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A Simple Benzimidazole Quinoline-conjugate Fluorescent Chemosensor for Highly Selective Detection of Ag^{+}

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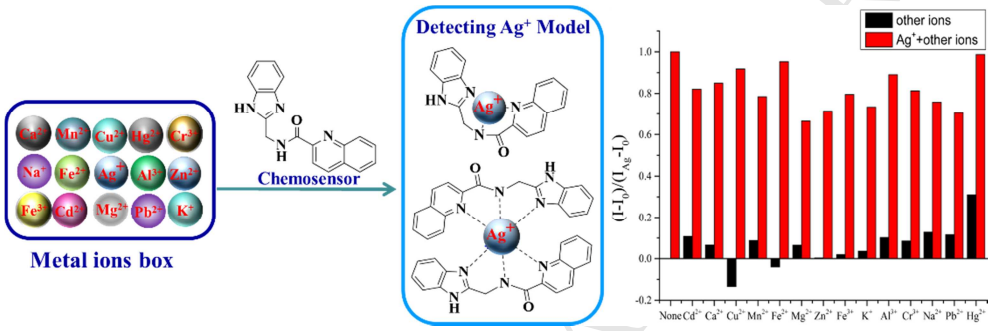
A quinoline benzimidazole scaffold based fluorescence probe was synthesized successfully, which had “turn on” effect for detecting Ag^{+} with high selectivity and good sensitivity.



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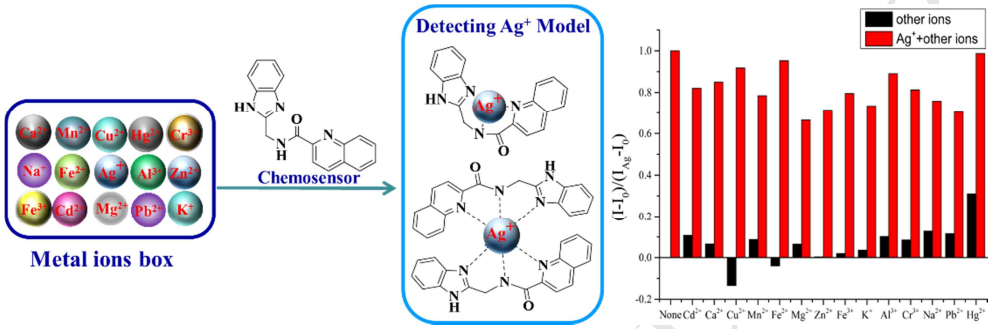

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A Simple Benzimidazole Quinoline-conjugate Fluorescent Chemosensor for Highly Selective Detection of Ag^+

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Abstract

A novel and simple fluorescent chemosensor (L), N-((1H-benzo[d]imidazol-2-yl)methyl)quinoline-2-carboxamide, based on quinoline benzimidazole scaffold was synthesized successfully, which had a "turn-on" effect for Ag^+ detection in methanol/Tris buffer(1:1, v/v, pH=7.35) and exhibited a strong fluorescence emission at 357 nm (λ_{ex} = 300 nm). The chemosensor had high sensitivity and selectivity for Ag^+ even in the presence of other metal ions with the detection limit of 4.4×10^{-7} M, which reached the standard of World Health Organization (WHO) for drinking water (5.0×10^{-7} M). The mechanism of the interaction between the sensor and Ag^+ was investigated in detail through NMR and MALDI Mass spectra analysis.

Keywords

Fluorescence chemosensor; Silver ion; Turn-on effect; High selectivity

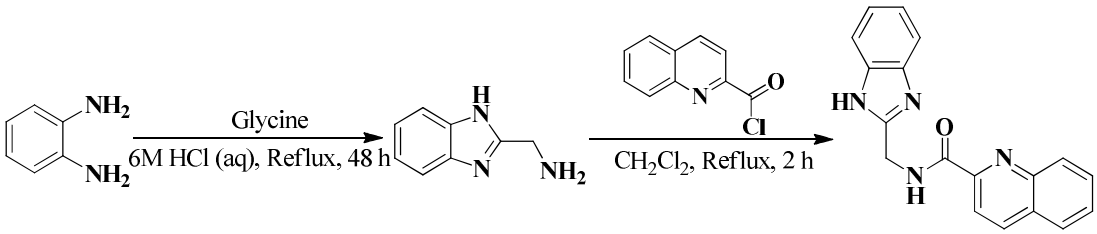
1. Introduction

Sliver is comprehensively applied in electric industry, photographic, imaging, pharmacy, and mirror. It is also widely used in the manufactory of tableware, jewellery, water distillation equipment and wearable accessory.[1,2] However, the overuse of silver and its related complexes in industrial processes has triggered serious environmental crisis. Even worse, the accumulation of silver ions (Ag^+) in organisms results in toxic effects because they can inactive sulfhydryl enzymes and combine with amine, imidazole and carboxyl groups of various metabolites.[3,4] Therefore, the development of rapid, high effective, sensitive and selective methods to detect silver ions is urgent needed for the environment and human health.

Up to now, various approaches have been developed to measure Ag^+ such as inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), electrothermal atomic absorption spectroscopy, atomic fluorescence spectrometry, X-ray fluorescence and electrochemical methods.[5-8] However, most of these methods have some drawbacks including the requirement of expensive equipment, skilled personnel and time-consuming. In comparison, fluorescence spectroscopy with its superiority of simplicity, high sensitivity and widespread availability has become a powerful analytical technique and draws lots of attention. Considerable efforts have contributed to

the silver fluorescent detection and several novel fluorescent probes for Ag^+ have been developed.[4,9-25] However, since Ag^+ pertains to the so-called "silent ions", most of the reported probes are based on a fluorescence quenching mechanism. Therefore, "turn-on" chemosensors for Ag^+ remained a great challenge.[26] Up to now, only a few fluorescence "turn-on" chemosensors have been reported.[27-30] In addition, some of the reported probes have the defects such as poor solubility in aqueous media; difficulty in synthesis methods; insufficient selectivity and sensitivity and so on.[27-29,31,32] As fluorescence "turn-on" sensors have many advantages over "turn-off" sensors such as increased sensitivity and reduced false-positive likability, it is of a great importance to design "turn-on" probes with high selectivity and efficiency for Ag^+ detection.

In view of the recent literatures, the quinoline-derived and benzimidazole-derived compounds are generally used as fluorescent chemosensors for recognition of metal ions.[32-36] Herein, we combined two units together and successfully developed a fluorescence probe, N-((1H-benzo[d]imidazol-2-yl)methyl)quinoline-2-carboxamide (**L**) (**Scheme 1**), which had high sensitivity and selectivity for Ag^+ detection with the advantages of fast response (<1 min), fluorescence turn-on ability and good detection limit.



Scheme 1. Schematic illustration for the synthesis of chemosensor L.

2. Experimental procedures

2.1 Materials and general methods

^{1}H and ^{13}C NMR spectra were measured on a Bruker 400MHz spectrometer. Fluorescence spectra were measured on a SPEX Fluorolog 3-TCSPC spectrometer with 1 cm path length cuvettes and absorption spectra was measured on a Beckman DU 800 spectrometer. Mass spectra were measured on a Waters Micromass Q-TOF Premier Mass Spectrometer and an UltrafleXtreme MALDI-tandem-time-of-flight (MALDI-TOF/TOF) analyzer (Bruker Daltonics, Bremen, Germany) equipped with a 2000 Hz, 355 nm, Nd: YAG laser (minimum spot diameter at 20 μm). Sample surface was irradiated with laser shots in the positive and reflectron mode of the mass spectrometer. Each spectrum was the cumulative average of 1000 laser shots. UV-vis spectra were measured on SCINCO S-4100.

2.2 Synthesis of L

As shown in scheme 1, **L** was synthesized *via* a simple procedure.(1H-benzo[d]imidazol-2-yl)methanamine was obtained *via* the method reported in our previous paper. [37] 2-Quinolinecarboxylic acid (0.38 g, 2 mmol) was refluxed in oxalyl dichloride (20 mL) for 2 h, and then the solvent

was removed. The crude quinoline-2-carbonyl chloride was obtained, which was added into (1H-benzo[d]imidazol-2-yl)methanamine (0.29 g, 2 mmol) dichloromethane solution containing 0.3 mL trimethylamine at 0 ^{o}C in a 0.5 h timescale. The reaction mixture was gradually returned to room temperature and maintained for 4 h, which was evaporated and separated *via* column chromatography. Pale yellow solid was obtained. Yield: 0.42 g, 70%. m.p., 212 ^{o}C; HR-MS (ESI): Calcd for $[M+H]^{+}$ 303.1246; found: 303.1236. ^{1}H NMR (400 MHz, CD_3OD, ppm): 8.49 (d, 1H, *J*=8.40 Hz), 8.20-8.25 (m, 2H), 8.02 (d, 1H, *J*=8.40 Hz), 7.85 (m, 1H), 7.71 (m, 1H), 7.53 (m, 2H), 7.21-7.23 (m, 2H), 4.97(s, 2H). ^{13}C NMR (100 MHz, CD_3OD, ppm): 166.08, 158.58, 151.92, 149.36, 146.68, 137.55, 130.11, 129.50, 129.45, 129.39, 128.01, 127.62, 122.13, 118.33, 115.12. anal. calcd for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.69; N, 18.53; Found: C, 71.39; H, 4.75; N, 18.19.

2.3 Analysis

The nitrate and chloride salts of the metal including Na^{+}, K^{+}, Fe^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ag^{+} were dissolved in deionized water to prepare stock solution (5 mM). Stock solution of **L** was prepared in DMSO (10 mM). The stock solutions were further diluted as needed with methanol-water (v/v=1:1 pH=7.35 10mM Tris-HCl). Therefore ion solutions were added into the buffer solution by using a pipette for UV-vis absorption spectrum and fluorescence spectrum. Both the excitation and

emission slit widths were 5.0 nm. The PH of Tris-HCl buffer was titrated *via* 0.1 M HCl and 0.1 M NaOH.

3. Results and discussion

3.1 Absorption spectroscopic studies

The binding properties of **L** (10 μM) with various metal ions including Na^+, K^+, Cd^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+} and Ag^+ were firstly investigated *via* UV-vis spectrum in methanol-water (v/v=1:1, pH=7.35, 10 mM Tris-HCl). As shown in Fig. S4. (Supporting Information), the absorption spectrum of **L** appeared two strong band at 272 nm and 280 nm. The two absorption band may contribute to the benzimidazole and quinolone segments of **L** respectively. Only upon addition of Cu^{2+}, Fe^{3+} and Ag^+, the spectra of **L** increased apparently, among which, **L** exhibited the most sensitive binding ability with Ag^+. Therefore, the binding capability of **L** with Ag^+ was further studied. As shown in Fig. 1, the absorbance of **L** increased gradually with the amount of Ag^+ increased. The result of UV-vis spectra indicated that **L** formed a complex with Ag^+.

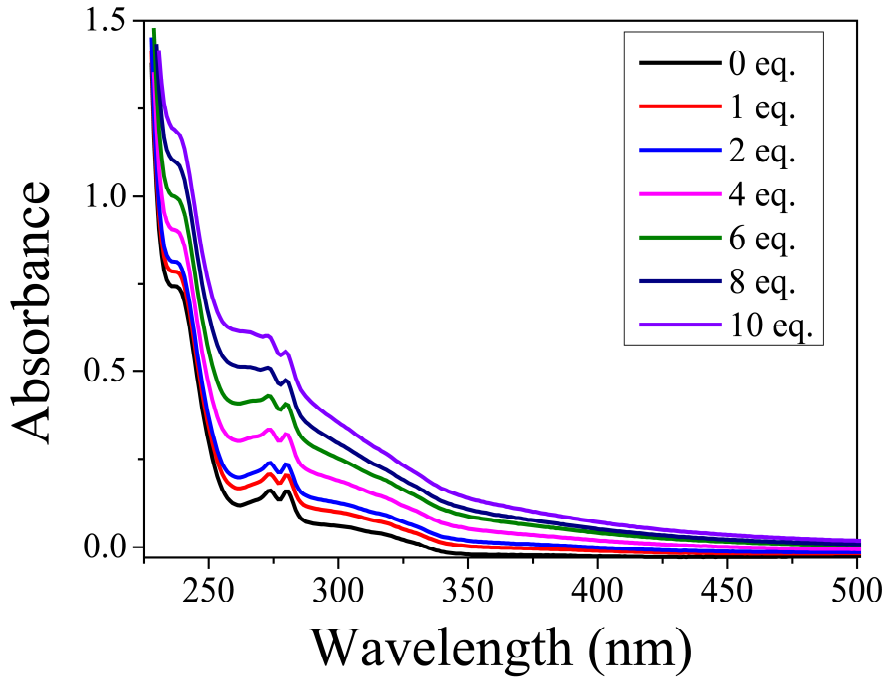


Fig. 1. UV-vis spectra of **L** (10 μM) with different Ag^+ in methanol-water (v/v=1:1, pH=7.35, 10 mM Tris-HCl). The concentrations of Ag^+ values ranged from 0 to 100 μM.

3.2 pH effect to the sensing system

In order to investigate the influence of pH on Ag^+ detection and evaluate the suitable pH span, the acid titration experiments were carried out. As shown in Fig. S5, the fluorescence titration curve of free **L** showed that pH had slight influence on fluorescence emission spectra. However, the spectra of **L** with Ag^+ showed the highest detection intensity from pH 6.0 to 9.0, which were the most common pH environment in nature and daily life. The decrease intensity might be caused by the increasing amount of hydroxyl ions and chloride ions of system which could form Ag(OH) and AgCl precipitations. The wide range of pH in detecting Ag^+ proved that it could be used in various area. Considering

the chemosensor applied to environmental detection, all the further fluorescence measurement were conducted in methanol/water buffer (pH=7.35).

3.3 Fluorescence spectroscopic studies

Fluorescence response properties of **L** (10 μM) with Ag^+ were also investigated in methanol-water (v/v=1:1, pH=7.35, 10 mM Tris-HCl) with the excitation at 300 nm. There were three emission bands which attributed to the benzimidazole and quinolone segments of **L** respectively.[38,39] As shown in Fig. 2, upon the addition of an increasing amount of Ag^+ (0-300 μM), the fluorescence emission intensity of **L** increased gradually, accompanied with a 7-fold improvement at 357 nm, which could be assigned to a chelation-enhanced fluorescence effect between Ag^+ and **L**.[33] Upon the addition of more than 30 equiv. of Ag^+, the complex of **L** and Ag^+ will be precipitated.

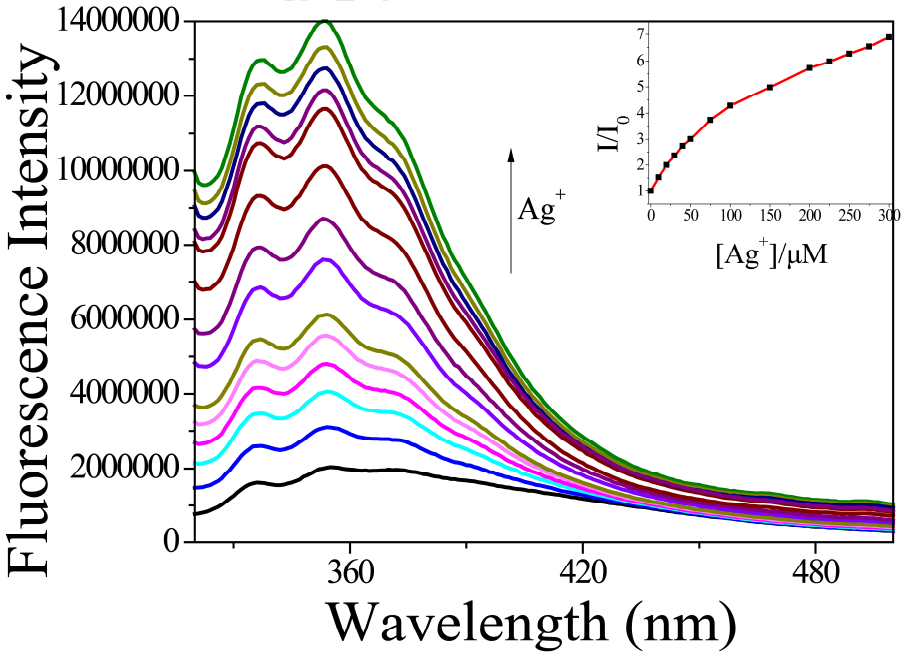


Fig. 2. The fluorescence spectra of **L** (10 μM) upon addition of Ag^+ (0, 10, 20, 30, 40, 50, 75, 100, 150, 200, 225, 250, 275, 300 μM) in methanol-water (v/v=1:1, pH=7.35, 10 mM Tris-HCl). (Inset) The fluorescence intensity I/I_0 upon the addition of Ag^+ (0, 10, 20, 30, 40, 50, 75, 100, 150, 200, 225, 250, 275, 300 μM), which I_0 was the fluorescence intensity of **L** without Ag^+. λ_{ex} = 300 nm, λ_{em} = 357 nm.

The fluorescence binding efficient was acquired *via* the Stern-Volmer equation, $I/I_0 = Ksv\ [Ag^+] + 1$, where I represented the fluorescence intensity of **L** with different concentration of Ag^+, I_0 represented the intensity of **L** without Ag^+, $[Ag^+]$ represented the concentration of silver ions and Ksv represented the Stern-Volmer constant.

According to Stern-Volmer equation, a linear Stern-Volmer plot was obtained with the Ksv value of $3.2 \times 10^4\ M^{-1}$, as shown in Fig. 3.

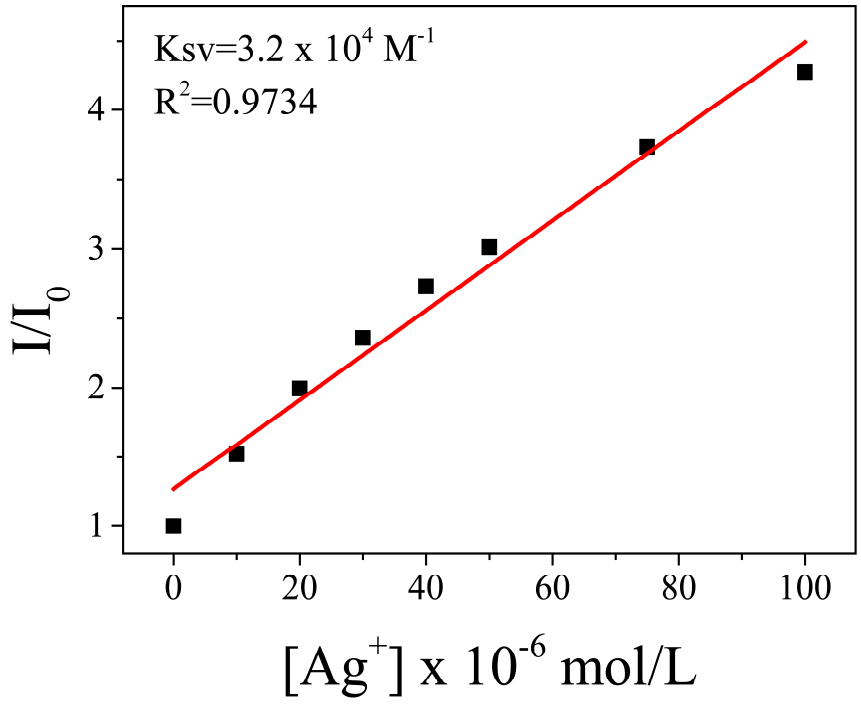


Fig. 3. Stern-Volmer plot for emission intensity enhancement of **L** in methanol-water (v/v=1:1, pH=7.35, 10 mM Tris-HCl) upon addition of Ag^+ (0-100 μM). λ_{ex} = 300 nm, λ_{em} = 357 nm.

The detection limit of Ag^+ was calculated through the following equation: detection limit=3k/σ, where σ was the standard deviation of blank measurements, and k was the slope between the intensity versus Ag^+ concentration.[40-42] According to the equation, the detection limit of Ag^+ reached 4.4×10^{-7} M (Fig. S6). According to the drinking water standard given by WHO, **L** was capable to distinguish between safety and toxic levels of silver ion in drinking water. Furthermore, the comparison between our probe and the reports has been added in the supporting information (Table S1), which indicated the detection limit of L is comparable or better than some similar fluorescent probes literature reported.

Furthermore, the selectivity of the target ion from the competition system is one of the vital features for a practical chemosensor. Therefore, the competition experiments were carried out by recording the changes of the fluorescence intensity before and after adding Ag^+ into the probe solution with interferants (10 μM **L** in methanol/water, λ_{ex} = 300 nm, λ_{em} = 357 nm). Addition of 500 μM of aqueous solution of Na^+, K^+, Fe^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}, no significant spectral changes were observed except Hg^+, (black bars in Fig. 4). Upon the addition of Ag^+, immediate increase in fluorescence emission were observed, (red bars in Fig. 4). The result showed that only Hg^{2+} caused minor increase on fluorescence intensity, other ions almost did not interfere the detection of Ag^+.

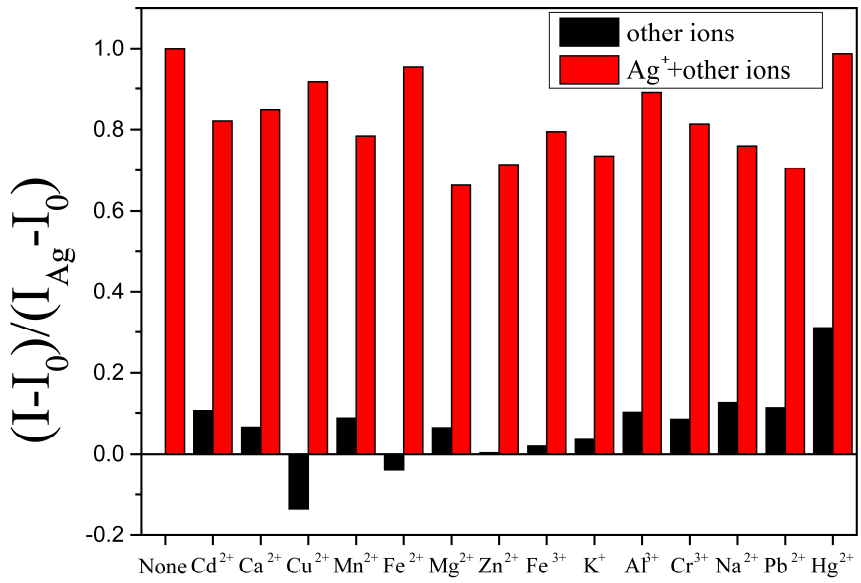


Fig. 4. Fluorescence intensity at 357 nm of **L** (10 μM) in the presence of Ag^+ (100 μM) containing 500 μM of various metal ions in methanol-water (v/v=1:1, pH=7.35, 10 mM Tris-HCl). Black bars represented the fluorescence intensity of **L** (10 μM) upon the addition of various metal ions (500 μM).Red bars represented the fluorescence intensity of the mixture of **L** with various ions followed by addition of Ag^+ (100 μM)) respectively.

Although it was shown that **L** had a strong absorbance upon the addition of Fe^{3+} in the UV-vis spectra (Fig. S4), fluorescence selectivity studies showed that Fe^{3+} only slightly quenched the fluorescence of **L** and had very minor effect on fluorescence detection upon addition of Ag^+. The results proved that **L** can be a potential chemosensor for Ag^+ with promising selectivity under the assay condition in the presence of competitive ions.

As the probe is used to detect Ag^+ ions in environment, **L** (10 μM) was applied to detect Ag^+ in tap water/methanol (v/v=1:1). Ag^+ was deliberately introduced to simulate contaminated tap water. As shown in Fig. S7, the fluorescence intensity gradually increased upon the addition of Ag^+ (0-50 μM).

The result indicated that this chemosensor was suitable for detecting Ag^+ in nature water sample.

3.4 Sensing mechanism of L with Ag^+

In order to gain more information for the complexation between **L** and Ag^+, the ^1H NMR spectra of **L** in CD_3OD solution were studied in the absence and presence of different concentration of Ag^+ (Fig. 5). With the increase of Ag^+ concentration (from 0.2 to 1 equiv.), the signals of all the protons of benzimidazole and quinolone moieties were shifted significantly upfield, which proved **L** formed a firmed binding with Ag^+. The reasons of chemical shifts may be illustrated as followed: when Ag^+ combined with **L**, the electrons of Ag^+ were shared with **L** and thickened the electron cloud of **L,** therefore the signals shifted upfield. When the Ag^+ concentration increased to 2 equiv., the chemical shifts displayed a little difference compared with 1 equiv. Ag^+, which indicated that the binding mode of Ag^+ and **L** changed.

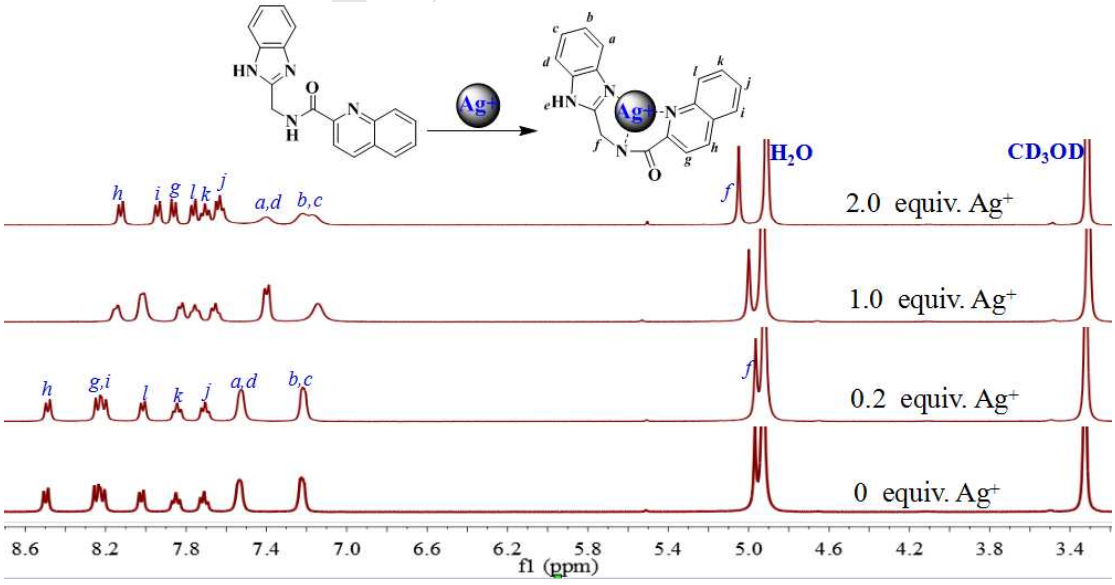


Fig. 5. ^1H NMR spectra of L (10 μM) with addition of Ag^+ from (0-2 eq.) respectively.

To prove the hypothesis, further studied was measured on MALDI mass spectra. As shown in Fig. 6a, the MS spectrum of **L** revealed one main ion, which was $[M+H]^+$. When Ag^+ was added to the **L** solution in a 1:1 molar ratio, a mixture of **L**-Ag^+ complexes was identified (Fig. 6b). The mixture of 1:1 and 2:1 **L**-Ag^+ complexes occurred. As the concentration of Ag^+ increased to 2 equiv., the peaks of complexes increased and almost all complexes turned to [**L** + Ag^+] (Fig. 6c), which was in accordance with the ^1H NMR data. All the results confirmed that **L** could formed a stable complex with Ag^+ and the binding mode of Ag^+ and **L** was dependent on the concentration of Ag^+.

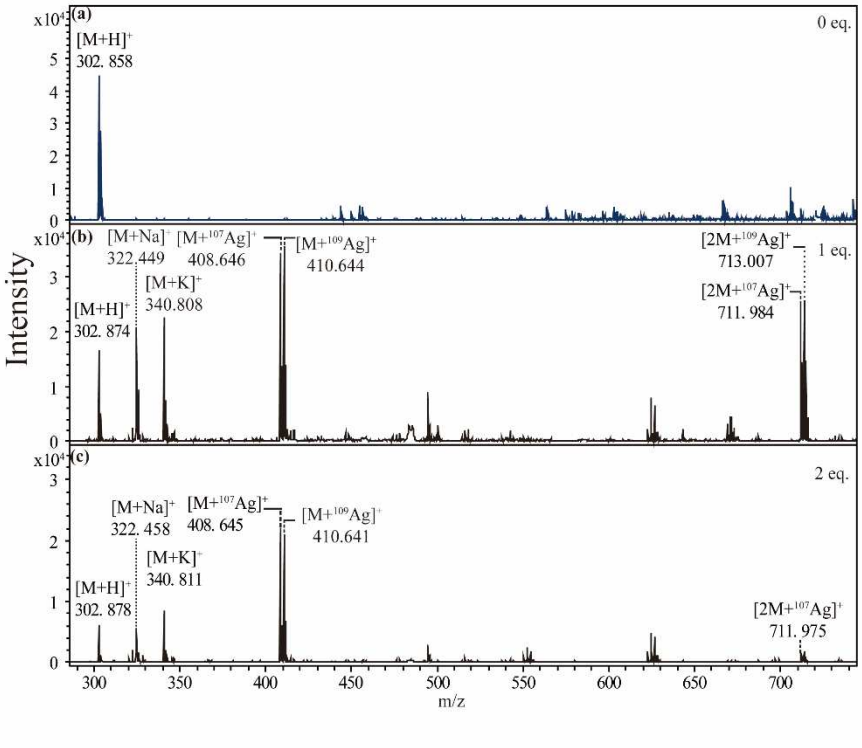
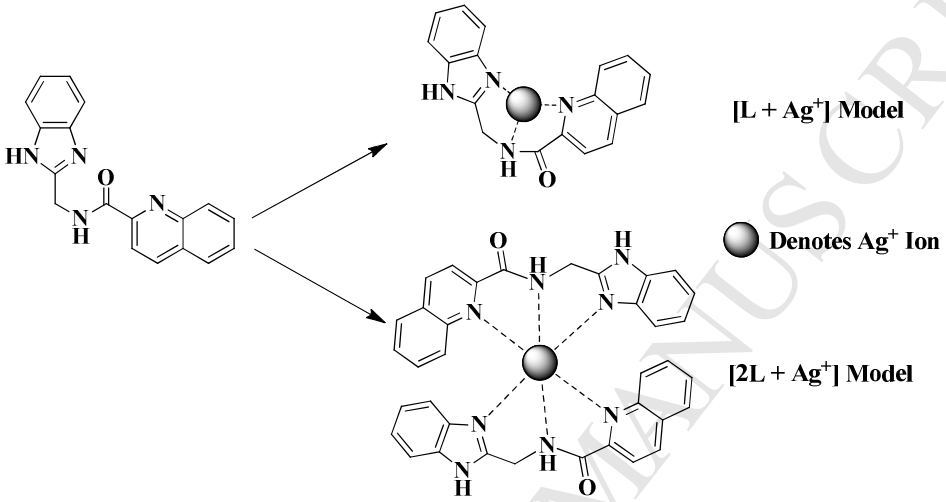


Fig. 6. Mass spectra of **L** with addition of Ag^+ from 0-2 equiv. (a) Mass spectra of **L**; (b) Mass spectra of **L** with addition of 1 equiv. of Ag^+.; (c) Mass spectra of **L** with addition of 2 equiv. of Ag^+.

According to the results above and literature[25,27,43-46], a possible interaction mode of sensor **L** with Ag^+ was proposed in Scheme 1. Ag^+ was supposed to bind to the nitrogen atom of **L** *via* coordination bond. In conclusion, Ag^+ formed alternative complex *via* chelation method and as Ag^+ increased, most of complex turned to [**L** + Ag^+].



Scheme 2. Proposed binding mode of **L** with Ag^+.

4. Conclusions

We synthesized a novel fluorescence chemosensor **L** with quinoline and benzimidazole scaffold, which exhibited high selectivity for Ag^+ over other metal ions. The probe could be easily synthesized and showed good sensitivity for Ag^+. The limit detection for Ag^+ was down to 4.4×10^{-7} M in aqueous solution, which reached the standard of WHO for drinking water. Considering its application area, we tested Ag^+ in tap water and the result proved that the probe can work in nature water sample as well. The complex formation and binding mode were determined by ^{1}H NMR studies and mass spectroscopy. It was found that as the concentration of Ag^+ increased, the **L**-Ag^+ complex

changed from [2**L** + Ag^+] to [**L** + Ag^+]. In conclusion, the ligand **L** can be a potential fluorescence "turn-on" probe for Ag^+ in aqueous system with promising selectivity and sensitivity.

Acknowledgements

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Supplementary data

See the supporting information for the ^{1}H NMR, ^{13}C NMR spectra and high resolution mass spectrometry of **L**, UV-vis spectra for **L** with various mental ions, and linear concentration of Ag^+ in methanol-water containing 10 μM **L**.

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