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Highly selective and sensitive fluorescent chemosensor for femtomolar detection of silver ion in aqueous medium



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ABSTRACT

The chemical sensing for the trace level detection of silver ion in aqueous solution still remains a challenge using simple, rapid, and inexpensive method. We report that thionine can be used as a fluorescent probe for the detection of Ag^+ ion. The successive addition of Ag^+ ion to the solution containing thionine quenches (turns-off) the fluorescence intensity of thionine. Association and quenching constants have been estimated by the Benesi–Hildebrand method and Stern–Volmer plot, respectively. From the plot, the nature of the fluorescence quenching was confirmed as static quenching. An important feature of our chemosensor is high selectivity towards the determination of silver ion in aqueous solution over the other competitive metal ions. The detection limit of the sensor achieved 5 fM for Ag^+ ion, which is superior to all previously reported chemosensors. The NMR and FT-IR studies were also carried out to support the complex formation between thionine and Ag^+ ion. The practicality of the proposed chemosensor for determination of Ag^+ ion was carried in untreated water samples.

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1. Introduction

Contamination of water and soil by heavy metal ions is a serious issue worldwide due to their toxicity and biological persistence [1]. Silver ions have strong tissue healing and antimicrobial properties against a wide range of bacteria, for which it has been used for hundreds of years [2]. Silver also plays a major role in different industrial fields such as photography imaging, soldering production, electrical & electronics, automobiles and as a catalyst in oxidation reactions [3]. However, the Ag^+ ions are highly toxic to aquatic organisms and may accumulate in the human body through the food chain [4]. When absorbed in the human body, silver ions can displace essential metal ions such as Ca^{2+} and Zn^{2+} ions in hydroxyl apatite in bone. Moreover, the bioaccumulation and toxicity of silver ions through binding with various metabolites such as amine, carboxyl groups, and inactivating sulfhydryl enzymes have also been disclosed [5]. The high concentration of Ag^+ ion can lead to a variety of adverse health effects, brain damage, nerve damage and immune systems. Therefore, the analysis of Ag^+ ions in water and food resources is of great importance. It is therefore of utmost importance to develop effective sensor with high sensitivity and

selectivity to detect Ag^+ ion in both environmental and food related samples. The U.S. Environmental Protection Agency (EPA) actively regulates silver contamination by setting a secondary maximum contaminant level (SMCL) for this metal at 0.1 mg L^{-1} ($0.93 \text{ }\mu\text{M}$) [6].

Some of the traditional methods such as spectrophotometry, atomic absorption spectrometry, stripping voltammetry, potentiometry and inductively coupled plasma atomic emission spectrometry have been used for the detection of silver ions. However, these methods are associated with many drawbacks including being labor-intensive, high-cost and involving complex processes. Fluorescence-based sensing recently offers significant advantage of simplicity, high sensitivity, high selectivity, easy operation and instantaneous response [7]. Hence, most of the sensors developed for heavy metal ions are based on the conventional fluorescence emission technique by quenching (turn off) of the fluorescence intensity [8]. Fluorescent chemosensors reported for detection of Ag^+ ions are mostly in organic solvent or mixed aqueous solution but we have used only water as medium in our study, ($>0.1 \text{ M}$).

Thionine, a small planar molecule, contains one heterocyclic nitrogen atom and two amine groups symmetrically distributed on each side. Thionine has been used to induce photodynamic inactivation of bladder cancer cells, *Escherichia coli* and *Saccharomyces cerevisiae* [9], as polymerization photoinitiators, in the decontamination of blood

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products, as nucleic acid probes and against bacteria viruses and yeasts [10]. The biological activity of thionine has also been employed in graphene-based immunosensors [11]. The studies on molecular aspects of the interaction of thionine with DNA [12] and RNA [13] are widely available in literature.

Heavy metal ions are relatively easy to chelate and detect in organic solvents, they are rather difficult to recognize directly in aqueous environments, due to their strong hydration. These limitations, together with the fluorescence output signal of sensors, need to be addressed when designing a silver ion sensor for biological and environmental practical applications. To date, many fluorescent probes for silver ion have been reported. Among these literatures, a very few sensors are reported in water for Ag^+ ion [14,15]. The most widely used methods for the separation and determination of the trace amounts of silver(I) ions are solid-phase extraction (SPE), cloud-point extraction (CPE), and dispersive liquid-liquid microextraction as well as various electrochemical methods such as stripping voltammetry and ion-sensitive electrodes. Herein, we designed a highly sensitive and selective fluorescent turn-off chemosensor for Ag^+ ion in pH 7 phosphate buffer solution based on thionine as thionine has higher solubility of in water (nearly >0.1 M). The detection limit of the sensor for Ag^+ ion was reached 5 fM. The sensitivity & selectivity of the sensor is superior to all reported chemosensors. Furthermore, no obvious interference by the other metal ions are observed.

2. Experimental sections

2.1. Materials and reagents

All the reagents and solvents were of analytical grade and used without further purification. All glassware's were cleaned with a diluted HNO_3 solution and rinsed with Milli-Q water prior to use. Thionine, silver nitrate (AgNO_3) and other metal salts were purchased from Sigma-Aldrich. Stock solutions of the metal ions (1 mM) were prepared freshly in Milli-Q water. These solutions were used for all colorimetric and fluorescence spectrophotometric experiments after appropriate dilution. The 0.1 M phosphate buffer solution was prepared from disodium hydrogen phosphate and monosodium dihydrogen phosphate.

2.2. Apparatus and procedure

UV-Vis absorption spectra were recorded by using the Agilent spectrophotometer 89090A in a 1 cm path length quartz cuvette at room temperature. Fluorescence emission spectra were performed using a

Cary Eclipse fluorescence spectrophotometer equipped with a xenon lamp excitation source. Both the excitation and emission slit width was set to 5.0 nm. Measurements of pH were made with EUTECH Instrument's pH meter. FT-IR spectra were recorded using Thermo FT-IR spectrophotometer. ^1H NMR spectra was measured with 300 NMR spectrometers (JEOL-ECX).

For absorption and emission spectra, stock solutions of metal salts (1 mM) were prepared in Milli-Q water. All the experiments were carried out with 12 μM solutions of thionine. The fluorescence measurements were carried out at the maximum excitation wavelength of 598 nm and the maximum emission wavelength of 608 nm. Before each measurement, the solution was allowed to stand for 2 min.

3. Results and discussion

3.1. Spectral studies of thionine

As shown in Fig. 1A, in the UV-Vis spectrum of thionine exhibits two characteristic absorption bands at 598 and 565 nm. The 598 nm band is a characteristic absorption feature of monomeric form, and the 565 nm shoulder can be attributed to the H-type dimer aggregate [16]. Of the various species of thionine in solution, only the monomer has fluorescent property. Moreover, Rabinowitch and Epstein have proposed [17] that thionine dimerizes in water solutions but does not in alcoholic solutions. Fluorescence emission spectrum of thionine was given in Fig. 1B. The maximum emission peak of thionine was appeared at 623 nm due to excitation of the free thionine molecule at 598 nm. The energy of the emitted photon was equal to the energy difference between the two states.

3.2. Effect of pH on spectral properties of thionine

The effect of pH on the spectral properties of thionine was investigated in aqueous medium (shown in Fig. 2). The thionine adsorption spectrum shows marked pH dependence [18–21]. The thionine molecule can exist in the following forms at different pH: (i) neutral form at $\text{pH} = 10$, (ii) monocationic form at $\text{pH} = 2$ to 8 and (iii) dicationic form at $\text{pH} < 2$ [21]. It can be seen that the fluorescence intensity of the thionine increases with increasing of pH from 2 to 7 and then the intensity slightly decreases up to $\text{pH} = 8$. Finally it remains constant up to $\text{pH} = 10$. Since, the pK_a value of thionine is 6.3 [22], when pH of the solution is increased from 2 to 7, the structure of the thionine has been changed from dicationic form (diprotonated) to monocation (monoprotonated) form up to $\text{pH} = 7$ and then decrease slightly up

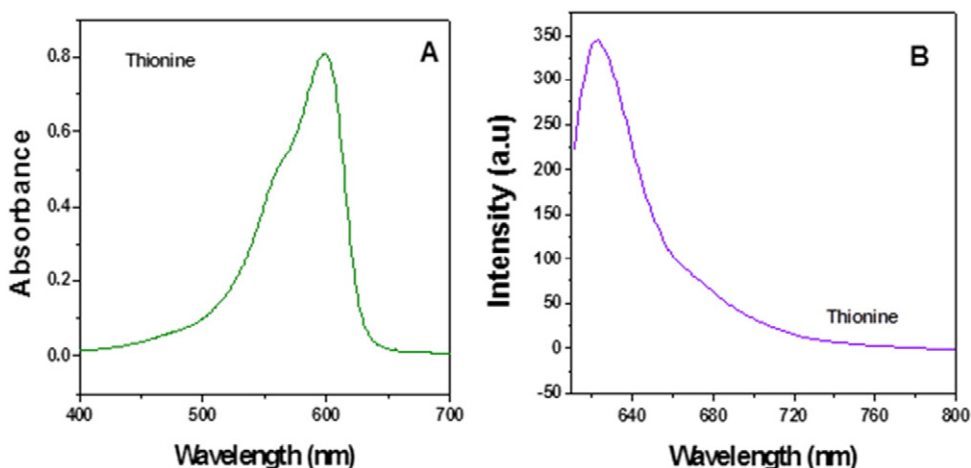


Fig. 1. UV-Vis spectra (A) and fluorescent spectra (B) (excitation was at 598 nm) for 12 μM of thionine in phosphate buffer solution (pH 7).

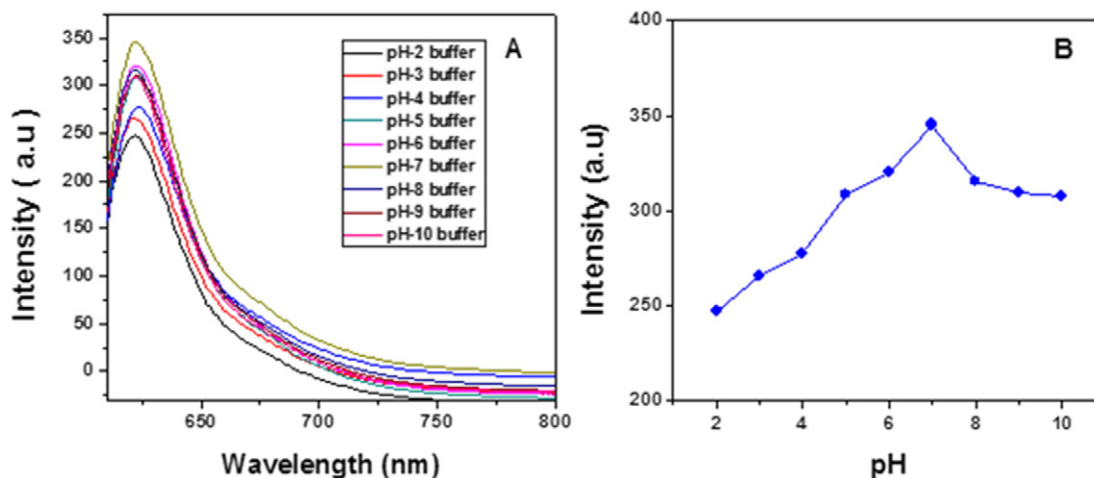


Fig. 2. Fluorescence responses of the thionine solution (12 μM) in the presence of various pH solutions.

to 8 and remains constant up to pH = 10, due to the existence of neutral form in equilibrium.

3.3. Sensing property of thionine towards silver ions

Fig. S1 shows the UV–Vis absorption spectra of thionine in the presence of different Ag^+ ion concentrations. It was observed that the absorbance of the thionine decreased with the increasing of Ag^+ ion concentration. In this plot, no further decrease of the absorbance up to 700 pM concentration of Ag^+ ions and then remained constant indicating the saturation of the absorbance intensity of thionine. The intensity of the peak decreased due to the formation of thionine- Ag^+ ion complex. According to Pearson's classification, metal ions, such as Ag^+ ions, being “soft” cations, prefers “soft donors” for complexation. In designing the chemosensor for Ag^+ ions, soft sulfur or nitrogen donor centers should be present in the sensing molecule. Therefore, the two amino groups of thionine may be providing a good binding site for Ag^+ ion [23,24]. Because the lone pair of electrons present in the N-atom of amino group is not involved in the resonance of the thionine molecule and presents free for binding with metal ions.

The spectral data were used to calculate the binding constant between the thionine and the Ag^+ ions by applying the Benesi–Hildebrand Eq. (1) [25].

$$\frac{1}{A-A_0} = \frac{1}{A_{\max}-A_0} + \left[\frac{1}{K[M^{n+}]} + 1 \right] \quad (1)$$

where A is the absorbance of thionine measured with different concentrations Ag^+ ions, A_0 is the absorbance of thionine, A_{\max} is the absorbance of thionine in the presence of maximum concentration of silver ions, $[M^{n+}]$ is the concentration of the metal ion and K is the binding constant. By plotting $1/(A - A_0)$ against $1/[M^{n+}]$ (Fig. S2), the binding constant (K) was determined from the ratio of intercept/slope as $9.94 \times 10^{11} \text{ M}^{-1}$ for Ag^+ ion. This value is very much higher than earlier reports. For example, Tilak Raj et al. reported binding constant value [26] of $4.30 \times 10^3 \text{ M}^{-1}$ using nanoaggregates of benzothiazole-based amidine and Meiling Wang et al. reported K value of $\sim 10^5 \text{ M}^{-1}$ using erythrosin B with Ag^+ ion [27]. The results indicate that the interaction between thionine and Ag^+ ion molecules is stronger than the above reported organic molecules and hence the stability of thionine and Ag^+ ion complex is very high.

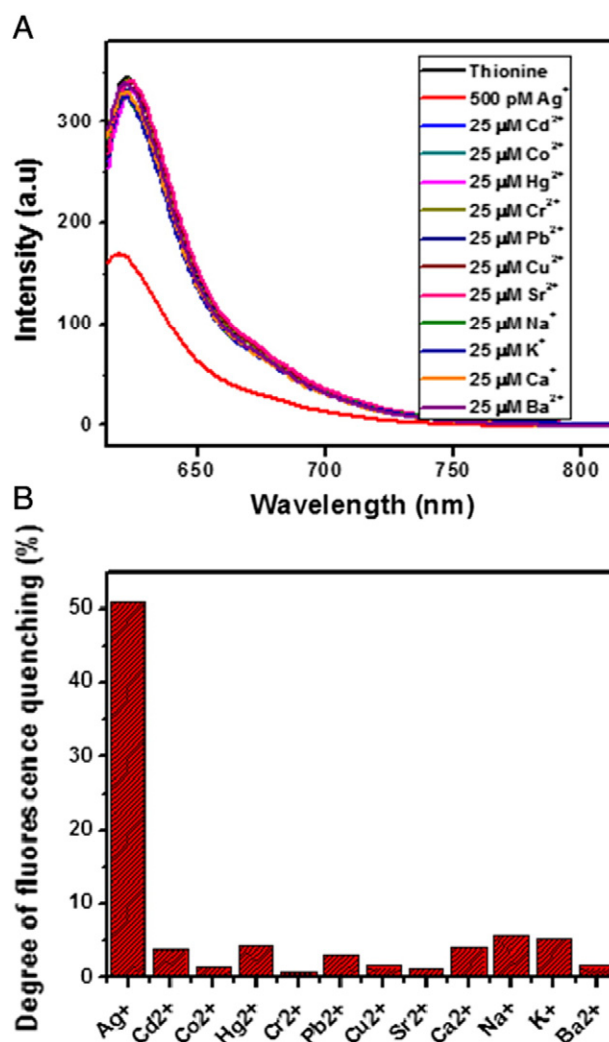


Fig. 3. A. Fluorescence response of thionine solution in the presence of various metal ions. The concentration of silver ion is 500 pM and other metal ions are 25 μM. B. Selectivity bar diagram of the fluorescence quenching of thionine towards Ag^+ ion, the concentration of Ag^+ ion is 500 pM while those of all the other metal ions are 25 μM. The degree of fluorescence quenching is defined as $[(I_0 - I) / I_0]$ multiplied by 100, where I_0 and I are the fluorescence intensities in the absence and presence of the corresponding metal ion at 622 nm, respectively.

3.4. Sensing of thionine towards other metal ions

The fluorescent property of the thionine in the presence different metal ions like Cd^{2+} , Co^{2+} , Hg^{2+} , Cr^{2+} , Pb^{2+} , Cu^{2+} , Sr^{2+} , Na^+ , K^+ , Ca^{2+} and Ba^{2+} was tested in pH = 7 phosphate buffer solution (Fig. 3A). The fluorescent response of thionine was quenched obviously in the presence of Ag^+ ions whereas for other metal ions such as Ag^+ , Co^{2+} , Cr^{2+} , Pb^{2+} , Cu^{2+} , Sr^{2+} , Ca^{2+} and Ba^{2+} ions no change in fluorescence intensity was seen. However, for some other metal ions like Na^+ , Cd^{2+} , Hg^{2+} and K^+ ions, it has minimal effect (Fig. 3B) i.e. 5% of fluorescence quenching. Therefore, thionine can be used to identify Ag^+ ion fluorescent sensor in aqueous medium.

3.5. Selectivity of thionine sensor

To evaluate the selectivity of the probe towards Ag^+ ion, we measured the fluorescence response of thionine – Ag^+ ion complex in the presence of some interfering metal ions individually (Figs. 4 and S3 & Visual color change Fig. S4). Firstly the selectivity of the probes towards biologically relevant metal ions such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ (which exists in high concentrations as in cells) was tested. The above metal ions do not cause any quenching on the fluorescence of the probe even at 50 μM level. Some other metal ions such as Cd^{2+} , Co^{2+} , Zn^{2+} , Hg^{2+} and Pb^{2+} have also no significant effect on the fluorescence spectrum even at same concentrations, whereas Ni^{2+} , Ba^{2+} and Cu^{2+} ions have slight turn on effect. Hence, Ag^+ ions can be easily deduced by the probe in the presence of above metal ions with several-fold of concentrations.

3.6. Sensitivity of the probe

To investigate sensitivity of the thionine towards Ag^+ ion, different concentrations of Ag^+ ions were added into the thionine solution. When the concentration of Ag^+ ion was increased, the fluorescent intensity of the probe decreased (Figs. 5 and 6). The linear range was observed from 5×10^{-15} M to 8×10^{-13} M with a correlation coefficient of $R^2 = 0.9945$. The quenching of fluorescent intensity of the thionine reached the saturation at 700 pM of Ag^+ ion with the 53% decrease in intensity. Hence, the quenching efficiency was very high even at pico molar level of Ag^+ ions. As shown in the inset of Fig. 5, the decrease in fluorescent intensity was directly proportional to the concentration of Ag^+ ions from 5×10^{-15} M to 8×10^{-13} M.

The K_{SV} , the Stern–Volmer constant was measured in the concentrations of Ag^+ ion from 5×10^{-15} M to 8×10^{-13} M using Stern–Volmer-type Eq. (2) [28].

$$I_0/I = 1 + K_{SV}[Q] \quad (2)$$

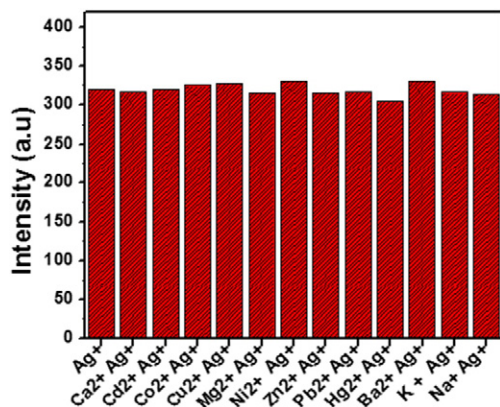


Fig. 4. The Fluorescence intensity of thionine (12 μM) in the presence of 50 μM of various metal ions with an added 200 fM of Ag^+ in Phosphate buffer solution (pH 7) 598 nm.

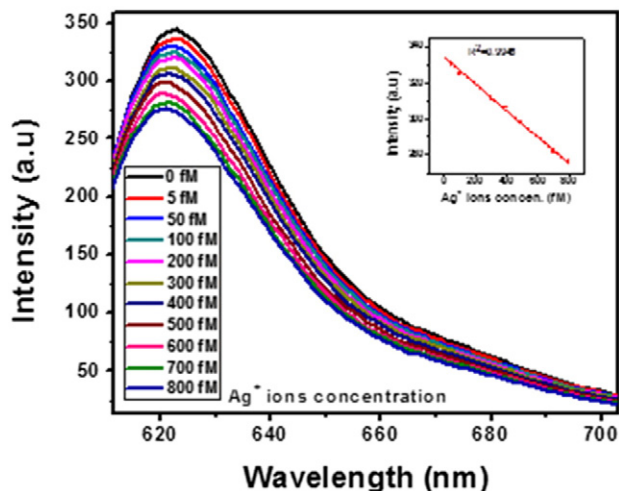


Fig. 5. Variance of the fluorescence intensity as a function of the concentrations of Ag^+ ion (0 fM to 800 fM from top to bottom). The inset shows the linear correlation between the fluorescence intensity and the concentration of Ag^+ ion.

where I and I_0 are the fluorescence intensity of the thionine in the presence and absence of Ag^+ ion, respectively, $[Q]$ is the concentration Ag^+ ion, K_{SV} is the Stern–Volmer constant (K_{SV} was obtained from the slope of the linear plot). Fig. 7 depicts the plot between fluorescence intensity ratio (I_0/I) and the concentration of Ag^+ ion. The Stern–Volmer quenching constant K_{SV} is found to be $2.7482 \times 10^{11} \text{ dm}^3 \text{ M}^{-1} \text{ v}$ with correlation coefficient of 0.9931 and this large K_{SV} value ensured the high sensitivity of thionine for Ag^+ ion. The detection limit of the sensor is 5 fM Ag^+ ion, this value is much lower than the US Environmental Protection Agency (EPA) limit of $[\text{Ag}^+]$ in drinking water (460 nM) [29], and which is 3 orders lower than in magnitude compared to that of bifunctional SDA and multiplexed QF probes based fluorescence sensor (16 pM) [30] and 6 orders lower when compared to a multiwalled carbon nanotube based electrochemical sensor (1.3 nM) [31].

Therefore, the lower detection limit and selectivity of our chemosensor are superior to all the reported chemosensors based on fluorescence method. Furthermore, no interference was observed obviously (see Table 1). To the best of our knowledge, a couple of reports are reported, in which fluorescent chemosensors display a significant selectivity for Ag^+ ion in aqueous solution.

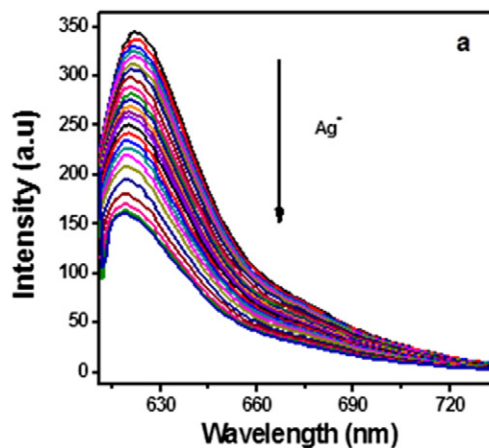


Fig. 6. Variance of the fluorescence intensity as a function of the concentrations of Ag^+ ion (0 fM to 800 pM) from top to bottom.

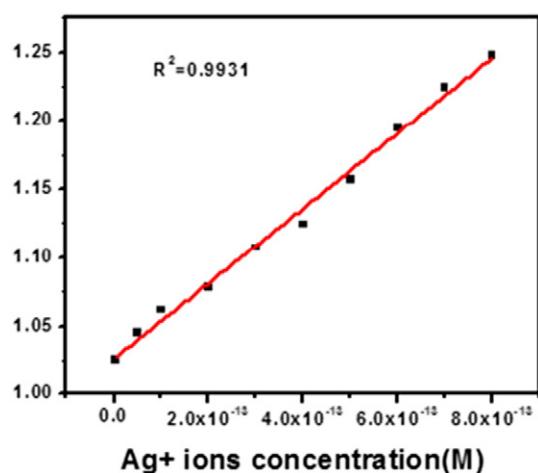


Fig. 7. Linear relationship between fluorescence intensity and Ag^+ ion concentration (5 fM to 800 fM).

3.7. Fluorescence quenching mechanism

As shown in Fig. 7, it is possible to analyze the fluorescence quenching mechanism by using Stern–Volmer kinetics. Since, Stern–Volmer plot is linear, which supports a static quenching process. Static quenching can arise due to the formation of nonfluorescent complex between the fluorophore and the quencher. This mechanism can also be supported by the absence of upward curvature in the Stern–Volmer plot [38]. In addition, the plot of $(I_0/I - 1) / (\text{Ag}^+)$ against Ag^+ ions is found to be non-linear as in Fig. S5, eliminating the possibility of simultaneous occurrence of static and dynamic quenching.

The bimolecular quenching constant K_q can be calculated from the relation $K_q = K_{SV} / \tau_0$ and it is found to be $2.7482 \times 10^{19} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 1, using the Stern–Volmer slope and the lifetime of thionine. In the present study, the higher value of K_q for Ag^+ -thionine system reveals that the quenching is not initiated by collision process but it is due to the formation of ground state complex and also suggests a highly effective static quenching. It is reasonable to reject the dynamic mechanism, because half lifetime of thionine in water is very short (10^{-8} s [39]) and it has relatively large value of the bimolecular quenching rate constant (k_q).

Reproducibility of the chemosensor (Fig. 8, Fig. S6) was tested by applying the sensor for seven times for the determination of Ag^+ ions at fixed concentration. The relative standard deviation was then calculated from the fluorescence intensity obtained for the thionine in the presence of 400 fM silver ions and found to be 0.48% (for all 7 repetitions). The thionine–silver ion complex formation was further confirmed by FT-IR and NMR studies as shown in Figs. S7 and S8 (in supplementary information).

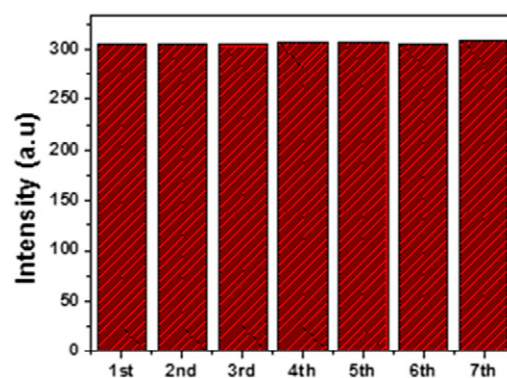


Fig. 8. Fluorescence response of the thionine solution (12 μM) in the presence of 400 fM Ag^+ metal ion. Total number of times are 7.

Based on the results obtained from the above studies, a tentative mechanism is proposed as the amino nitrogen atoms are responsible for capturing the Ag^+ cation. Because the other nitrogen and sulfur atoms of the central heterocyclic ring of thionine are less electron-rich due to delocalization of electrons with the phenyl ring. [16]. As a result of the complexation between Thionine and Ag^+ ions, the number of the free thionine molecules decreases, as indicated by the decrease of the intensity of fluorescence spectrum of thionine molecules. Therefore, thionine can be applied as fluorescent sensor to Ag^+ ions.

In addition, we tested tap water samples with the addition of Ag^+ ions. The analytical recoveries are measured to be in the range of 98% to 99.6%. (Table S1). The results suggest that the proposed method shows a great promise for real water analysis with great accuracy and reliability.

4. Conclusions

In summary, thionine based fluorescent sensing for Ag^+ ion has been developed. It displays high selectivity and sensitivity for Ag^+ ion in aqueous medium, which also showed a good selectivity towards Ag^+ ion over other competitive metal ions. This probe was successfully applied for the detection of Ag^+ ion in aqueous solution containing femto molar level of silver ion with the linear range from 5×10^{-15} M to 8×10^{-13} M, which are superior to most of the current approaches for silver ion analysis. Stern–Volmer quenching constant K_{SV} was determined as $2.7482 \times 10^{11} \text{ dm}^3 \text{ M}^{-1}$ for Ag^+ ion. The NMR and FT-IR studies also support strongly for the formation of complex between thionine and silver ion.

Acknowledgments

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Table 1

Comparison of analytical data for the determination of silver ion.

Compound	Selectivity	Type of sensor Turn on/off	LOD (M)	Linear range (M)	Ref.
Erythrosin B	Ag^+	Turn off	5×10^{-7}	$0-27 \times 10^{-6}$	[26]
NBD-armed thiocalix[4]arene and 7-nitrobenzo-2-oxa-1,3-diazole (NBD)	Ag^+	Turn off	6.5×10^{-7}	—	[32]
Bifunctional SDA and multiplexed QF probes.	Ag^+	Turn on	16×10^{-12}	$16 \times 10^{-12}-10 \times 10^{-9}$	[29]
2,2-disulfediyl bis-(N-anthracen-9-ylmethylene) ethanamine	Ag^+	Turn on	2.797×10^{-7}	$10 \times 10^{-6}-100 \times 10^{-6}$	[33]
Molecular light switch Ru complex Ru(bpy) ₂ (dppz) ₂ ⁺ and CdTe quantum dots (QDs)	Ag^+	Turn off	0.1×10^{-6}	$2 \times 10^{-6}-10 \times 10^{-6}$	[34]
CdTe quantum dots (QDs) and dye-labeled single-strand DNA (DNA dye) probes	Ag^+ and Hg^{2+}	Turn off	$2.1 \times 10^{-9} \text{ Ag}^+$ $1.5 \times 10^{-9} \text{ Hg}^{2+}$	$0-20 \times 10^{-9}$	[35]
Heptamethine cyanine	Ag^+	Turn on	34×10^{-9}	0.6×10^{-7} to 50×10^{-7}	[36]
Pyrrolo-dC (PdC)-modified duplex DNA	Ag^+	Turn off	9.2×10^{-9}	$0-100 \times 10^{-9}$	[37]
Thionine	Ag^+	Turn off	5×10^{-15}	5×10^{-15} to 8×10^{-13}	Present work

Appendix A. Supplementary data

Supplementary data of this article can be found online at <http://dx.doi.org/10.1016/j.sbsr.2015.10.004>.

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