



A borondipyrromethene-based turn-on fluorescent probe for silver ion with high sensitivity and selectivity and its application in water samples and living cells



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ABSTRACT

A borondipyrromethene-based compound (**1**) is synthesized and used as a “turn-on” fluorescent probe for silver ions (Ag^+). The probe displays highly sensitive fluorescence response toward Ag^+ with a 40-fold fluorescence enhancement when $60 \mu\text{M}$ of Ag^+ is added. The fluorescence intensity of the probe is linearly dependent on Ag^+ concentration ranging from 0.05 to $60 \mu\text{M}$. And the detection limit (LOD) can reach $0.02 \mu\text{M}$, which complies with the standard of World Health Organization (WHO) for drinking water ($0.9 \mu\text{M}$). Moreover, the probe shows remarkable selectivity for Ag^+ over other metal ions. Furthermore, the response behavior of **1** toward Ag^+ is pH independent in the neutral range from 6.0 to 8.0. The response of **1** toward Ag^+ is fast (response time is less than 2 min) and reversible chemically. What's more, the sensing mechanism of probe **1** toward Ag^+ is verified by mass spectra (MS) and density functional theory (DFT) calculations. In particular, the probe is applied for detection of Ag^+ in water samples and living cells successfully.

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Introduction

Silver is one of most important resources, which has been widely used in the electronic industry, pharmaceutical industry and photographic and imaging industry.^{1,2} Therefore, with the development of modern industry, more and more Ag^+ is released which makes water sources polluted and further affects the food and agriculture.^{3,4} Silver ions are assigned to the highest toxicity class of heavy metal pollutants. Excessive Ag^+ intake may damage skin and eyes and cause cardiac enlargement, growth retardation and degenerative changes in the liver.^{5,6} According to the World Health Organization (WHO) data, the content of Ag^+ in drinking water should not exceed $0.9 \mu\text{M}$ (approx. 0.1 mg/L). Therefore, it is very urgent to develop sensitive and selective methods for the detection of trace quantities of silver ions in water samples and biological sample such as living cells.

In order to detect silver ions at trace quantity levels, several methods such as atomic absorption spectroscopy (AAS),^{7–9} inductively coupled plasma-mass spectroscopy (ICP-MS)^{10,11} and ion-selective electrodes (ISEs)^{12–14} 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.^{15–25} Recently, several fluorescent probes have been developed for Ag^+ ,^{26–43} but one, two or all of the following disadvantages in these probes are still existing. Firstly, some reported probes are based on fluorescence quenching because Ag^+ is the so-called “silent ions”, unfavorable for a high signal output.^{26–30,40} Secondly, the proposed probes exhibit only moderate fluorescence variations (<20-fold),^{31–42} and thus the sensitivity of these probes is frequently not enough to detect trace quantities of silver ions in water samples.^{27,36–39,43} Finally, it is difficult for the reported probes in the literatures to discriminate Ag^+ from other metal ions such as Hg^{2+} , Cu^{2+} and so on (Table S1).^{39–43} Therefore, it is significant to develop new fluorescent probes that can detect Ag^+ sensitively and selectively in real samples.

Borondipyrromethene (BODIPY) possesses excellent spectral properties such as high molar absorptivity and fluorescence quantum yield, narrow absorption and emission bandwidths, and good stability against photobleaching.^{44,41,45–48} And thus it is an ideal fluorophore for fluorescent probe. To date, a number of BODIPY-based probes have been constructed for the detection of various metal ions including Hg^{2+} ,^{49–52} Cu^{2+} ,^{53–55} Fe^{3+} .^{56–58} However, only a few reports are available for the fluorescent assay of Ag^+ .^{30,38,39,43}

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Herein, a BODIPY-based probe (**1**) is designed and synthesized for fluorescent determination of Ag^+ . The probe shows fluorescent enhancement (turn-on) about 40-fold when $60 \mu\text{M}$ Ag^+ is added. The detection limit ($0.02 \mu\text{M}$) is low, which matches the allowable level of Ag^+ in drinking water by WHO. Two oxygen atoms and two nitrogen atoms are used as binding site and the probe exhibits a high selectivity to Ag^+ over other metal cations. Furthermore, probe **1** has been applied in the detection of Ag^+ in real water samples and living cells successfully.

Results and discussion

Synthesis and structural characterization of compound **1**

The synthetic route for compound **1** from commercially available reagents was depicted in Fig. 1. Compound **2** was obtained through the reaction of 3,4-dihydroxybenzaldehyde with 2-(chloromethyl) pyridine and K_2CO_3 in N,N-dimethylformamide at room temperature for two days. Under the protection of N_2 atmosphere, compound **2** then reacted with 2,4-dimethylpyrrole at room temperature for 6 h to provide compound **1**. The obtained products were well characterized by ^1H NMR, ^{13}C NMR, MS and elemental analysis (Fig. S1–S3).

To study the sensitivity of probe **1**, the fluorescence spectra of the probe with addition of different concentrations of Ag^+ were measured in Tris- HNO_3 buffered solutions (Fig. 2). In the experiment, we found that probe **1** itself displays almost no fluorescent emission of BODIPY at 508 nm. The fluorescence quantum yield (Φ) of free probe **1** is 0.004 using quinine as standard. The addition of Ag^+ to the solution of probe **1** led to a significant increase of fluorescence signal with the peak at 508 nm. And the fluorescence

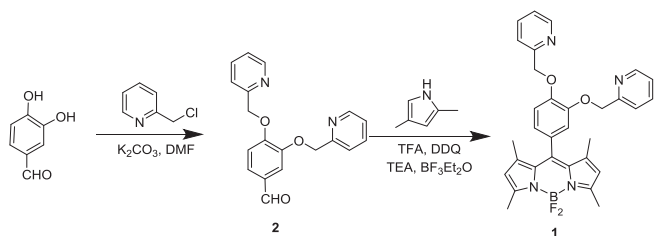


Fig. 1. The synthetic route of compound **1**.

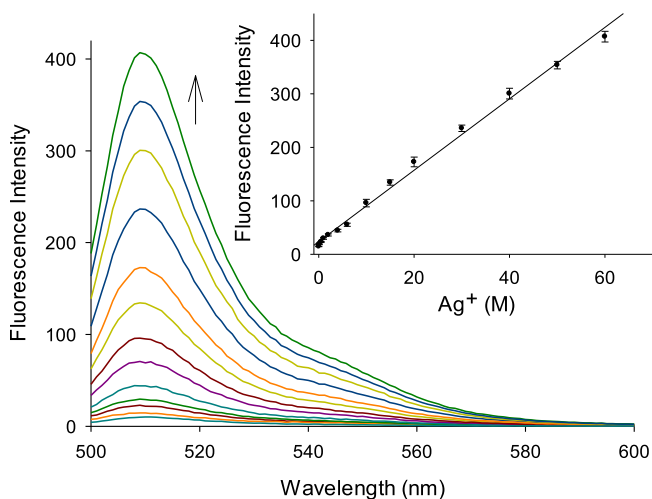


Fig. 2. The fluorescence spectra of probe **1** ($10 \mu\text{M}$) at different concentrations of Ag^+ ($0, 0.05, 0.5, 1, 4, 6, 10, 15, 20, 30, 40, 50, 60 \mu\text{M}$) in Tris- HNO_3 buffer solution (pH 7.0). The excitation wavelength is 490 nm. Inset: the plot of the fluorescence intensity versus Ag^+ concentrations.

quantum yield of the probe with Ag^+ is 0.568. The fluorescence intensity of the probe enhances gradually with concomitant increasing of Ag^+ concentration. The fluorescence intensity of the probe increases about 40-fold when $60 \mu\text{M}$ of Ag^+ is added. As the inset of Fig. 2 shows, the fluorescence intensity is linearly proportional to Ag^+ concentration in the range of 0.05 – $60 \mu\text{M}$. And the detection limit (LOD) can reach $0.02 \mu\text{M}$ ($3\sigma/\text{slope}$), which complies with the standard of World Health Organization (WHO) for drinking water ($0.9 \mu\text{M}$).

To understand better the variation of fluorescence of probe **1** toward Ag^+ , the UV–visible spectra of **1** upon the gradual addition of Ag^+ were recorded in Fig. 3. The absorption spectrum of the probe shows an absorption band at 500 nm ($\epsilon = 1.05 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Upon the addition of Ag^+ , the band centered at 500 nm shows an obvious increase ($\epsilon = 1.74 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption of the probe at 500 nm enhances gradually with the increase of Ag^+ . These spectroscopic features support that there is interaction between probe **1** and Ag^+ .

The selectivity is an important index for rating fluorescent probe. The fluorescence spectra of the probe based on **1** before and after adding the competitive metal ions (Ag^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Cr^{3+} , Fe^{3+} and Al^{3+}) was investigated. As shown in Fig. 4 and Fig. S4, remarkable

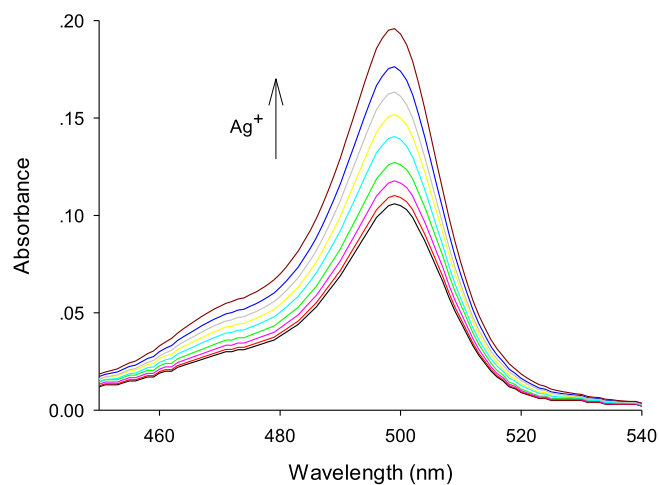


Fig. 3. The absorbance spectra of probe **1** ($10 \mu\text{M}$) at different concentrations of Ag^+ ($0, 10, 20, 30, 40, 50, 60, 80, 100 \mu\text{M}$) in Tris- HNO_3 buffer solution (pH 7.0).

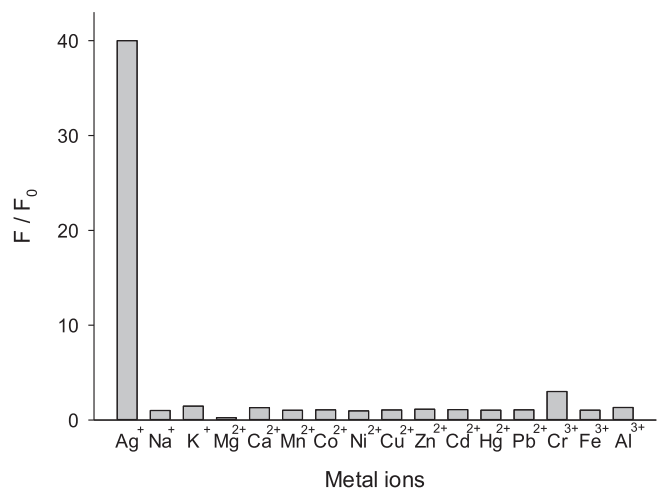


Fig. 4. Fluorescence spectra of **1** ($10 \mu\text{M}$) with Ag^+ ($60 \mu\text{M}$) or other metal ions (1 mM) in Tris- HNO_3 buffer solution (pH 7.0).

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