



RECENT PROGRESS OF FLUORESCENT PROBE FOR SELECTIVE DETECTION OF SILVER (I)

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ABSTRACT

Silver and its complexes, are toxic to bacteria, algae, and fungi while it is the least toxic for humans among. Silver ions and silver nanomaterials irreversibly bind with the key enzyme systems in the cell membranes of pathogens. In fact, recent study has shown that silver ion can cause severe damage to both humans and the environment. Thus, blood silver (argyriaemia) and urine silver excretion are useful clinical indices of human silver exposure. In order to detect silver ions, some traditional methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectroscopy (ICP-MS), ion-selective electrodes (ISEs) etc. have been proposed in literature. However, these methods often require expensive equipment and complicated techniques. In contrast, detection by fluorescence techniques is highly attractive due to its high sensitivity and real-time detection approach in a non-destructive way. This review article covers the design of fluorogenic probes, mechanistic behaviour of Ag(I) detection and their application in living cell imaging.

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INTRODUCTION

Silver has long been valued as a precious metal that is beneficial to humans. During several years, it has been well known that silver ions have the ability to kill harmful bacteria [1-3]. It can damage benign bacteria and affecting their reproduction through inhibition their growth [4]. Silver ion has extensive usage especially in the imaging, photographic and electronic industries. Upon release into the environment silver ions can bind readily to various metabolites and enzymes [5-10]. In fact, recent study has shown that silver ion can cause severe damage to both humans and the environment [11,12]. Eyes secrete mucus and make the skin dark due to the excessive silver ion intake that can cause insoluble substances in eye and skin cells [13]. Thus, blood silver (argyriaemia) and urine silver excretion are useful clinical indices of human silver exposure. Every year over 2500 tons of silver are discharged as industrial wastes into the environment, including 150 tons into the sludge of sewage treatment plants, and 80 tons into surface water [14]. In recent years, with the rapid progress of nanoscience, nano-Ag catalyzer and antimicrobial reagents have been widely used in research and in clinics. After being discharged into the environment, some of the silver nanoparticles are oxidized to silver ions and easily dissolve in environmental water and also contaminate slowly the ground water.

In this way, silver ion can cause more serious pollution to the environment and damage to human health. According to the World Health Organization (WHO) data, the permissible limit of Ag⁺ in drinking water should not exceed 0.9 μM (approx. 0.1 mg/L). In contrast, excessive Ag⁺ intake can cause cardiac enlargement, growth retardation and degenerative changes in the liver [15,16]. Therefore, it is of great significance to develop a rapid, selective, sensitive and simple detection method for silver ion in environmental samples and human fluids.

In order to detect silver ions at trace quantity levels, several methods such as atomic absorption spectroscopy (AAS) [17-19] inductively coupled plasma-mass spectroscopy (ICP-MS) [20,21] and ion-selective electrodes (ISEs) [22-23] have been proposed. However, these methods often require expensive equipment and complicated techniques. Fluorescent probe is preferential tool because of its high sensitivity, easy operation and suitable for the biological system.

Fluorescence probes for Ag(I)

Yoon and co-worker described a fluorescent chemosensor for silver ion in CHCl₃-ethanol (7:3, v/v) medium [24]. They have synthesised new fluorescent chemosensors, 1 & 2 based on anthracene (Figure 1). The probe 1 & 2 were based on 1,8- and 9,10- isomer types compound of anthracene respectively, whereas the 1,8-isomer showed selective fluorescent quenching effects with Ag(I) and Cu(II) and on the other hand, the 9,10-isomer displayed a selective fluorescent quenching effect only with Ag(I). The binding of probe 1 and 2 with silver ion were shown in Scheme 1. The 1,8-isomer contains a

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relatively rigid binding pocket compared to the 9,10-isomer. On the other hand, the 9,10-isomer provides an additional binding site (π -cation interaction) in addition to the two pyrazole groups. In the case of these two isomers, the preorganized receptor **1** showed a better binding with the silver ion than receptor **2**.

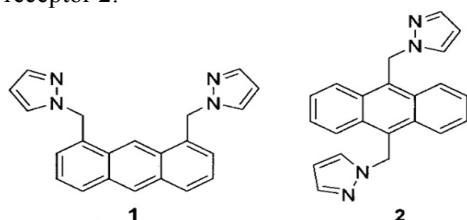
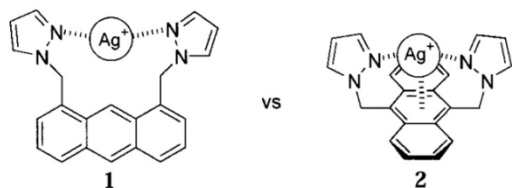


Figure 1 Structure of Probe 1 and 2



Scheme 1 Proposed binding modes of **1** and **2** with Ag(I). Reprinted with permission from ref. 24, Copyright 2002 ACS.

Jiang co-worker designed reported a new fluorescent sensor (**3**) for Ag(I) by incorporating Ag(I)-selective receptor based on aza-crown [NS₂O₂] to the 4-isobutoxy-6-(dimethylamino)-8-methoxyquinoline fluorophore (Figure 2) [25]. Both absorption and emission spectra of the protonated species exhibit a bathochromic effect in comparison with the neutral form. The coordination of Ag(I) with the protonated form of **3** would lead to the deprotonation of the ligand and consequently generates a significant ratio signal output through Ag(I)-induced inhibition of the resonance (Scheme 2). It displayed ratiometric detection of Ag(I) with high sensitivity and selectivity in aqueous solution. They also showed that the resultant silver complex, **3-Ag(I)** can be an excellent sensory system for detecting I⁻ in aqueous solution by sequestering Ag(I) from the **3-Ag(I)** complex.

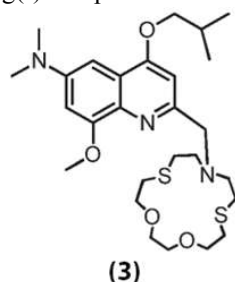
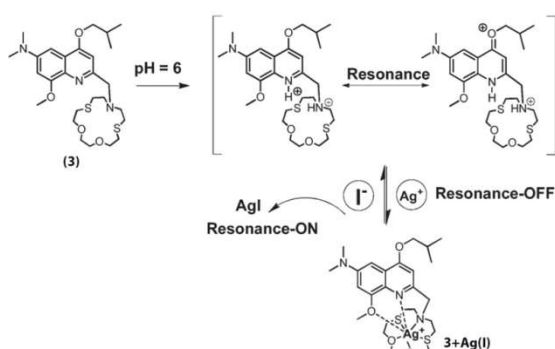
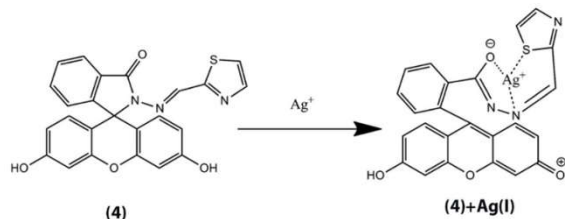


Figure 2 Structure of the probe **3**.



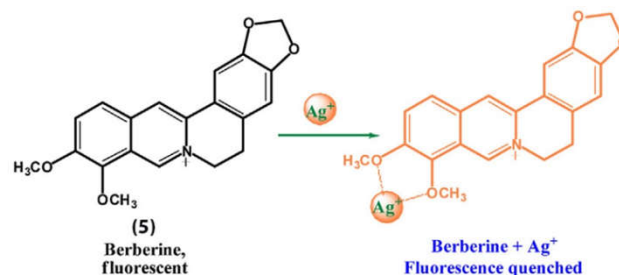
Scheme 2 Proposed binding mechanism of **3** with Ag(I). Reprinted with permission from ref. 25, Copyright 2011 ACS.

Lai, Sun and researchers have reported a fluorescein spirolactam derivative, **4**, was designed and synthesized that displayed a turn-on fluorescence probe (**4**) for the detection of silver ion in aqueous solution [26]. The probe exhibited high selectivity towards Ag(I) in a 20% ethanol solution with a satisfactory detection limit of 0.08 μM . The response of **4** towards Ag(I) is expected to be based on the opening-closing function of the spirolactam ring. The proposed binding mechanism is shown in Scheme 3. In presence of Ag(I), the spirolactam ring is opened and a ternary complex is formed between the Ag(I) ion and O, S, N atoms, which leads to the effect of fluorescence enhancement. In addition, the present probe has been further used for the detection of Ag(I) in tap water, river water and lake water.



Scheme 3 Proposed mechanistic route of sensing Ag(I). Reprinted with permission from ref. 26, Copyright 2014 RSC.

Pitchumani and researchers have reported berberine (Bn), **5**, an alkaloid of pharmacological interest, as a probe for silver ion sensing for the first time [27]. The effect of different metal ions including Ag(I) ion with Bn were investigated by UV-Vis., absorbance and fluorescence spectroscopies analysis with a detection limit of $0.1 \times 10^{-4} \text{ mol L}^{-1}$. They found that Bn is found to be highly selective for sensing Ag(I) over other metal ions such as Cu²⁺, Zn²⁺, Sn²⁺, Ni²⁺, Ba²⁺, Bi²⁺, Pb²⁺, Co³⁺, In³⁺, Mn²⁺, Fe²⁺, Fe³⁺, Li⁺, Hg²⁺ and Ca²⁺. The overall quenching of Bn upon binding with Ag(I) ion, is ascribed to suppression of intramolecular charge transfer (ICT) (Scheme 4).



Scheme 4 Plausible mechanism for the sensing of silver ion using Bn (**5**) as a probe via ICT mechanism.

Recently, Wang et al reported a potential colorimetric and far-red fluorescent probe **6** for Ag(I) based on a dicyanomethylene-4H-chromene chromophore [28]. The probe displayed significant changes in both colour and fluorescence that allowed on-site and naked-eye detection of Ag(I) easily and quickly. The detection procedure was established with high sensitivity. Also, this system was selective towards various metal ions. The fluorescence intensity of this probe showed a linear response to Ag(I) in the concentration range of 0-10 μM with a very low detection limit of 21.1 nM. The mechanism of these fluorescent probes for the selective detection of Ag(I) is depicted in Scheme 5. Ag(I) shows a high tendency to coordinate with soft Lewis base such as sulfur containing donor site of the ligand due its soft nature and thereby this probe would form complex with Ag(I). This phenomenon accompanied with color change and turn-off far-

red emission. In addition, this probe had low toxicity to cells and gave distinct fluorescence changes in cell imaging (Figure 3). All these results demonstrate its promising application prospects for Ag(I) sensing in both environmental and biology fields.



Scheme 5 Chemical structures of fluorescent probe **6** and its complex with Ag(I).

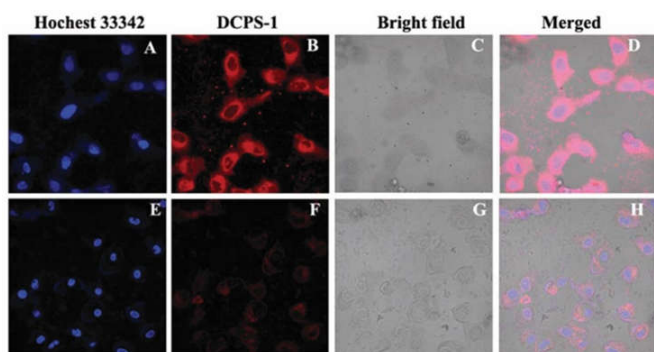
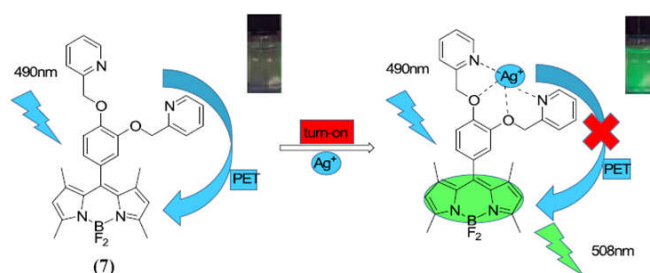


Figure 3 Confocal fluorescence images of living HeLa cells using a 488 nm laser. HeLa cells were co-stained with Hoechst 33342 (10 μ M) and probe **6** (10 μ M), without (A–D) and with (E–H) incubation of Ag(I) (30 μ M) for 30 min.

Very recently, Li and co-workers reported a “turn-on” fluorescent probe (**7**) for Ag(I) based on borondipyrromethene [29]. The probe displayed highly sensitive fluorescence response toward Ag(I) with a more than 40-fold fluorescence enhancement towards 60 μ M of Ag(I) addition. The fluorescence intensity of the probe was linearly dependent on Ag(I) concentration ranging from 0.05 to 60 μ M with a low detection limit (LOD) of 0.02 μ M. Such a very low LOD value complies with the standard of World Health Organization (WHO) for drinking water (0.9 μ M). Moreover, the probe shows excellent selectivity for Ag(I) over other interfering metal ions. Moreover, the response of **7** toward Ag(I) is pH independent in the neutral range from 6.0 to 8.0. Also the response toward Ag(I) is very fast i.e. less than 2 min. In the structure of probe **7**, the nitrogen of pyridine and the oxygen of ether linkage, connected with BODIPY fluorophore, displayed the characteristic of a strong photo-induced electron transfer (PET) to the BODIPY fluorophore. So, the fluorescence of probe **7** is in “off state”. After the addition of Ag(I), the PET process was inhibited by the formation of complex with donor sites (nitrogen and oxygen), responsible for PET process. Thus the fluorescence of the BODIPY restores and showed a “turn-on” fluorescence (Scheme 6). In particular, the probe **7** was applied for detection of Ag(I) in water samples and living cells successfully.



Scheme 6 The proposed sensing mechanism of probe **7** with Ag(I).

CONCLUSION

The methods discussed above in this review provide examples of the designing aspects of recently reported fluorogenic probes for detection of Ag(I). Most of the reported probes are based on the complex formation with Ag(I). The changes in fluorescence response were initiated by the photo induced electron transfer, opening of spirolactam ring etc. with the simultaneous formation of probe-Ag(I) complex. Also, some of the probes were able to monitor the changes in intracellular Ag(I) concentrations by fluorescence microscopy using living cells. This will help to understand the fascinating role of Ag(I) in biological system in further.

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