Tetrahedron Letters 54 (2013) 4620-4623

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

An ICT based highly selective and sensitive sulfur-free sensor for naked eye as well as fluorogenic detection of Hg²⁺ in mixed aqueous media

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ARTICLE INFO

Article history: Received 3 April 2013 Revised 6 June 2013 Accepted 10 June 2013 Available online 14 June 2013

Keywords: Sensor Hg²⁺ Colorimetric Fluorometric ICT

ABSTRACT

A new internal charge transfer (ICT) based colorimetric as well as fluorogenic sulfur-free probe for highly selective and sensitive monitoring of Hg^{2+} has been developed and reported in this Letter. It gives a colorimetric and fluorometric response upon addition of Hg^{2+} in acetonitrile:water (1:1) solution at a physiological pH, with no significant interference of other competitive metal ions. Receptor (**TPM**) shows a distinct color change from light yellow to orange upon progressive addition of Hg^{2+} , so that it can serve as a naked-eye sensor for Hg^{2+} ion. It exhibits excellent reproducibility, reversibility, and selectivity with the detection limit at micro-molar level.

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In recent times, the development of chemosensors for the recognition and detection of physiologically and environmentally important analytes has been receiving considerable attention.¹ Mercury pollution is a global problem and remains a significant threat to human health, yet global mercury emissions continue to rise.² Mercury is one of the most dangerous metal elements to humans and the environment, and exists in nature mainly in three forms, namely elemental, inorganic, and organic. Various forms of mercury and its compounds have high chemical activity. They can associate strongly with thiol, carboxyl, and phosphate in biological bodies and cause great damage on human health.³ Due to the high toxic effect of mercury in biological bodies and in environment the recognition of mercury is a great area of research.⁴ Keeping in view the roles played by mercury in day to day life, the development of techniques for mercury hazard assessment and mercury pollution management is in great demand.

Therefore, easy and affordable detection methods are in great demand for various situations. In this regard, optical sensors for mercury, in which a change in color is monitored, have been studied actively over the recent decades due to their simple, inexpensive, and rapid implementation.⁵ Especially, colorimetric sensors are promising because the color change can easily be observed by the naked-eye, thus requiring less labor and no equipment.⁶ In the past few years, fluorescence chemosensors are widely re-

garded as one of the most effective ways for sensor design due to the high sensitivity, specificity, simplicity of implementation, and ability for real-time monitoring.⁷ Therefore, the development of new fluorescence chemosensor for Hg²⁺ detection, especially those that exhibit selective Hg²⁺ amplified absorption color change in aqueous media, is still a challenging task.

Here, we report the synthesis and cation binding properties of a new triphenyl amine based Schiff's base derivative. Experimental studies revealed that the present sulfur-free sensor exhibits remarkable affinity for Hg²⁺ in aqueous media which is associated with a color change from light yellow to orange due to the enhancement of ICT⁸ (internal charge transfer) effect.

The receptor (**TPM**) is synthesized starting from triphenyl amine as shown in Scheme 1. 4,4'-diformyl triphenyl amine is synthesized using the known literature procedure.⁹ The treatment of diaminomaleonitrile with 4,4'-diformyl triphenyl amine in ethanol at refluxing condition affords the receptor as a yellow powder in 94% yield. The receptor is characterized by ¹H NMR, ¹³C NMR, and mass spectrometry analysis.

The photophysical properties of the sensor are investigated by monitoring the absorption spectral behavior upon addition of several metal ions such as Na⁺, Mg²⁺, Cr³⁺, Al³⁺, Mn²⁺, Fe³⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺, and Co²⁺ in aqueous medium [1:1, water/MeCN, pH 7.1]. pH of the solution was maintained using HEPES [4-(2hydroxyethyl)-1-piperazineethanesulfonic acid] buffer (50 mM) solution. Now from Figure 1, it is clear that the sensor (10 μ M) exhibits an absorption maximum centered at 447 nm. Upon





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Scheme 1. Synthesis of the receptor (TPM). Reagents and conditions: (i) DMF/POCl₃, 90 °C, 12 h; (ii) diamino maleonitrile, EtOH, reflux, 6 h.



Figure 1. UV-vis spectra of **TPM** (10 μ M) in (CH₃CN:H₂O, 1:1, v/v, pH 7.1) in the presence of different metal ions (5 equiv).

addition of Hg²⁺ a new band appears at 508 nm and the color of the solution has changed from light yellow to orange.

The other competing metal ions have no or insignificant effect on the absorbance of the receptor. After addition of Cu^{2+} ion the absorbance of the receptor decreases whereas no red shifted band appeared. From this point of view, it is clear that the receptor is highly selective toward Hg²⁺.

An absorption study of the receptor (**TPM**) upon gradual addition of increasing concentrations of Hg^{2+} (0–5.0 equiv) is shown in Figure 2. The absorption band at 447 nm gradually decreases and a new band appears at 508 nm and gradually increases with the incremental amount of Hg^{2+} .

The intensity of the new band (at 508 nm) increases regularly as the amount of Hg^{2+} is added progressively (up to 5 equiv) (Fig. 2) resulting a color change of the solution from light yellow to orange.



Figure 3. Change of absorbance of TPM at 508 nm as a function of Hg^{2+} concentration.

This red shift (60 nm) of the absorption spectra is observed which may be due to the enhancement of ICT effect after complexation of the receptor with Hg^{2+} .

The absorbance of the receptor at 508 nm increases linearly with the incremental amount of Hg^{2+} in the range of 0–20 μ M (Fig. 3). The detection limit of the sensor for Hg^{2+} is determined from the absorption spectral change, upon addition of Hg^{2+} to be 4.15 μ M, using the equation DL = $K \times Sb1/S$, where K = 3, Sb1 is the standard deviation of the blank solution, and *S* is the slope of the calibration curve¹⁰ (Supplementary data).

Job's continuous variation method has been used to determine the stoichiometry of the interaction between the receptor (**TPM**) and Hg^{2+} . Now Job's plot obtained from absorbance spectral change showed 1:2 stoichiometric complexation between **TPM** and Hg^{2+} in [CH₃CN:H₂O, 1:1, v/v, pH 7.1] (Fig. 4). From the absorption spectral data, we have evaluated the association constant of **TPM** using



Figure 2. UV-vis spectra of **TPM** (10 μ M) in (CH₃CN:H₂O, 1:1, v/v, pH 7.1) in the presence of increasing amounts of Hg²⁺ (0–5 equiv). Inset: photograph of **TPM**, before and after addition of Hg²⁺.



Figure 4. Job's plot diagram of receptor for Hg^{2*} ion (where Xg is the mole fraction of the guest and ΔI indicates the change of absorbance at 447 nm).



Scheme 2. Probable binding mode of receptor with Hg²⁺.

Benesi–Hildebrand equation¹¹ and it is found to be 1.7×10^5 M⁻¹. Assuming the (1:2) stoichiometry between TPM and Hg²⁺, we plot $1/[A - A_0]$ versus $1/[Hg^{2+}]^2$ and the data obtained from the graph give a linear fit, which also support the (1:2) binding stoichiometry of **TPM** and Hg²⁺.¹²(Supplementary data)

The colorimetric sensor **TPM** is an electronically conjugated form of two subunits, triphenyl amine (signaling unit) and diaminomaleonitrile (binding unit). The binding interaction between **TPM** and Hg²⁺ induces the ICT (internal charge transfer) from the electron rich nitrogen atom of the triphenylamine moiety to Hg²⁺ coordinating unit, which is responsible for the bathochromic shift of the UV spectra. The plausible binding mode of TPM with Hg²⁺ in a 1:2 manner is shown in Scheme 2.

The selectivity and the interference are the two very important parameters to evaluate the performance of a receptor. Now the sensitivity and the selectivity of the **TPM** toward Hg^{2+} are examined by employing different metal ions (Al^{3+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Mg^{2+} , Na^+ , Pb^{2+} , and Zn^{2+}) in aqueous acetonitrile solution of **TPM**. **TPM** shows an extraordinary selective enhancement of absorbance toward Hg^{2+} in $CH_3CN:H_2O$ (1:1) solution at 508 nm, whereas, no notable change is observed upon addition of other competing metal ions in the **TPM** solution at 508 nm. So the selectivity of TPM toward Hg^{2+} is well proved in this section.

The interference of other competing metal ions is investigated by the competition experiment which is demonstrated in Figure 5. When **TPM** is treated with 2.0 equiv of Hg^{2+} in the presence of other metal ions in the same concentration, the detection of Hg^{2+} in the presence of other metal ions is not hampered, that is, the interference for the detection of the Hg^{2+} is not observed. So TPM can be used as a selective and sensitive colorimetric sensor for the Hg^{2+} ion.

In order to examine the sensitivity of the receptor (**TPM**), the fluorescence spectra of TPM (10 μ M, λ_{ex} = 390 nm) are explored in aqueous acetonitrile (H₂O:CH₃CN, 1:1, v/v) solution buffered



Figure 5. Metal ion selectivity profile of the receptor (10 μ M): (yellow bars) change of absorbance intensity of receptor + 2 equiv Mⁿ⁺; (brow bars) change of absorbance intensity of receptor + 2 equiv Mⁿ⁺, followed by 2 equiv Hg²⁺.

with 50 mM HEPES (pH 7.1). **TPM** shows a strong broad emission band centered at about 575 nm in the absence of Hg^{2+} . Now the gradual addition of Hg^{2+} shows a distinct change in the emission spectrum (Fig. 6). On continued addition of Hg^{2+} a gradual decrease in the emission intensity at 575 nm is observed whereas a new band at 475 nm appears. Essentially these changes in the fluorescence spectrum stop when the addition of Hg^{2+} reaches 5 equiv. The difference between the two emission intensities is very large (100 nm), which not only explains the accurate measurement of the intensities of the two emission peaks but also holds a good ratiometric value. The detection limit was found to be 5.2 μ M, which indicates the sensitivity of the receptor toward Hg^{2+} is in micro molar scale (Supplementary data).

Analogous experiments in fluorescence are carried out with other series of cations such as Al^{3+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Mg^{2+} , Na^+ , Pb^{2+} , and Zn^{2+} using their perchlorate salts.

In these cases small quenching of emission intensity at 575 nm is observed whereas no blue shifted spectrum is found (Fig. 7). Thus the sensor is exclusively selective for Hg^{2+} , observed from the fluorescence titration experiment.

Taking the advantage of thiophilic nature of Hg^{2+} , in order to show the reversibility of the receptor (**TPM**), absorption titration experiment is performed using the **TPM**–Hg²⁺ complex with S²⁻. Now from the titration experimental data it is clear that the return of the original **TPM** spectra is restored and disappearance of the orange color is also well defined (Fig. 8). It indicates the decomplexation of **TPM**–Hg²⁺ complex, as S²⁻ strips away Hg²⁺ from the binding side.



Figure 6. Change of emission spectra of TPM (10 μ M) upon gradual addition of Hg²⁺ (0–6 equiv) in [H₂O:CH₃CN, 1:1, v/v, pH 7.1]. Inset: Plot of [Hg²⁺] versus fluorescence intensity at two different wavelengths (right). Photograph of TPM before and after addition of Hg²⁺ (left).



Figure 7. Fluorescence spectra of TPM (10 μ M) in (CH₃CN:H2O, 1:1, v/v, pH 7.1) in the presence of different metal ions (5 equiv).



Figure 8. Absorption titration spectra of $TPM\text{-}Hg^{2+}$ (10 $\mu M)$ upon increasing concentrations of S^{2-} (0–5 equiv.).

In summary, we have designed and synthesized a simple (internal charge transfer) ICT based probe **TPM** which exhibits a selective, sensitive, colorimetric, and ratiometric sensing toward the Hg^{2+} ion in an aqueous acetonitrile solution. Thus from the UVvis and fluorescence data, it is clear that this sulfur-free receptor is solely selective to the Hg^{2+} ion over other ions. Water solubility, reversibility, and high sensitivity make this probe suitable to use as an excellent chemosensor for Hg^{2+} .

Acknowledgments

The authors thank CSIR and DST, Government of India for financial support. S.D. and K.A. acknowledge CSIR for providing them with fellowships.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013. 06.035.

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