3} M) and diluted with a mixed solution of $MeCN/H_2O$ to prepare the analytical solution (5.0×10^{-6} M) in $MeCN/H_2O$ (8/2, *v*/v) solution. The stock solution of the metal cations and I3TEA was used directly in the spectroscopic measurement. For the sensitivity measurement, different concentrations of Hg^{2+} ions were added to the assay solution, and the fluorescence spectra were recorded. The selectivity was checked by addition of Mn^{2+}, Cr^{6+}, Na^+, K^+, Ag^+, Ca^{2+}, Fe^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Fe^{2+} and Cr^{3+} in to the stock solution.

Results and Discussion

To explore the sensing ability of I3TEA, 17 metal cations including Mn^{2+}, Cr^{6+}, Na^+, K^+, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Pb^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Al^{3+}, Cr^{3+} and Fe^{2+} has been studied using both UV–Vis and fluorescence techniques. The UV-Vis absorption spectrum of sensor I3TEA (5 μM) was investigated in the presence of metals cations (10 μM) in $MeCN/H_2O$ (8:2, *v*/v) solution. As is shown in Fig. 1, sensor I3TEA exhibited strong absorption in the range 300–450 nm, however, almost no remarkable changes were observed in absorption spectra upon the addition of various metal cations such as Mn^{2+}, Cr^{6+}, Na^+, K^+, Ca^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, Al^{3+}, Cr^{3+} and Fe^{2+} ions. Surprisingly, the strong absorption intensity of peak of sensor I3TEA highly quenched upon addition of Hg^{2+} to the solution. These obvious observations indicate that sensor I3TEA shows high selectivity towards Hg^{2+} in $MeCN/H_2O$ (8:2, *v*/v) solution.

To further research the availability of I3TEA as a highly selective sensor for Hg^{2+}, the selectivity studies were performed by recording the fluorescence spectra of I3TEA after the addition of representative metal cations in $MeCN/H_2O$ (8:2, *v*/v) solution. All the results indicated that the fluorescence intensity of I3TEA strongly quenched in the presence of the Hg^{2+} ion (2.0 equiv.) (Fig. 2), accompanied by a green-yellow color fluorescence turn-off response (Fig. 2, inset), while, other metal cations induced no or small significant change in the fluorescence emission spectra relative to the free I3TEA. These dramatical observations also indicate that sensor I3TEA displays considerably high selectivity toward Hg^{2+} in $MeCN/H_2O$ (8:2, *v*/v) solution over other competitive metal cations.

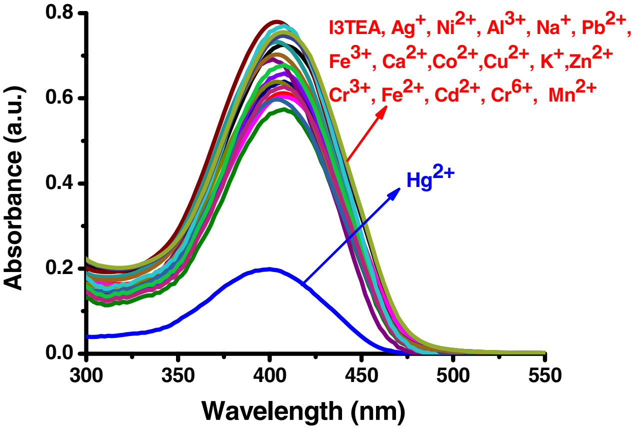


Fig. 1 Fluorescence spectra of I3TEA (5.0×10^{-6} M) in aqueous solution ($MeCN/H_2O$, 8/2, *v*/v) in the presence of various cations (2.0 equiv). Inset: Photos of I3TEA without and with addition of Hg^{2+} under the irradiation of UV light at 365 nm

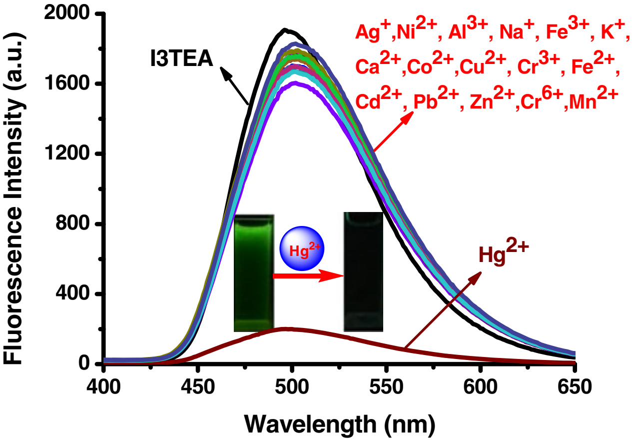


Fig. 2 UV–vis absorption spectra of I3TEA (5 μM) in the presence of 2.0 equiv. of different metal ions

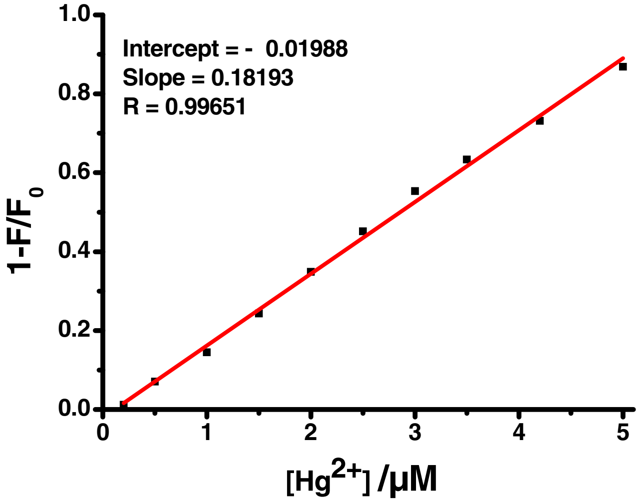


Fig. 4 Calibration curve of I3TEA–Hg^{2+} in MeCN/H_2O (8/2, *v*/v) solution

The binding stoichiometry between the sensor and metal cation is very important in relation to the sensing properties. The fluorescence titration of I3TEA (5 μM) with Hg^{2+} (0–2.0 equiv) was therefore carried out in MeCN/H_2O (8/2, *v*/v) solution shown in Fig. 3. Upon addition of Hg^{2+} ion, the fluorescence intensity decreased gradually at 498 nm and then tended to be saturated with 1.0 equiv. of Hg^{2+}. However, when more Hg^{2+} solution was titrated, the fluorescence intensity showed negligible changes and the curve (Fig. 3, inset) remained relatively constant, indicating the formation of a 1:1 binding between I3TEA and Hg^{2+}. From the fluorescence titration experimental results (Fig. 4), a good liner relationship between the fluorescence intensity and the Hg^{2+} concentration was found in the concentration range (0–5 μM) with corresponding correlation coefficient (*R*) of 0.99651. The "*R*" value demonstrated a 1:1 stoichiometric ratio between I3TEA and the binding metal cation Hg^{2+}. In addition, the fluorometric titration data was used to obtain the detection limit of I3TEA for Hg^{2+}. The detection limit was calculated to be 5.92×10^{-7} M for Hg^{2+} ion based on the equation DL = K × SD/S, where K = 3, SD is the standard deviation of the blank solution, and S is the slope of the calibration curve [30, 31]. The DL was sufficiently low to detect submillimolar concentration of the Hg^{2+} ion, which belongs to the range found in many chemical and biological systems. To further determine the stoichiometry of the I3TEA–Hg^{2+} complex, the fluorescence intensity of sensor I3TEA at 498 nm were plotted as a function of their molar fraction under a constant total concentration (5.0 μM). Figure 5 shows the result of Job's plot analysis, the maximum emission intensity was reached at a molar fraction of 0.5, which further gave solid evidence for the formation of a 1:1 complex of I3TEA-Hg^{2+}.

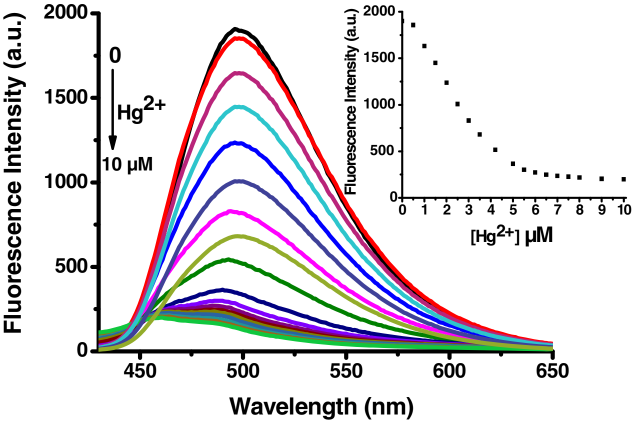


Fig. 3 Fluorescence emission spectra of I3TEA (5 μM) was titrated with Hg^{2+} (0–2.0 equiv) in aqueous solution (MeCN/H_2O, 8/2, *v*/v). Inset: Plot of the fluorescence intensity at 498 nm as a function of Hg^{2+} concentration

Sensor I3TEA likely chelates metal ion via the amine N atom of the aniline moiety, as other reported [32–34]. Mercury nitrate has structure in which covalent bonding is important

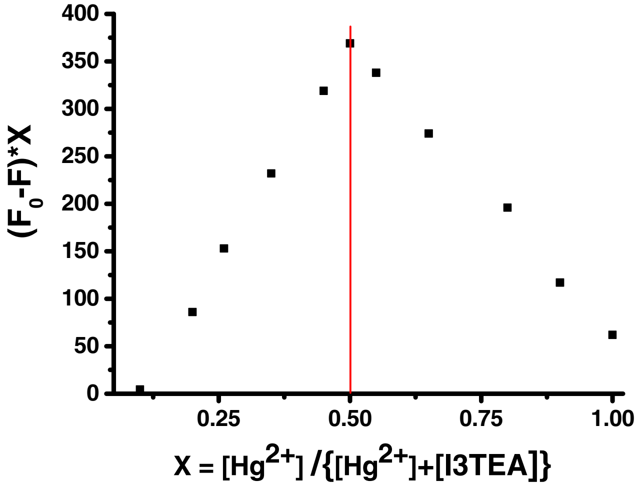


Fig. 5 Job's plot for determining the stoichiometry for I3TEA and Hg^{2+} in MeCN/H_2O (8/2, *v*/v). The total concentration was 5 μM

and easily form amine-mercury(II) salt π-complexes with amine ligand, specially primary amine I3TEA. The proposed binding model between I3TEA and Hg^{2+} was suggested in Scheme S1. The IR spectra of I3TEA was recorded in the presence of Hg^{2+} ion (Fig. S1). IR spectra of I3TEA and I3TEA-Hg^{2+} complex exhibited that the peak at 3332 and 3411 cm^{-1} corresponding to the characteristic NH_2 group stretching vibration absorption of I3TEA was shifted to a higher wavenumber (3534 and 3589 cm^{-1}) upon addition of Hg^{2+} (1.0 equiv). A substantial blue shift upon coordination of the N-donor atom of the amine group indicates electron transfer from oligothiophene to phenylamine after coordination to the mercury center in the case of I3TEA. Our experimental results presented are in good agreement with the reported literature. Thus, the changes above can be explained by the amine group of I3TEA participated in the formation of amine-mercury(II) salt π-complex.

High selectivity for the analyte of interest over a complex background of various competitive metal cations is an important feature for an effective sensor. To further gauge selectivity of the sensor I3TEA toward Hg^{2+}, the competition experiments were carried out by recording the fluorescence spectra of I3TEA (5 μM) with Hg^{2+} (2.0 equiv.) in the presence of other competing metal cations (2.0 equiv.) shown in Fig. 6. No significant variation in the fluorescence was observed in the presence and absence of other metal cations, and the relative error was less than ±5 %. These results above indicate that the recognition of Hg^{2+} by I3TEA is almost uninfluenced by other coexisting metal cations.

The reversibility of the chemosensor is particularly attractive properties for practical application. The EDTA experiments were conducted to examine the reversibility of I3TEA toward Hg^{2+} ion in MeCN/H_2O (8/2, *v*/v) solution as shown in Fig. 7, the solution changed from colorless to green-yellow when EDTA (5.0 equiv) was added to the solution of I3TEA/Hg^{2+}, and the fluorescence was turned on in several seconds. These obvious results indicate that the coordination process is reversible and thus I3TEA is a reversible chemosensor for Hg^{2+} ion in aqueous solutions.

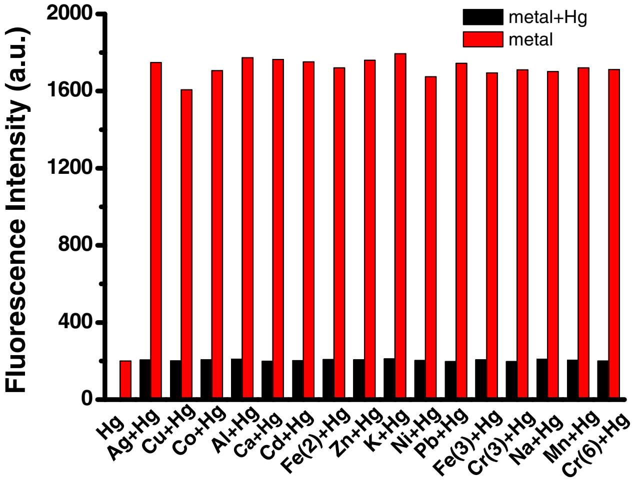


Fig. 6 Fluorescence intensity of I3TEA (5 μM) compared to various metal cations in MeCN/H_2O (8/2, *v*/v) solution. The *red bars* represent the emission of the MeCN in the presence of 2.0 equiv. of metal ions; the *black bars* represent the emission of the above solution upon the addition of 2.0 equiv. of Hg^{2+}

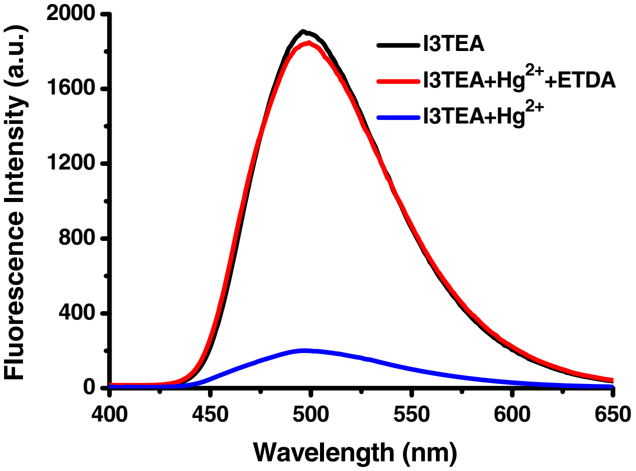


Fig. 7 Fluorescence spectra of I3TEA in the absence and presence of Hg^{2+} and EDTA. [Hg^{2+}] = 10 μM, [I3TEA] = 5 μM, [EDTA] = 50 μM

Reaction time is an important factor for sensors, thus the effect of the reaction time on the binding process of Hg^{2+} ion to I3TEA was investigated (Fig. 8). Following the addition of Hg^{2+} ion (10 μM) to I3TEA (5 μM), the fluorescence intensity of I3TEA was quenched rapidly, reaching a stable value within 3 min and then remaining constant from 3 to 10 min. Thus the rapid, stable complexation of Hg^{2+} ion by I3TEA and the resulting fast response profile are important features for robust, real time detection of Hg^{2+} ion by portable device in field.

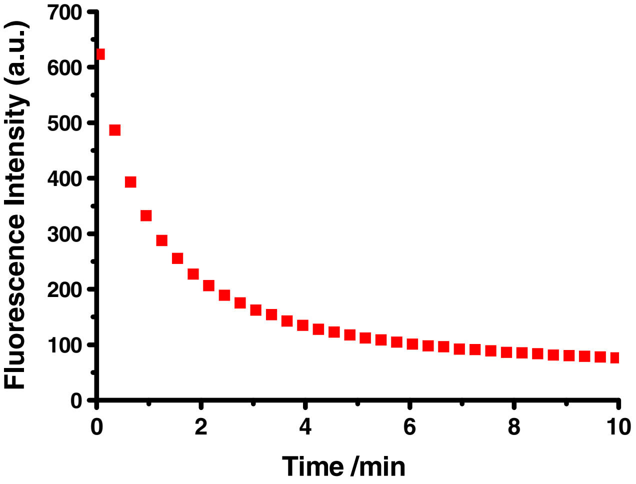


Fig. 8 Fluorescence quenching profile of addition Hg^{2+} (10 μM) to I3TEA (5 μM) in MeCN/H_2O (8/2, *v*/v) solution from 1 to 10 min

Conclusions

In summary, a phenylamine-oligothiophene-based fluorescent sensor I3TEA was reported, and its sensing ability toward metal cations was investigated. I3TEA exhibited highly selective, sensitive and rapid fluorescence turn-off response to Hg^{2+} ion in aqueous solution (MeCN/H_2O, 8/2, *v*/v). The quite low detection limit was found to be 5.92×10^{-7} M. The coordination process of sensor I3TEA and Hg^{2+} was chemically reversible with EDTA. In addition, this sensor could detect Hg^{2+} ion in real time, permitting its incorporation into a portable mercury detection kit in aqueous environment.

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