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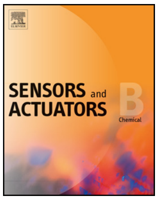

# Fluorogenic detection of $Hg^{2+}$ and $Ag^{+}$ ions via two mechanistically discrete signal genres: A paradigm of differentially responsive metal ion sensing

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ABSTRACT

Selective and specific detection of $Hg^{2+}$ and $Ag^{+}$ ions has been enabled by a prudently developed new schiff base probe (L) in a differentially responsive manner of emission intensity. An exciting aspect of the devised ligand is its efficient detection ability of $Hg^{2+}$ and $Ag^{+}$ ions by two different fluorometric responses: a TURN-ON signal for $Hg^{2+}$ and a TURN-OFF response for $Ag^{+}$. The sensing aptitude of the analytes in concern in 1:1 (v/v) acetonitrile/HEPES Buffer (10 mM, pH 7.4) mixed aqueous medium further make it an encouraging prospect for practical applications. The functioning of two different mechanisms for judicious distinction and detection of the $Hg^{2+}$ and $Ag^{+}$ ions has also been successfully validated. Sensing of $Hg^{2+}$ proceeds via conventional metal chelation enhanced fluorescence mechanism (CHEF) whereas detection of $Ag^{+}$ follows from the formation of nano-sized aggregates in the working medium.

## 1. Introduction

The toxicity and hazardous level of mercury ions can be estimated by the fact that they are wholly banned in electrical and electronic equipment by the European Union's Restriction on Hazardous Substances (RoHS) directive [1]. Its ill-effects range from critical harm to the nervous as well as endocrine systems, even at very low concentrations, in human beings [2,3] to severe environmental damage [4–7]. Accumulation of mercury can also lead to the infamous Minamata disease [8]. Mercury accumulation in the environment results from a number of natural as well as human sources such as volcanic eruptions, burning of fossil fuels and gold mining [9,10]. Mercury in the form of methyl mercury is considered to be particularly damaging to the central nervous system [11,12]. Therefore, selective and sensitive chemosensors for mercury detection are highly desirable.

Silver, on the other hand, has for long been extensively used commercially in electronics, imaging and pharmaceutical realms [13]. As a result of excessive use for industrial purposes, the accumulation of silver in the environment has become a grave concern. The involvement of silver in biological systems including its ability to displace $Zn^{2+}$ and $Ca^{2+}$ ions in hydroxyapatite and its propensity to deactivate a series of sulfhydryl enzymes poses serious health hazards as well [14–17]. Surplus amount of silver ions can also lead to buildup of insoluble precipitates in the body causing severe damage to eyes and skin [18]. Therefore, specific detection of silver ions remains a task of seeming urgency.

The area of differential multi metal ion sensing by a single probe remains to be one of the unusual and exceptional field of research [19–21]. The importance of this domain can be gauged from its ability to open avenues for further applicability prospects such as utilization as molecular keypads, lab-on-a-chip and logic gate operation [22,23]. However, selective sensing of important toxic metal ions commonly involves the utilization of sophisticated synthetic and purification procedures. The process of building on simple known systems is invaluable for selective detection of such important species. In our continuous efforts towards moving in this direction [24–31], we have synthesized a new fluorogenic chemosensor that selectively detects both $Hg^{2+}$ and $Ag^{+}$ through distinct fluorogenic responses: 'off-on' for $Hg^{2+}$ and 'on-off' for $Ag^{+}$ ions. Another exciting feature of the probe was that without the use of any exceptional high wavelength emitting fluorophore we were able to achieve emission close to 600 nm in aqueous medium which to a great extent, eliminates prospects of biological interference [32,33].

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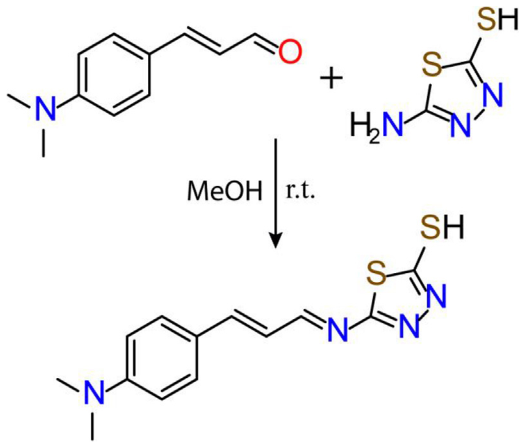

**Scheme 1.** Synthesis of the ligand L.

Present day methodologies for detection of both these metal ions include their recognition by inductively coupled plasma mass spectrometry (ICP-MS) [34], stripping voltammetry [35] and atomic absorption spectrometry [36]. However, the problem with the aforementioned analysis methods lie in their comparatively difficult operational procedures, cost ineffectiveness, immobile nature of the instrument and challenging sample pre-treatment aspects. The use of fluorescence based methodologies is preferable owing to their ability to overcome these difficulties.

## 2. Experimental

### 2.1. General information and materials

All materials for synthesis were purchased from commercial suppliers. The absorption spectra were recorded on a Perkin-Elmer Lamda-25 UV–vis Spectrophotometer using 10 mm path length quartz cuvettes in the range 300–700 nm wavelengths, while the fluorescence measurements were conducted on a Horiba Fluoromax-4 Spectrofluorometer using 10 mm path length quartz cuvettes with a slit width of 3 nm at 298 K. The mass spectrum of L was obtained using Waters Q-ToF Premier Mass Spectrometer. The NMR spectra were recorded on a Bruker Avance 600 MHz Instrument and the chemical shifts were presented in parts per million (ppm) on the scale. The following abbreviations were used to describe spin multiplicities in $^1$H NMR spectra: s = singlet; d = doublet; t = triplet; m = multiplet.

### 2.2. Synthesis of the probe L

4-(Dimethylamino)cinnamaldehyde (1.05 mmol) and 5-Amino-1,3,4-thiadiazole-2-thiol (1 mmol) were stirred at room temperature in methanol to afford a dark red precipitate (L). The obtained precipitate was subsequently filtered and washed with cold methanol to give pure L. The synthetic scheme is shown in Scheme 1. The structure of the probe was fully characterized by NMR spectroscopy and mass spectrometry. Yield = 85%; $^1$H NMR (600 MHz, DMSO, TMS): 14.30 (s, 1H), 8.30–8.28 (d, 1H), 7.58–7.51(m, 2H), 6.97–6.91(m, 3H), 6.76–6.74 (d, 1H), 3.02 (s, 6H). $^{13}$C NMR (600 MHz, DMSO, TMS): 152.71, 131.15, 122.77, 121.43, 112.33 ESI–MS: *m/z* Calculated for $C_{13}H_{14}N_4S_2$ [M] = 290.06, Found [M+H$^+$] = 291.07.

### 2.3. UV–vis and Fluorescence spectroscopic studies

Stock solutions of various ions ($50 \times 10^{-3}$ mol L$^{-1}$) were prepared in milliQ water. Chloride, nitrate or perchlorate salts were used for various metal ions. A stock solution of L ($5 \times 10^{-3}$ mol L$^{-1}$) was prepared in DMF. All UV–vis and fluorescence experiments were carried out in 1:1 (v/v) acetonitrile/HEPES Buffer (10 mM, pH 7.4) medium. For the titration experiments, a $1 \times 10^{-3}$ M solution of L in a quartz optical cell of 1 cm optical path length was titrated with increasing concentration of the concerned ion solution.

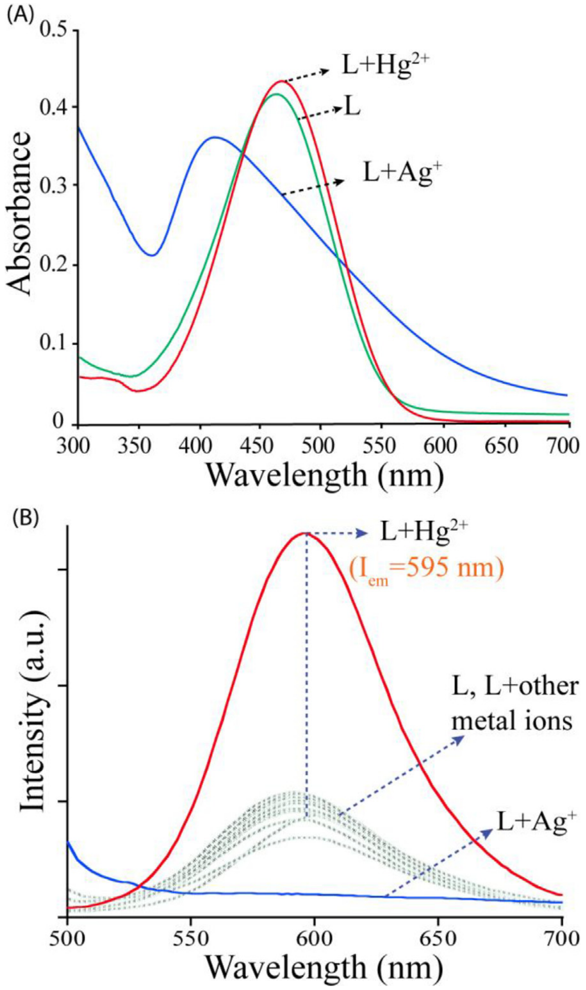

**Fig. 1.** **A)** Changes in the absorbance spectrum of L upon addition of $Hg^{2+}$ and $Ag^+$ in 1:1 (v/v) acetonitrile/HEPES Buffer (10 mM, pH 7.4) medium at room temperature. **B)** Fluorescence intensity change of L upon addition of different metal ions in the same working medium.

### 2.4. Evaluation of the apparent binding constant

The ligand L with an effective concentration of $10.0 \times 10^{-6}$ M was used for the fluorescence emission titration studies with $Hg^{2+}$ solution. The effective $Hg^{2+}$ concentrations were varied between 0 and 20 μM for this titration. The apparent binding constants for the formation of the respective complexes were evaluated using the Benesi–Hildebrand (B–H) plot (Eq. (1)) [37,38].

$$1/(I - I_0) = 1/\{K(Imax - I_0)C\} + 1/(Imax - I_0) \quad (1)$$

$I_0$ is the emission intensity of L at λ = 595 nm, I is the observed emission intensity at the particular wavelength in the presence of a certain concentration of the metal ion (C), Imax is the maximum emission intensity value that was obtained at λ = 595 nm during titration with varying metal ion concentration, K is the apparent binding constant (M$^{-1}$) and was determined from the slope of the linear plot, and C is the concentration of the $Hg^{2+}$ added during titration studies.