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# Selective colorimetric and fluorescence ‘turn-on’ sensor for $Ag^+$ and in-situ sensing of $CN^-$ (off–on–off) via displacement approach

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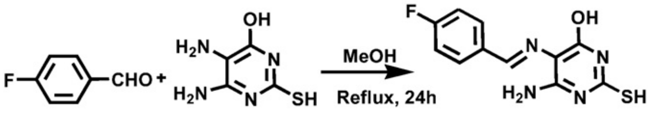
ABSTRACT

In this contemporary work we designed and synthesized a simple tetra dentate Schiff base, which displays colorimetric and fluorescence “turn on” sensing behavior towards $Ag^+$ in aqueous DMF (50%) solution. Benesi Hildebrand–plot reveals 1:2 binding mode between probe and $Ag^+$ with limit of detection down to 1.12 μM. Cyclic voltammograms exhibits high anodic shift with $Ag^+$ due to the charge transfer from ligand to metal ion. The binding mode was proved by NMR titrations, FE-SEM elemental analysis & advance DFT calculation. Additionally, the subsequent $Ag^+$-complex also shows an extremely selective response to $CN^-$ among other anions due to the displacement of $Ag^+$ via $CN^-$, forming $[Ag(CN)_x]^-$ species into the medium. Probe was used as coated paper test strip which served as mini colorimetric device for detection of $Ag^+$ and $CN^-$.

## 1. Introduction

Many human syndromes are activated by interaction of poisonous metal ions and anions like copper, silver, mercury, lead, cyanide and acetate. Among transition metals, silver is very essential but extreme consumption causes more serious pollution to the environment and harm to human health [1,2]. Some diseases like stomach distress, skin irritation, nervous damage, organ edema and even death occurs after accumulation of $Ag^+$ into the human body [3–5]. $Ag^+$ inactivates the function of sulfhydryl enzymes and changes the protein confirmation and its function [6]. Therefore it is of great importance to develop a selective, rapid, sensitive and simple detection method for determination of $Ag^+$. Although many recent instrumental analytical techniques such as atomic absorption spectroscopy [7,8], differential pulse anodic stripping voltammetry [9,10], potentiometric method [11] and inductively coupled plasma-mass spectroscopy [12,13] have been used for detection of $Ag^+$. However, these techniques require complicated instruments and time-consuming processes, so not frequently used. Meanwhile, optical probes, especially the fluorescence probes have high sensitivity, good selectivity, low detection limit, ease of operation and large dynamic concentration range [14,15,32] have substantial attention in recent years. Most $Ag^+$ probe function as 1:1 binding mode, the 1:2 binding mode has similarly like nature's binding or appreciation like protein-metal ion binding [16] and antigen-antibody [17]. We assumed that 1:2 binding between a probe and $Ag^+$ would afford a valuable sensing mechanism. Among conflicting anions $CN^-$ is enormously poisonous and voluntarily absorbed via lungs and gastrointestinal tract, which causes vomiting, convulsion, loss of consciousness etc. [18,19]. It has robust binding affinity towards cytochrome $a_3$, thus decreases oxidative metabolism due to disturbing the electron-transport chain in mitochondria [20]. It rises the $Ca^{2+}$ absorption inside the cell and increases the level of reactive oxygen species (ROS) thus obstruct antioxidant resistance systems [21,22]. Since $CN^-$ can easily forms complex with $Cu^{2+}$, $Ag^+$, $Ni^{2+}$, $Hg^{2+}$, $Fe^{2+}$ and high stabilization ligand field effect reassures development of stable $[M(CN)_x]^-$ species. Recently many copper–cyanide “off–on” type fluorescent probes have been reported [23–26]. However, only a few examples of $Ag^+$-complex are used for anion sensor [27,28]. We anticipated that a silver complex could be exploited for sensing of $CN^-$ through removing $Ag^+$ from the composite and form very stable $[Ag(CN)_x]^-$ which $K_{asso} = 1.1 \times 10^{18}$ L-mol$^{-1}$ in aqueous medium. This method would release probe from $Ag^+$-complex and subsequently encourages substantial signal productivity.

With this objective in mind, we planned a novel probe i.e. 5,6-diamino-4-hydroxy-2-mercaptopyrimidine (Hdahmp) (Scheme 1) ligand. The synthesized probe shows naked eye and emission “turn-on” for $Ag^+$ in aqueous DMF (50%) solution. The in-situ $Ag^+$ complex was



**Scheme 1.** Synthesis of 5-(-4-fluorobenzylideneamino)-6-amino-2-mercaptopyrimidin-4-ol.

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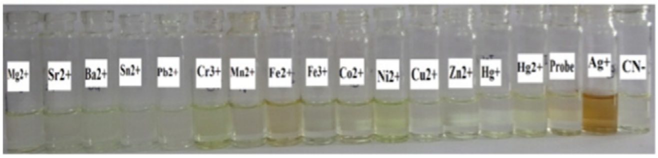

**Fig. 1.** Naked eye detection of $Ag^+$ and $CN^-$ with probe.

supplementary used for fluorescence "on-off" appreciation of $CN^-$ via displacement approach. The applicability of the probe for the analysis of $Ag^+$ in drinking water and actual environmental were also evaluated and discussed.

## 2. Result and discussions

### *2.1. Synthesis and characterization of 5-(4-flurobenzylidenenamino)-6-amino-2-mercaptopyrimidin-4-ol*

Probe was synthesized by coupling of 4-5 diamino-6-hydroxy-2-mercaptopyrimidin (158 mg, 1.0 mmol) and *p*-fluoro-benzaldehyde (124 mg, 1.0 mmol) in methanol by addition of catalytic amount of $H_2SO_4$ (2 drops) with constant stirring. The reaction mixture was refluxed for 1 day; light yellow precipitate was obtained, filtered and washed with hot methanol (Scheme 1).

Anal. calc. for $C_{11}H_9N_4SFO$- Theoretically- C-49.99; H-3.43; N-21.20; S-12.13; F-7.19; O-6.05; Experimentally- C-49.23; H-3.46; N-21.5; S-12.23.

FE-SEM calc.- C-49.45; N-21.47; S-12.75; F-7.28; O-6.05 (Fig. 9a).

IR (KBr/$cm^{-1}$); $\nu_{as}$-$NH_2$-3492, $\nu_s$-$NH_2$-3367, $\nu$-OH-3134, $\nu$-NH-2905, $\nu$-NH-1629, $\nu$-C = N-1546, $\nu$-C = S-1246 (Fig. S1).

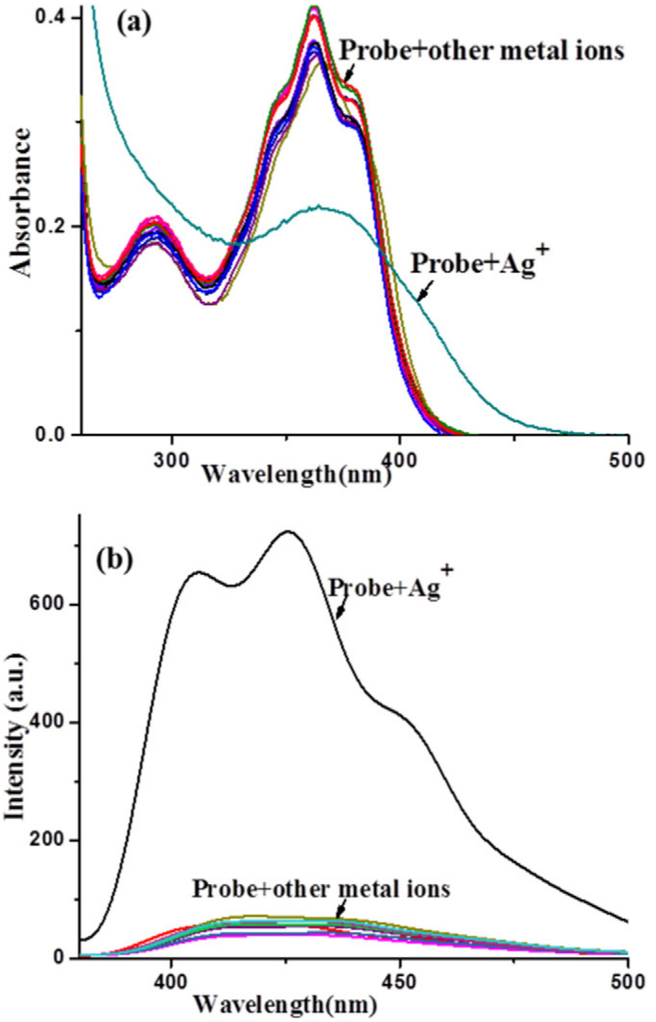

**Fig. 2.** Selectivity of probe on interaction with different metal ions (a) absorption spectra (20 μM), (b) emission spectra (5 μM) in aqueous DMF (50%) HEPES buffer (pH −7).

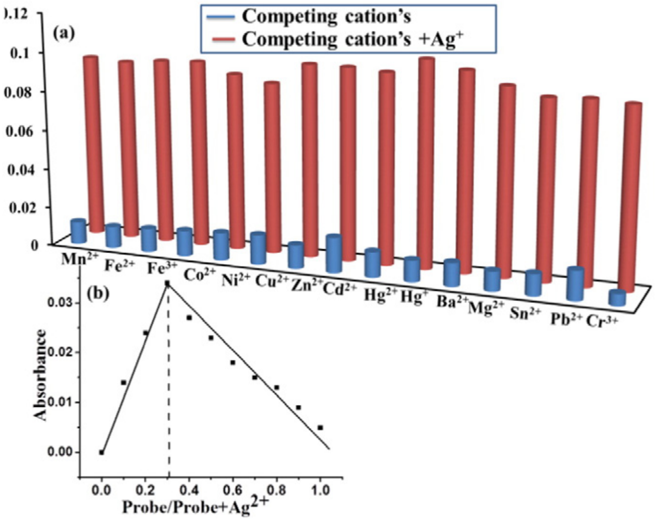

**Fig. 3.** (a) Interference study by the addition of different cations (2 eq.) to a solution of probe-$Ag^+$ in aqueous DMF (50%) HEPES buffer (pH −7). (b) Job's plot shows the 1:2 complex formations between probe and $Ag^+$.

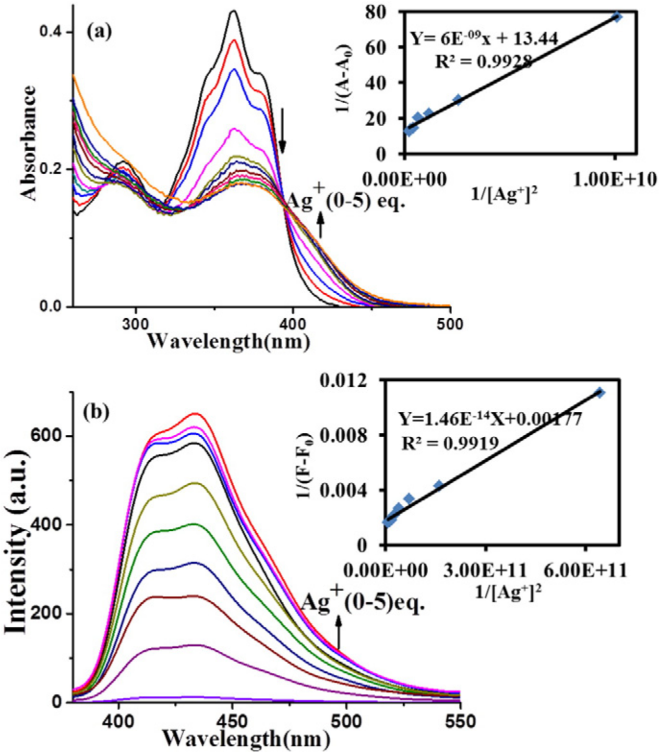

**Fig. 4.** (a) Absorption titration spectra (20 μM) and (b) emission titration spectra (5 μM) of Probe with $Ag^+$ ions (0–5 equiv.) in aqueous DMF (50%) HEPES buffer (pH −7). Inset: Benesi–Hilderbrand plot for the binding of $Ag^+$.