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ORIGINAL ARTICLE

Triazole-Coupled Benzimidazole-Based Fluorescent Sensor for Silver, Bromide, and Chloride Ions in Aqueous Media

Yoon Gun Ko[1] · Won Sik Na[1] · Mayank[2] · Narinder Singh[2] · Doo Ok Jang[1]

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Abstract
A triazole-coupled benzimidazole-based fluorescent probe **S1** with nitrogen and oxygen binding sites was synthesized and its properties as a probe for cations were investigated. Probe **S1** was found to be highly selective toward Ag^+ ions in aqueous media. The fluorescence intensity of **S1** was quenched as a function of the concentration of Ag^+ ions in the presence of potential interfering cations with a detection limit of 2.70 μM. The resulting **S1**-Ag^+ complex was subsequently studied for its anion recognition abilities and found to recognize $Br^−$ and $Cl^−$ ions, revealing the concentration-dependent fluorescence enhancement with detection limits of 22.2 and 23.0 μM, respectively. Revival of the fluorescence profile of probe **S1** indicated that Ag^+ ion was released from the **S1**-Ag^+ complex. Probe **S1** is a sensor that can be single-handedly utilized for the qualitative and quantitative determination of Ag^+, $Br^−$, and $Cl^−$ ions in aqueous media.

Keywords Triazole · Benzimidazole · Fluorescence · Sensor

Introduction

In recent decades, considerable efforts have been devoted to the development of chemosensors for the selective sensing of cations and anions because of their important roles in chemical, biological, and environmental processes [1–5]. Fluorescence methods are frequently employed for sensing analytes because they have several advantages over other methods, including high sensitivity, nondestructive detection, and fast response time [6–8]. As traces of elements in environmental resources are a major source of pollution, serious efforts have been made to detect these elements in natural resources [9]. For instance, excess of silver pollution within the natural resources poses a particularly high threat. Owing to the broad range of applications of silver in industry, including photography, electronics, pharmacy, and water purifier filters, the annual output of silver waste is massive on global scale [10, 11]. A large dose of silver ions has a negative effect on organisms and environments, although they are not harmful in a small amount. Therefore, both qualitative and quantitative determinations of silver are important to monitor its concentrations in industrial wastes and environment. Bromide and chloride ions are also hazardous pollutants and found in marine water resources and various biological fluids such as serum, saliva, and urine [12]. The exposure of bromide and chloride ions is hazardous to health and may cause various health problems such as skin and tissue damage, malfunctioning of the respiratory system, and malignant diseases [13]. Therefore, easy-to-use methods for qualitative and quantitative determination of silver [14–20] and bromide [21] and chloride ions [22–25] are in high demand.

Estimation of anions in aqueous media is an especially important task because the majority of environmental and biological real samples are aqueous solutions. However, probing of anions in aqueous media is problematic when the recognition process mainly relies on hydrogen bonding interactions. This is because of the competition of anions with water molecules for the binding sites in the receptor. In this context,

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✉ Narinder Singh
nsingh@iitrpr.ac.in

✉ Doo Ok Jang
dojang@yonsei.ac.kr

[1] Department of Chemistry, Yonsei University, Wonju 26493, Republic of Korea

[2] Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, Punjab 140001, India

cation displacement is an ingenious method to resolve the problem. A reversible sensor that can selectively recognize a particular cation interacts with an anion, which then releases the ligand [26–37]. Based on this idea, we have developed a fluorescence chemosensing probe **S1**, which is based on a triazole-coupled benzimidazole that detects silver ions and the resultant complex is capable of probing bromide and chloride ions in aqueous media via cation displacement mechanism.

Materials and Method

General

Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (230–400 mesh, Merck). TLC was performed on glass sheets pre-coated with silica gel (Kieselgel 60 $PF_{254,}$ Merck). The ^{1}H- and ^{13}C-NMR spectra were obtained using a Bruker 400 NMR spectrometer which operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei and were internally referenced to residual solvent signals. Chemical shifts are reported in parts per million (ppm). IR spectra were recorded on a Perkin–Elmer 16 PC FT IR spectrometer. Microanalyses were performed on a CE instrument EA1110 elemental analyzer. UV-Vis absorption studies were performed using a Perkin-Elmer Lambda 25 UV-Vis spectrometer. The fluorescence emission spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. The XEVO G2-XS QTOF HR-Mass instrument by Waters was used to record mass spectra.

Synthesis of Compound 1

A solution of propargyl bromide (1.17 g, 9.80 mmol), salicylaldehyde (1.00 g, 8.20 mmol), and K_2CO_3 (2.30 g, 16.3 mmol) in CH_3CN (60 mL) was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and EtOAc was added. After washing with water, the organic layer was dried over anhydrous $MgSO_4$. Then, after filtration and evaporation, the residue was purified with column chromatography on silica gel (eluent: hexane/EtOAc, 7:3) to obtain compound **1** as a dark brown solid (1.17 g, 89%) [38]; mp = 66–69 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.65 (t, J = 2.1 Hz, 1H), 5.00 (t, J = 2.2 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.66–7.70 (m, 1H), 7.72 (d, J = 7.7 Hz, 1H), 10.36 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.4, 78.6, 79.0, 114.3, 121.5, 124.8, 127.8, 136.1, 159.5, 188.9.

Synthesis of Compound 2

A solution of compound **1** (400 mg, 2.5 mmol), benzyl azide (499 mg, 3.75 mmol), and CuI (25 mg, 0.1 mmol) in dry THF (10 mL) was stirred at room temperature under argon for 40 h. After evaporation, the residue was dissolved in EtOAc, and washed with brine. The organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified with column chromatography on silica gel (eluent: hexane/EtOAc, 7:3) to obtain compound **2** as a white solid (930 mg, 73%) [38, 39]; mp = 116–119 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.34 (s, 2H), 5.62 (s, 2H), 7.10 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 6.7 Hz, 2H), 7.33–7.39 (m, 3H), 7.43 (d, J = 8.4 Hz, 1H), 7.65–7.70 (m, 2H), 8.37 (s, 1H), 10.33 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 53.1, 62.5, 114.5, 121.3, 124.8, 124.9, 127.8, 128.1, 128.3, 128.9, 136.2, 136.5, 142.8, 160.6, 189.3.

Synthesis of Probe S1

A solution of compound **2** (300 mg, 1.0 mmol), 1,2-phenylenediamine (111 mg, 1.0 mmol), H_2O_2 (0.13 mL, 4.1 mmol, 30% solution in H_2O), and CAN (56 mg, 0.10 mmol) in CH_3CN (30 mL) was stirred at room temperature for 1.5 h. After evaporation, the residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc, 3:7) to obtain probe **S1** as a pale yellow solid (125 mg, 31%); mp = 151–154 °C; IR (KBr) ν 3443, 1239, 1017, 749 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.53 (s, 2H), 5.62 (s, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.17–7.24 (m, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.32–7.37 (m, 3H), 7.40 (d, J = 8.4 Hz, 1H), 7.43–7.47 (m, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 8.29 (t, J = 3.9 Hz, 2H), 12.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 52.9, 62.2, 111.7, 114.0, 118.6, 118.9, 121.4, 121.6, 122.2, 124.3, 127.9, 128.2, 128.8, 130.0, 131.1, 134.6, 136.0, 142.8, 143.2, 148.9, 155.4. Anal. calcd for $C_{23}H_{19}N_5O$: C, 72.42; H, 5.02; N, 18.36; S, 4.19; found: C, 72.31; H, 5.23, N, 18.47.

UV-vis and Fluorescence Spectra Measurements

A stock solution of probe **S1** (300 μM) was prepared by dissolving **S1** (0.003 mmol) in DMSO (10 mL). A sample solution of probe **S1** (3 μM) was prepared by diluting 50 μL of the stock solution with 4950 μL of water (10 mM HEPES, pH 7.3). Nitrate salts of different cations (Zn^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Ag^+, Na^+, and K^+ ions) and sodium or ammonium salts of different anions (OAc^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^-, F^-, Cl^-, Br^-, and I^-) were used for different titration experiments. UV-Vis and fluorescence titrations were performed in 10-mm quartz cuvettes by successive addition of the corresponding cation or anion using a microliter pipette at ambient temperature. Upon addition of every aliquot, the solution was mixed, and the spectrum was measured with a slit width of 10 nm.

Results and Discussion

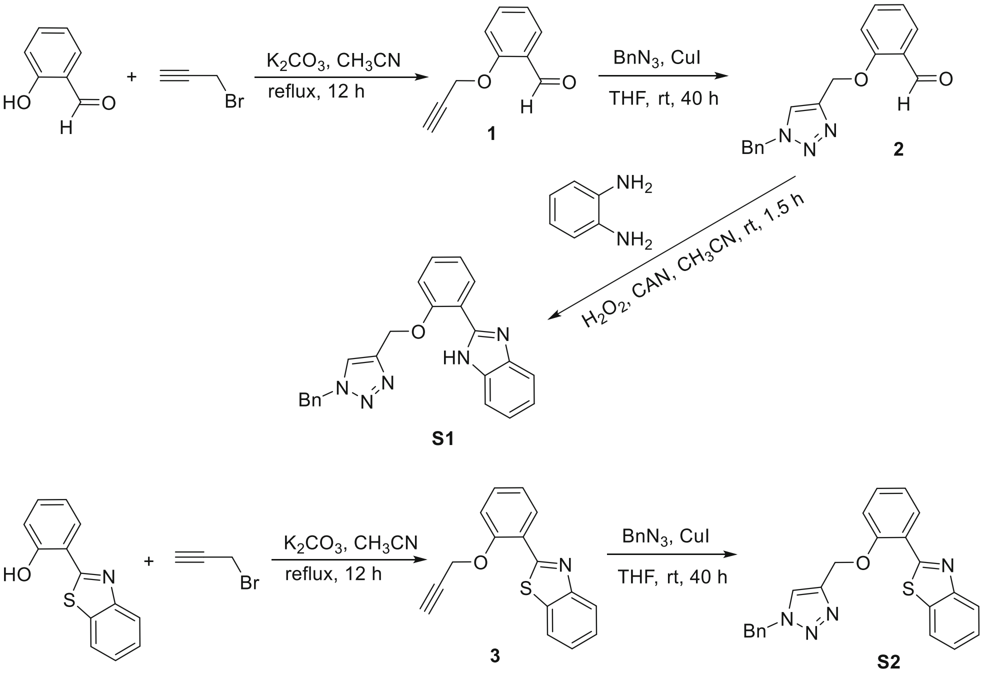
Synthesis of Probes S1 and S2

Probe **S1** was synthesized by a multi-step procedure (Scheme 1). The reaction of salicylaldehyde with propargyl bromide in the presence of K_2CO_3 afforded compound **1**, which was transformed to compound **2** by reacting with benzyl azide in the presence of CuI in THF [38, 39]. Treatment of compound **2** with 1,2-phenylenediamine, H_2O_2, and ammonium cerium(IV) nitrate (CAN) in CH_3CN resulted in the formation of probe **S1**. Probe **S2** was prepared in a similar manner from 2-(benzo[*d*]thiazol-2-yl)phenol.

Cation Binding Studies

The UV-Vis absorption spectrum of probe **S1** showed a characteristic absorption band at 307 nm, which was attributed to a π-π* transition of the benzimidazole unit. The fluorescence emission profile of probe **S1** upon excitation at 307 nm revealed an emission band at 358 nm. The cation binding studies were conducted by recording the fluorescence emission profile of probe **S1** in water (10 mM HEPES, pH 7.3) along with nitrate salts of different cations such as Zn^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Na^+, and K^+. There was negligible change in the fluorescence profile upon addition of these cations (Fig. 1a). However, upon addition of Ag^+ ions, a dramatic change was observed in the emission profile of probe **S1**. Therefore, the size, shape, and morphological factors of the Ag^+ ions were found to be optimum for the binding cavity of probe **S1**. Furthermore, there was no major change in the UV-Vis absorption profile in the case of all the studied cations (Fig. S1). Probe **S2** exhibited no changes in the UV-Vis and fluorescence profiles upon addition of the metal ions. To examine the ability of probe **S1** as a sensor, titration experiments were performed with an increasing concentration of Ag^+ ions (0–10 equivalents). As shown in Fig. 1b, the fluorescence profile of probe **S1** was not changed except that the fluorescence intensity decreased gradually without changing λ_{max} upon incremental addition of Ag^+ ions, which implied that the photoinduced electron transfer (PET) mechanism was operative [40]. The fluorescence intensity of probe **S1** at 358 nm decreased gradually with the incremental addition of Ag^+ ions, and revealed a good linear correlation with Ag^+ concentration from 0 to 24 μM (correlation coefficient, $R^2 = 0.96$) (Fig. 1c). This implied that probe **S1** might be used for the quantitative estimation of Ag^+ ions. The detection limit of probe **S1** towards Ag^+ ion sensing was calculated to be 2.70 μM (Fig. 1d) [41]. Job's plot showed that the binding of probe **S1** to Ag^+ ions took place in 1:1 stoichiometry (Fig. S2) [42]. ESI-MS analysis of **S1**-Ag^+ complex also indicated a 1:1 stoichiometry of the complex, exhibiting a peak at *m/z* = 488.04, which corresponded to the **S1**-Ag^+ complex (calcd. *m/z* = 488.06) (Fig. S3). The association constant

Scheme 1 Synthesis of probes **S1** and **S2**



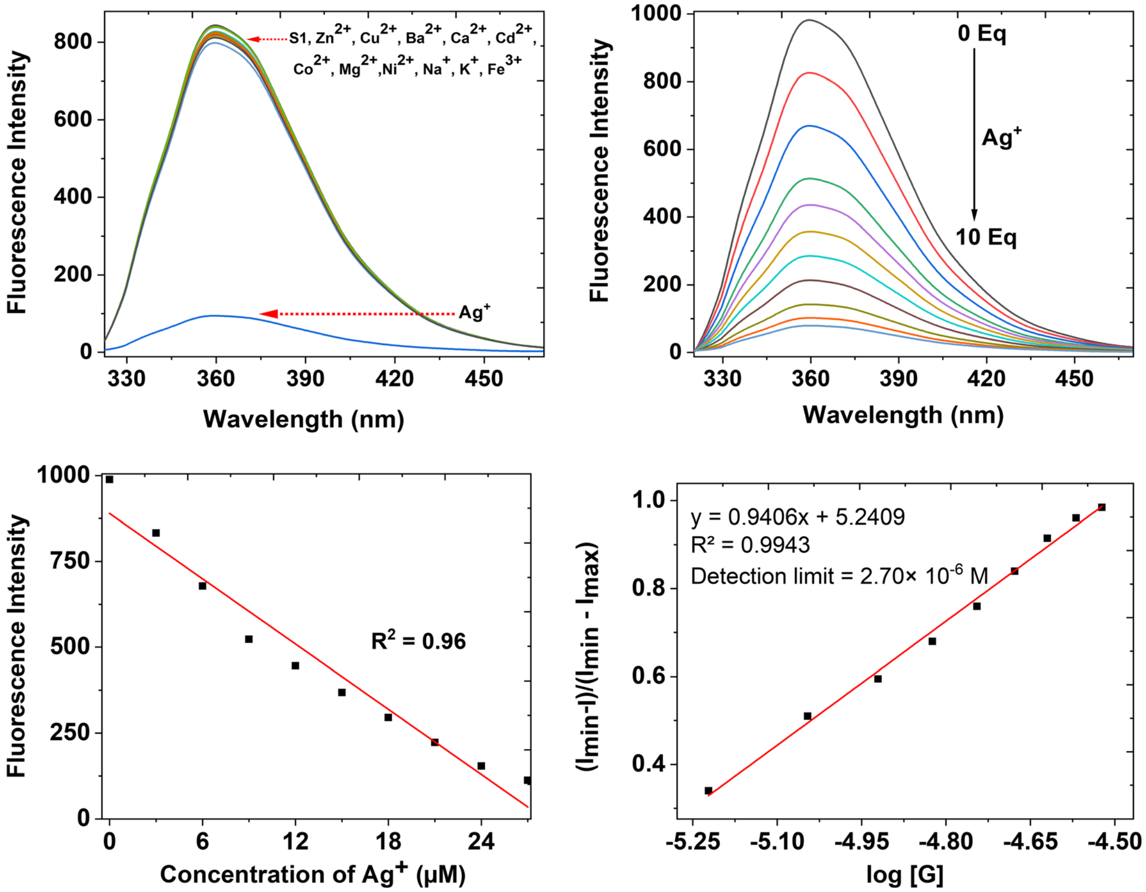


Fig. 1 (**a**) Changes in the fluorescence intensity of probe **S1** (3 μM) upon addition of a particular metal salt (50 μM) in water (10 mM HEPES, pH 7.3) excited at $\lambda_{ex} = 307$ nm. (**b**) Fluorescence titration study of probe **S1** (3 μM) upon addition of Ag^+ ions (0–10 equivalents) in water (10 mM HEPES, pH 7.3) excited at $\lambda_{ex} = 307$ nm. (C) Fluorescence intensity changes of probe **S1** (3 μM) at 358 nm as a function of Ag^+ ion concentration. (D) Detection limit of Ag^+ ions with probe **S1**

(K_a) was calculated to be $(5.2 \pm 0.2) \times 10^4$ M^{-1} by the Benesi-Hildebrand plot (Fig. S4) [43]. The fluorescence intensity of **S1**-Ag^+ complex in the presence of other competitive cations was also investigated, and showed that there was no interference of the other competing cations (Fig. 2).

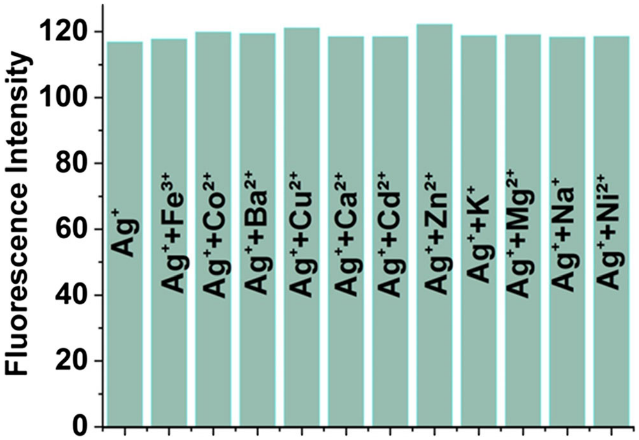


Fig. 2 Interference study of probe **S1** for Ag^+ ion detection in the presence of other cations

Anion Binding Studies

Based on the finding that probe **S1** selectively recognized Ag^+ ions by forming the complex **S1**-Ag^+, the anion sensing abilities of the complex **S1**-Ag^+ were examined. An aqueous solution (10 mM HEPES, pH 7.3) of **S1**-Ag^+ was prepared by adding the same equivalents of probe **S1** and Ag^+ ions. The resulting solution was subsequently screened for its sensing ability towards anions. The anions used in this study included tetrabutylammonium (TBA) salts of OAc^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, CN^-, and ClO_4^- ions. The anion binding studies were conducted by monitoring the fluorescence intensity of the **S1**-Ag^+ complex (4 μM) in the presence of various anions (50 μM). All of the examined anions were unable to change the fluorescence profile of **S1**-Ag^+ complex. Halides in the form of TBA salts were also used to investigate the sensing ability of

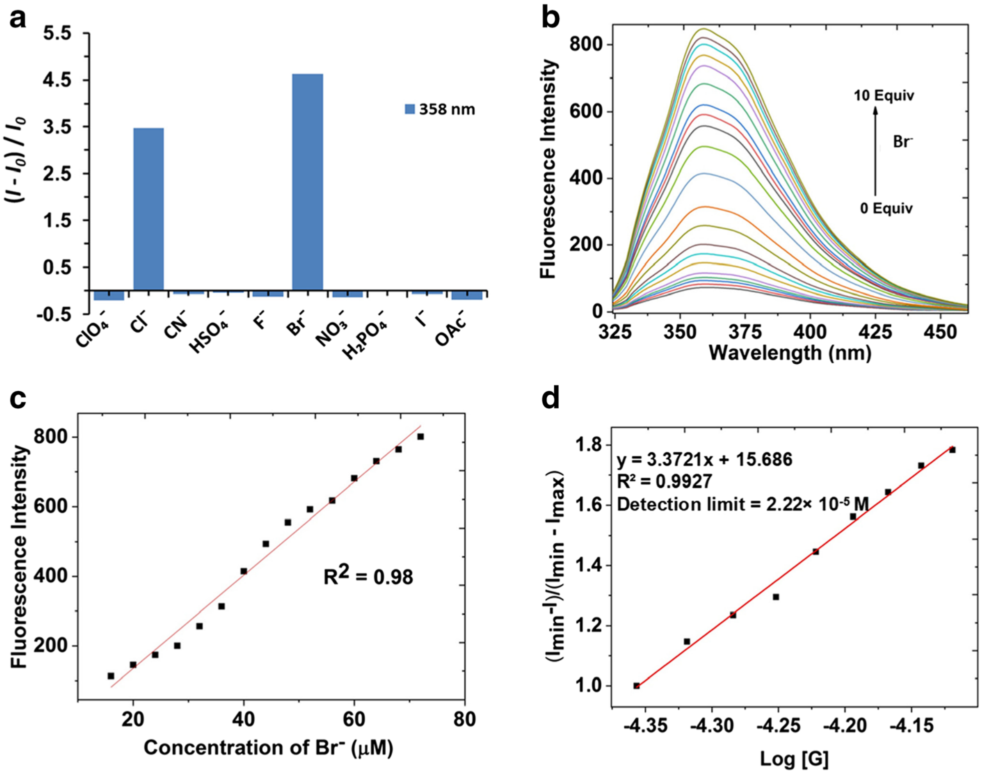


Fig. 3 (**a**) Changes in the fluorescence intensity of the **S1**-Ag^+ complex (4 μM) upon addition of TBA anion salt (50 μM) of various anions in water (10 mM HEPES, pH 7.3) excited at λ_{ex} = 307 nm. (**b**) Fluorescence titration study of **S1**-Ag^+ complex (4 μM) upon addition of 0–10 equivalents of Br^- ions. (**c**) Fluorescence intensity changes of **S1**-Ag^+ complex (4 μM) at 358 nm as a function of Br^- concentration. (**d**) Detection limit of Br^- with **S1**-Ag^+ complex

the **S1**-Ag^+ complex, and it was found that the **S1**-Ag^+ complex could recognize Br^- and Cl^- ions but not F^- and I^- ions. Upon addition of Br^- or Cl^- anions, there was a significant enhancement in the fluorescence intensity of the **S1**-Ag^+ complex (Fig. 3a). These results showed that the **S1**-Ag^+ complex could potentially act as a sensor for Br^- and Cl^- anions in aqueous media.

Titration studies were performed with an increasing concentration of Br^- ions (0–10 equiv), and the results revealed the ion concentration-dependent enhancement in the fluorescence intensity of the **S1**-Ag^+ complex (Fig. 3b). At the final stage of the titration, the observed fluorescence profile was found to be the same as that of probe **S1**, implying that the Ag^+ ion in the **S1**-Ag^+ complex had been displaced by the Br^- ion (Fig. S5). The biding constant of the **S1**-Ag^+ complex with the Br^- ions was determined to be $K_a = (1.6 \pm 0.3) \times 10^4\ M^{-1}$ by the Benesi-Hildebrand plot (Fig. S6) [43]. An analogous titration profile for Cl^- ions was obtained and the binding constant was determined to be $(5.0 \pm 0.4) \times 10^3\ M^{-1}$, implying that the **S1**-Ag^+ complex had a higher affinity toward Br^- ions as compared to Cl^- ions (Figs. S7 and S8). The calibration curves of the fluorescence intensity of **S1**-Ag^+ complex versus Br^- or Cl^- ion concentration at 358 nm had correlation coefficients (R^2) of 0.98 and 0.99, respectively, revealing a high

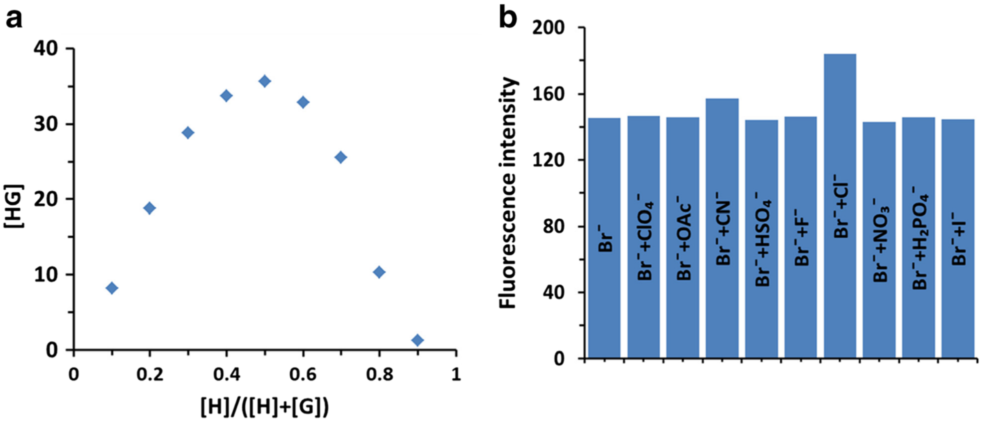


Fig. 4 (**a**) Job's plot for the binding of **S1**-Ag^+ complex with Br^- revealing the 1:1 (H:G) stoichiometry. Fluorescence intensity at 358 nm was plotted as a function of the mole ratio $[Br^-]/([Br^-] + [\mathbf{S1}\text{-}Ag^+])$; (**b**) Interference study of **S1**-Ag^+ complex for Br^- detection in the presence of other anions

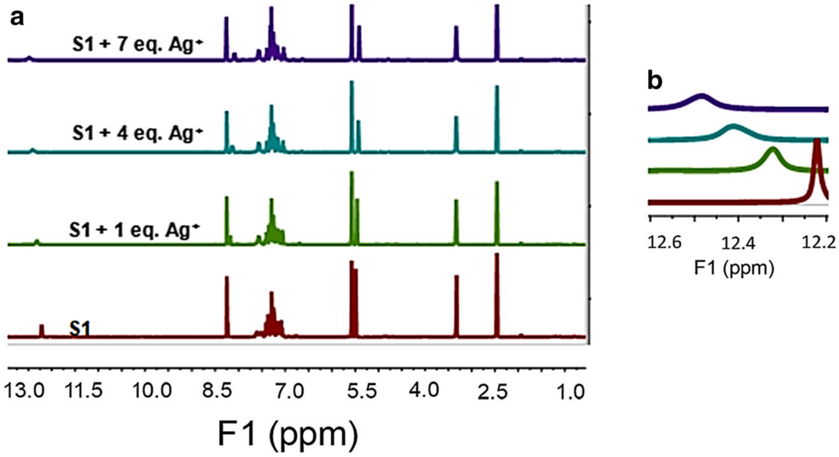


Fig. 5 (**a**) ^{1}H NMR study of probe **S1** with increasing concentration of Ag^+ ions; (**b**) Enlarged portion of the ^{1}H NMR spectra, showing the downfield shift of the peak at 12 ppm

correlation between the fluorescence response and Br^- or Cl^- ion concentration (Figs. 3c and S9). This indicated that the **S1**-Ag^+ complex could be applied as a chemosensor for the qualitative and quantitative determination of Br^- or Cl^- ions. The detection limits of the **S1**-Ag^+ complex for Br^- or Cl^- ions were calculated to be 22.2 and 23.0 μM, respectively (Figs. 3d and S10).

Job's plot for the binding of complex **S1**-Ag^+ with Br^- or Cl^- ions was explored, revealing a 1:1 host (H):guest (G) binding stoichiometry (Figs. 4a and S11) [42]. The fluorescence intensity of the **S1**-Ag^+ complex in the presence of potential interfering anions such as ClO_4^-, AcO^-, CN^-, F^-, Cl^-, NO_3^-, and $H_2PO_4^-$ along with Br^- was relatively unchanged. This implied that there was no significant interference of the ions in the sensing system, although chloride showed a slight interfering effect (Fig. 4b).

Sensing Mechanism

Once the sensing ability of probe **S1** toward Ag^+ ions was confirmed, the **S1**-Ag^+ binding mechanism was investigated. A ^{1}H NMR spectroscopy study of probe **S1** was performed with increasing concentration of Ag^+ ions (Fig. 5). The NH peak of benzimidazole in probe **S1** that appeared at 12 ppm provided evidence of the hydrogen bonding of this proton. This peak shifted continuously downfield as the amount of Ag^+ ions was increased, indicating that the hydrogen bonding was maintained, and that the Ag^+ ions were bound to the oxygen that formed a hydrogen bond with the NH of the benzimidazole moiety in probe **S1**.

Theoretical studies were also performed to investigate the **S1**-Ag^+ binding mechanism. The density functional theory (DFT) calculations for probe **S1** and **S1**-Ag^+ complex were performed with gaussian molecular modeling software [44,

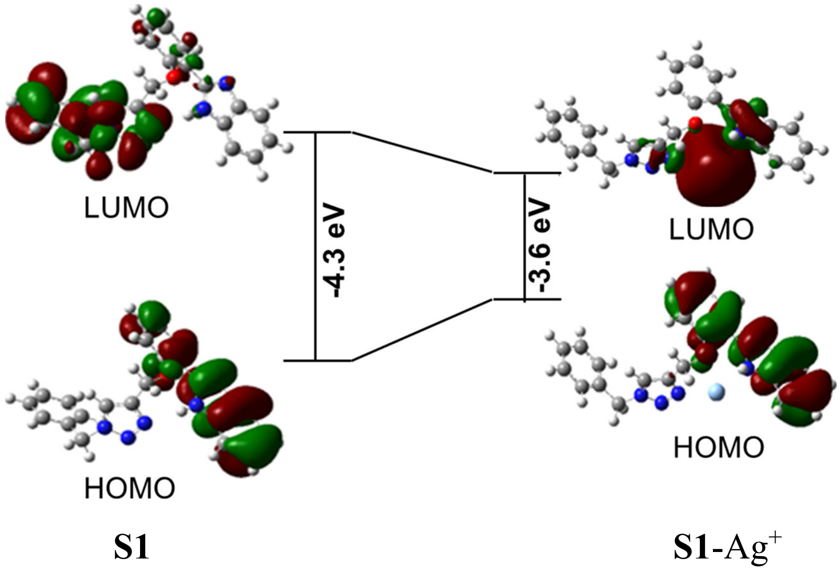
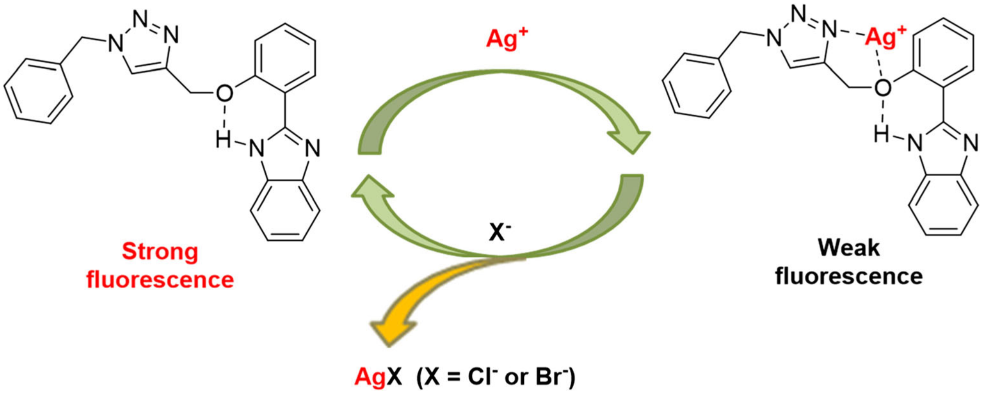


Fig. 6 Energy correlation of HOMO-LUMO gaps of **S1** and **S1**-Ag^+ complex

Scheme 2 Proposed mechanism for the detection of Ag^+ and Br^-/Cl^- ions with florescent probe **S1**



45]. The HOMO-LUMO energy difference calculated for probe **S1** and the **S1**-Ag^+ complex were − 4.3 and − 3.6 eV, respectively (Fig. 6). The energy gap between HOMO and LUMO of **S1**-Ag^+ complex was smaller than that of **S1**.

The sensing mechanism by which **S1** detected Ag^+ and Br^-/$Cl^-$is presented in Scheme 2. Binding of probe **S1** with the Ag^+ ion to the nitrogen of the triazole unit and the oxygen of the ether linkage in probe **S1** quenched the fluorescence intensity of the probe via the PET mechanism. When Br^-/Cl^- ions were added to the solution of the **S1**-Ag^+ complex, the Br^-/Cl^- ion assisted in the elimination of the Ag^+ ion from the cavity, restoring the fluorescence profile of probe **S1**. It is well known that silver ions react with halides, forming silver halides. However, due to its large size, it is impossible for iodide to approach the silver ion within the binding cavity of **S1** due to steric constraints. Therefore, displacement of the silver ion was only observed with Br^- and Cl^-.

Conclusion

A triazole-coupled benzimidazole-based probe **S1** with a combination of oxygen and nitrogen binding sites was synthesized and utilized for sensing Ag^+ ions in aqueous media. Upon adding Ag^+ ions, probe **S1** revealed a concentration-dependent fluorescence quenching behavior, which allowed estimation of Ag^+ ions even in the presence of potential interfering cations. The resulting **S1**-Ag^+ complex was further explored as a sensor for anion detection. Upon adding Br^- or Cl^- ions to the **S1**-Ag^+ complex, the fluorescence intensity increased and the emission profile of probe **S1** was restored, indicating the replacement of Ag^+ ion from the complex. The fluorescent probe **S1** is a single sensor that can be used for the quantitative and qualitative determination of Ag^+ ions as well as Br^-/Cl^- ions in aqueous media.

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Compliance with Ethical Standards

Conflict of Interest The authors declare no conflict of interest.

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