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Graphical Abstract

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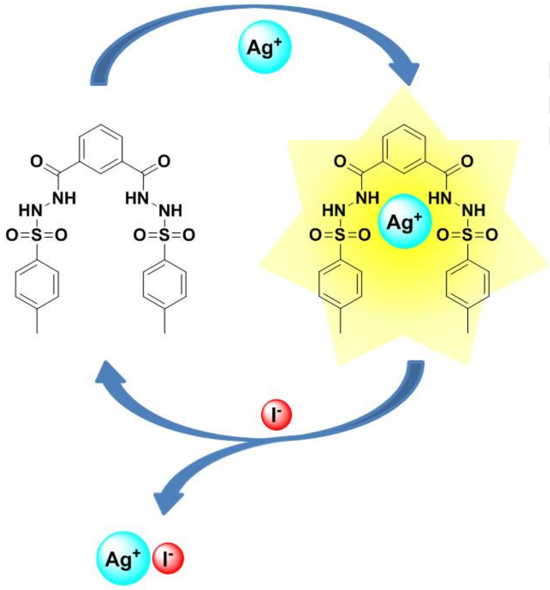

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Dipodal colorimetric sensor for Ag^+ and its resultant complex for iodide sensing using a cation displacement approach in water

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ABSTRACT

We synthetized a sulfonamide-based dipodal receptor capable of recognizing Ag^+ selectively in water in the presence of other possible competing cations through color change. The resultant Ag-complex showed suitability as a chemosensor for the sensing of I^- ions in water in the presence of other anions through a cation displacement process. The detection limits of the receptor for Ag^+ and of the resultant complex for I^- were identified as 2.43 and 5.31 μM, respectively.

1. Introduction

The visual detection of analysts, particularly in water, has been receiving substantial attention in supramolecular chemistry.[1–5] Colorimetric sensors present several advantages over other analytical techniques – including electrochemical sensors,[6–8] atomic absorption spectroscopy, inductively-coupled plasma spectroscopy, and gas chromatography. In terms of manufacturing costs and time consumption.[9-11] Generally, colorimetric sensors are built from highly conjugated organic receptors such as rhodamine[11,12] and salen.[13–15] These receptors are used in organic solvents, as they are mostly insoluble in water. Other approaches involve the use of metal complexes, inorganic-organic hybrid polymers, or nanoparticles-based sensors.[16,17] However, these classes of receptors present major issues in their stability and non-uniform size distribution.[18] Therefore, simple and cheap colorimetric receptors with high sensitivity are highly needed. Although many sensors highly sensitive to metal ions and anions have been developed,[19–22] multifunctional and reverse sensors are rare.[23,24] Dual sensing can be achieved with a cation displacement assay,[25-40] which is a promising method for the detection of anionic species in water. Generally, anion receptors consist of hydrogen bonding sites. However, competitive binding by polar solvents can happen.[41,42] This problem can be resolved by introducing ionic interactions provided by metal ions.

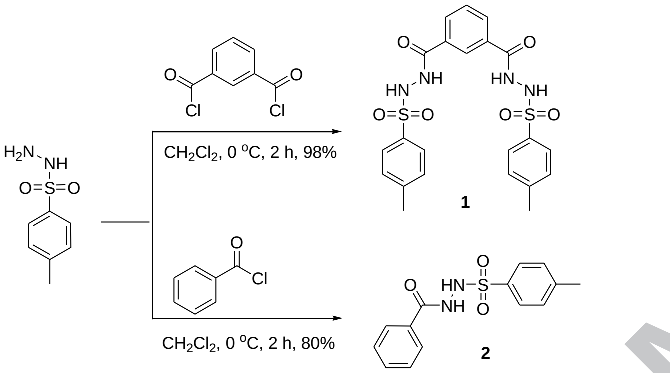
Among all transition metal ions, silver is one of the most important cations used in the electronic and photographic industries.[43,44] Its consumption has increased significantly over the last two decades. Therefore, to limit its harmful effects – particularly on plants, the silver concentrations in the environment and in industrial waste should be monitored. Iodide has attracted considerable attention for its important role in the biological system.[16,45,46] It plays a key role in the thyroid gland function and in normal human growth.[47] A deficit or excess of iodide in the thyroid can cause serious health problems. Therefore, the monitoring of iodide concentrations is used to diagnose many diseases. Due to the strong affinity of silver for iodide, high-sensitivity anion sensors can be constructed using a cation displacement approach.[25-40] In this approach, a primary receptor is used as a sensor for an analyte that is readily eliminated by the second analyte, causing a release of the primary receptor.

In this context, we designed and synthesized a sulfonamide-based dipodal receptor for the sensing of Ag^+. The resultant complex was used as a colorimetric sensor for the probing of I^- in water. We expected the receptor to be capable to encapsulate a cation selectively thanks to its multiple binding sites, and its Ag-complex to recognize I^- based on the high affinity of silver with iodide. In addition, considering the high polarity of the sulfonamide group, the receptor was expected to be soluble in water.

2. Results and discussion

Receptor **1** was prepared as per Scheme 1. The condensation of *p*-toluenesulfonylhydrazide with isophthaloyl dichloride in CH_2Cl_2 at 0 °C afforded receptor **1** in a 98% yield. For control experiments, a second receptor (**2**) was similarly prepared from the reaction of *p*-toluenesulfonylhydrazide with benzoyl chloride instead of isophthaloyl dichloride.

Photophysical studies of receptor **1** were performed in water (10 mM HEPES, pH 7.5). The absorbance spectrum of receptor **1** (10 μM) showed absorbance maxima at 226 nm. Further binding studies of receptor **1** were conducted with various metal ions (Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Mg^{2+}, Ag^+, Co^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Na^+, and K^+), as per Figure 1. None of these showed significant changes in absorbance, except for Ag^+ ions, which showed a new absorbance band at 426 nm. This new absorbance band was attributed to a metal-to-ligand charge-transfer (MLCT) mechanism, which confirmed that a complex was formed. As seen in Figure 2, the bar diagram at 426 nm showed a high selectivity of receptor **1** for Ag^+ over other metal ions, with a 350-fold increase in intensity. This was accompanied by a color change in the solution, from colorless to yellow (Figure 3). The emission spectrum of receptor **1** was also recorded in the presence of various cations (excitation at λ_{max} = 226 nm) (Figure S1). It remained almost the same with most of the metal ions, although the emission profile was changed with a cut-off around 450 nm for Ag^+ ions. To analyze the binding pattern of receptor **1**, binding experiments with mono-podal receptor **2** were performed using absorbance spectroscopy. The absorbance spectrum of receptor **2** was recorded in the presence of different metal ions (Figure S2). Although Ag^+ ions showed some enhancement of the absorbance intensity at 426 nm, it was significantly lower than with receptor **1**. Along with Ag^+ ions, Fe^{3+} ions also showed a small enhancement in the absorbance intensity. This revealed that the sensitivity and selectivity of the receptors depend on their cavity size and number of pods.



Scheme 1. Synthesis of receptors **1** and **2**

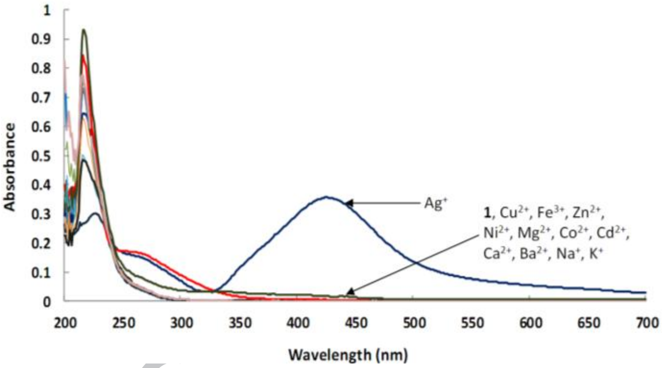


Figure 1. UV-vis absorbance of receptor **1** (10 µM) upon addition of particular metal (5 equiv) in water (10 mM HEPES, pH 7.5).

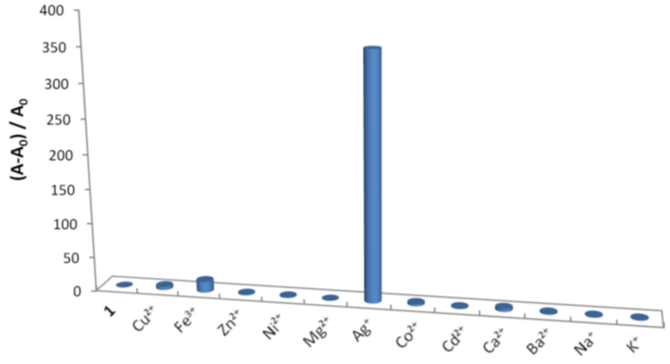


Figure 2. UV-vis absorbance of receptor **1** (10 µM) upon addition of particular metal (5 equiv) in water (10 mM HEPES, pH 7.5) at 426 nm.

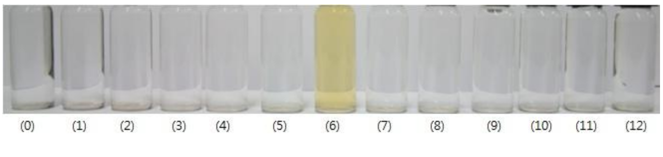


Figure 3. Photographic images of receptor **1** (10 µM) in water (10 mM HEPES, pH 7.5) in the presence of metal ions (5 equiv) (From 0 to 12: receptor **1**, Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Mg^{2+}, Ag^+, Co^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Na^+, and K^+).

Titration experiments were performed to understand the photophysical behavior of receptor **1** for the recognition of Ag^+ ions (Figure 4). Upon the stepwise addition of Ag^+ ions to a 10 µM solution of receptor **1** in water (10 mM HEPES, pH 7.5), the intensity at 426 nm increased gradually. From the titration data, the binding constant of receptor **1** to Ag^+ ions was calculated as 3.23 (±0.2) x 10^3 M^{-1} with the Benesi-Hildebrand plot (Figure S3).[48]

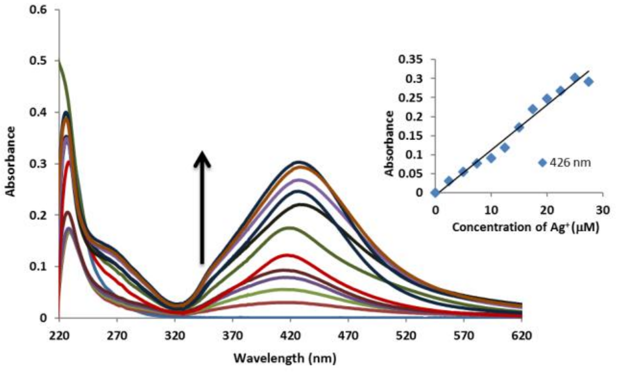


Figure 4. Absorbance changes in receptor **1** (10 µM) upon addition of Ag^+ ions (0-2.7 equiv) in water (10 mM HEPES, pH 7.5).

To evaluate the stoichiometry of complex formation, a Job's plot was constructed (Figure S4).[49] The x-axis of the Job's plot—the mole fraction—is the ratio of Ag^+ concentration to the total concentration of Ag^+ and receptor **1**, whereas the y-axis—labeled [HG]—is the concentration of the complex **1**-Ag calculated from spectroscopic techniques. The Job's plot indicated that receptor **1** and Ag^+ formed a 1:1 complex. The formation of the complex **1**-Ag was also confirmed with a comparison of the IR spectrum of receptor **1** (Figure S5) with that of the complex (Figure S6). The IR absorption frequency of the S=O asymmetric stretch moved from 1340 to 1366 cm^{-1}. The frequency of the S=O symmetric stretch also changed from 1166 to 1193 cm^{-1}. These changes in the IR spectrum imply that the Ag^+ ion coordinates with the oxygen atoms of sulfonyl groups. The IR spectrum of the complex **1**-Ag had a strong band at 3427 cm^{-1}, which implied the presence of H_2O. Furthermore, a FAB HRMS was used to verify the stoichiometry of the complex and the presence of H_2O in it (Figure S7). It showed m/z = 663.1517, which corresponded to (**1** + Ag + $3H_2O$) (calcd: 663.0349). The detection limit of receptor **1** for the estimation of Ag^+ was determined as 2.43 µM (Figure S8).[50]

To examine the effects of other metal ions on the detection of Ag^+ ions, competing binding tests were performed. The absorbance spectra of receptor **1** were recorded in the presence of different concentrations of Ag^+ ions with other possible competing metal ions at a ratio of 1:1. As per Figure 5, there was no obvious perturbation in the UV-vis intensity of receptor **1** irrespective of the presence or absence of other metal ions in low concentrations, although a small perturbation was observed after 15 equivalents of metal ions. These results confirmed that receptor **1** can estimate Ag^+ ions without interference in the presence of other metal ions.

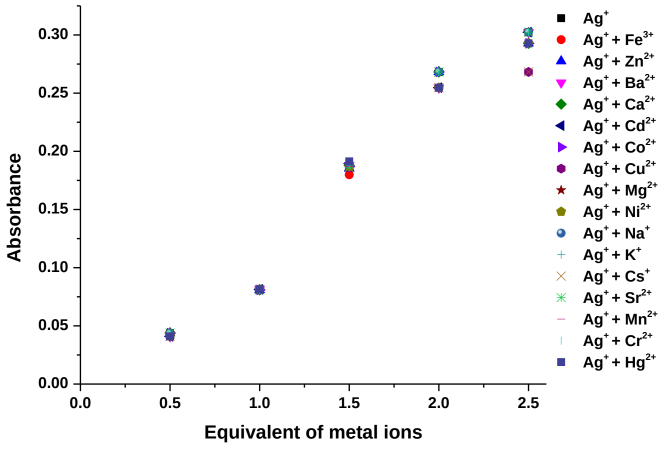


Figure 5. UV-vis absorbance of receptor **1** (10 uM) at 426 nm in the presence of various metal ions in water (10 mM HEPES, pH 7.5).

The silver complex of receptor **1** was prepared in situ, and binding studies were performed with anions through UV-vis spectroscopy. The absorbance spectrum of the complex **1**-Ag (10 µM) was recorded in water (10 mM HEPES, pH 7.5), as per Figure 6. Upon the addition of 5 equiv of I^- ions, the original absorbance of receptor **1** was regained. However, no significant change was observed with other anions. Figure 7 presents a bar diagram of the absorbance at 426 nm upon the addition of various anions. The addition of I^- brought a significant decrease in the intensity of receptor **1**, whereas other anions caused only small changes. Color changes from yellow to colorless in the complex **1**-Ag (10 µM) were also observed upon the addition of iodide ions (Figure 8). The recovery of the spectrum and color of receptor **1** revealed the release of Ag^+ ions from the complex **1**-Ag upon the addition of I^- ions.

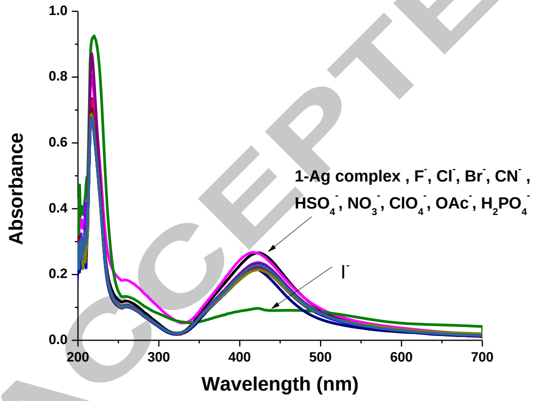


Figure 6. Changes in UV-vis absorbance of the complex **1**-Ag (10 µM) upon addition of particular TBA salt (5 equiv) in water (10 mM HEPES, pH 7.5).

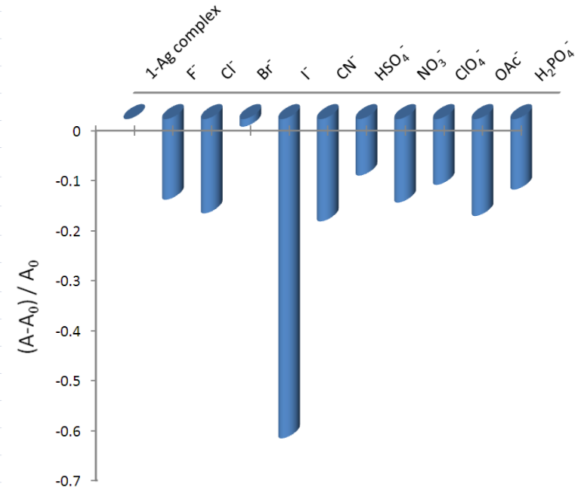


Figure 7. Plot of UV-vis absorbance of the **1**-Ag complex (10 µM) upon addition of particular TBA salt (5 equiv) in water (10 mM HEPES, pH 7.5) at 426 nm.

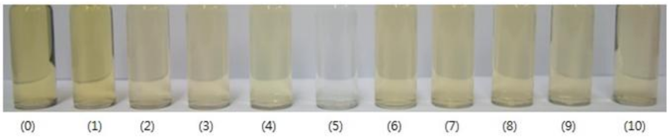


Figure 8. Color changes in the complex **1**-Ag (10 µM) upon addition of anions (5 equiv). [(0): **1**-Ag complex, (1): F^-, (2): Br^-, (3): Cl^-, (4): ClO_4^-, (5): I^-, (6): CN^-, (7): NO_3^-, (8): OAc^-, (9): HSO_4^-, and (10): $H_2PO_4^-$.

To confirm the interaction of the complex **1**-Ag with I^-, titration experiments were performed with the successive addition of I^- to a solution of the complex **1**-Ag (Figure 9). As the concentration increased, the MLCT band at 426 nm decreased, indicating the abstraction of Ag^+ from the complex **1**-Ag by I^-. The detection limit of the complex **1**-Ag as a I^- sensor was determined as 5.31 µM (Figure 10).[50]

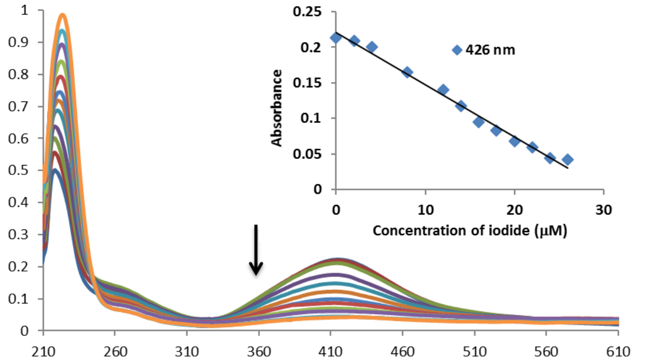


Figure 9. Absorbance changes in the complex **1**-Ag (10 µM) upon addition of I^- (0-2.6 equiv) in water (10 mM HEPES, pH 7.5).

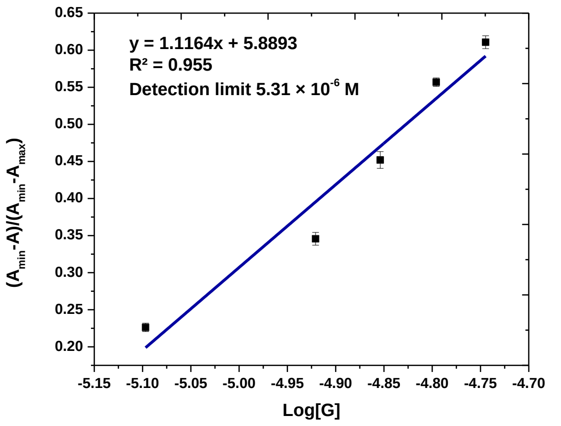


Figure 10. Detection limit of the complex **1**-Ag for estimation of I^-.

The amount of I^- was measured in the presence of potential competitive anions, including F^-, Cl^-, Br^-, CN^-, HSO_4^-, NO_3^-, ClO_4^-, OAc^-, $H_2PO_4^-$, CO_3^{2-}, and S^{2-}. As shown in Figure 11, no significant changes in the absorbance were observed, suggesting that the complex **1**-Ag recognized I^- ions selectively. There was also no observation of interference according to the concentrations of the competitive anions.

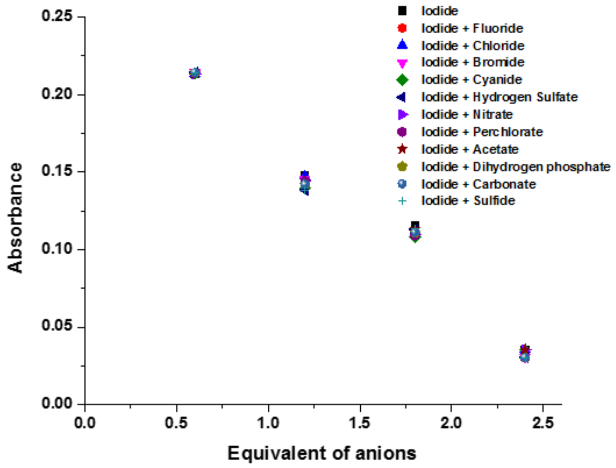


Figure 11. UV-vis absorbance of the complex **1**-Ag (10 µM) at 426 nm in the presence of various metal ions in water (10 mM HEPES, pH 7.5).

To validate the interaction of Ag^+ ions with receptor **1**, the ^1H NMR spectrum of receptor **1** was recorded in the presence of Ag^+ ions, showing that the chemical shifts of the aromatic protons shifted downfield. The downfield shifts and peak broadening confirm the interaction of Ag^+ ions with receptor **1** (Figure S9).

Density functional theory (DFT) calculations for receptor **1** were performed with the DMol3 GGA-DFT package.[51] Receptor **1** was optimized in the presence of $AgNO_3$. As shown in Figure 12, a silver ion coordinates to sulfonyl oxygens and a nitrate ion. The HOMO-LUMO diagrams of the complex **1**-Ag reveal that the band at 426 nm is due to an MLCT mechanism. As shown in Figure 13, the electron density of the HOMO concentrates on the silver ion whereas the LUMO is spread over the conjugated ligand, which leads to an MLCT transition. The MLCT transition enhances the population of transition, resulting in the detection of silver ions at low concentration.[52]

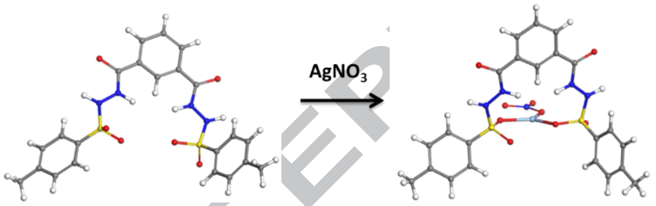
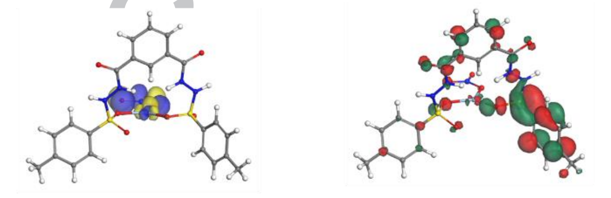


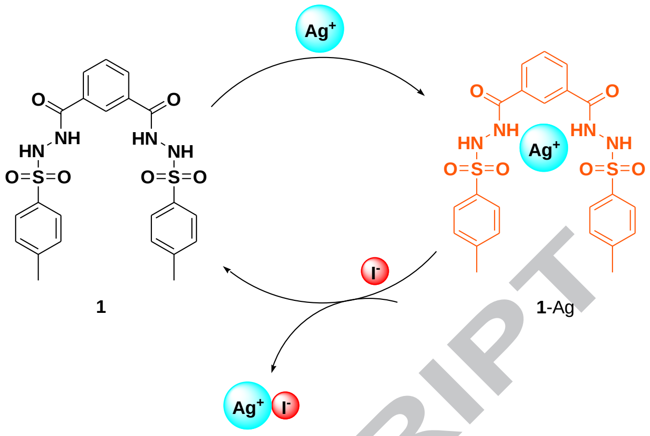
Figure 12. DFT computed optimized structure of receptor **1** and the complex **1**-Ag.



Highest Occupied Molecular Orbital Lowest Unccupied Molecular Orbital

Figure 13. The HOMO and LUMO of the complex **1**-Ag, showing that the electron density of HOMO spreads over the silver ion and the LUMO spreads over the conjugated receptor.

The changes in frequency of the sulfonyl group in the IR spectra implied that Ag^+ coordinated with the oxygen atoms of sulfonyl groups. The HRMS analysis and Job's plot also evidenced the formation of the complex **1**-Ag. The latter interacted with I^- ions selectively, resulting in the restoration of the absorbance profile of receptor **1**. The revival of the receptor **1** absorbance profile indicated that the Ag^+ ions in the complex **1**-Ag were released from the complex upon the addition of I^-. Receptor **1**'s binding mode involving Ag^+ and I^- ions is illustrated in Scheme 2.



Scheme 2. Proposed mechanism for I^- sensing with the complex **1**-Ag^+.

3. Conclusions

In summary, we demonstrated that a sulfonamide-based dipodal receptor, receptor **1**, could be used as a colorimetric chemosensor for the sensing of Ag^+ in water even in the presence of possible competing cations. The resultant complex **1**-Ag was capable of sensing iodide in the presence of other anions with a detection limit of 5.31 µM using a metal displacement process. Receptor **1** and the complex **1**-Ag are capable of selectively and sensitively estimating Ag^+ and I^-, respectively.

4. Experimental

Synthesis of compound 1: A solution of *p*-toluenesulfonylhydrazide (458 mg, 2.46 mmol) and isophthaloyl dichloride (200 mg, 0.98 mmol) in CH_2Cl_2 (20 mL) was stirred at 0 ^oC. After 2 h, the precipitate was filtered and washed with saturated $NaHCO_3$, MeOH, and ether, yielding 482 mg (98%): mp = 190 ~ 191 ℃; IR (KBr) ν 3143, 3032, 1340, 1166 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.34 (s, 6H, CH_3), 7.33 (d, J = 8.1 Hz, 4H, Ar), 7.52 (t, J = 7.7 Hz, 1H, Ar), 7.74 (d, J = 8.1 Hz, 4H, Ar), 7.83 (d, J = 7.7 Hz, 2H, Ar), 7.99 (s, 1H, Ar), 10.01 (s, 2H, CONH), 10.78 (s, 2H, $NHSO_2$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.0, 126.7, 127.7, 128.8, 129.3, 130.7, 132.2, 136.0, 143.4, 164.9; HRMS (FAB) calcd. for $C_{22}H_{22}N_4O_6S_2$ (M + H): 503.1070, Found 503.1059.

Synthesis of compound 2: A solution of p-toluenesulfonylhydrazide (397 mg, 2.13 mmol) and benzoyl chloride (200 mg, 1.42 mmol) in CH_2Cl_2 (20 mL) was stirred at 0 ^oC. After 2 h, the precipitate was filtered and washed with saturated $NaHCO_3$, MeOH, and ether, yielding 329 mg (80%): mp = 175-176 ^oC (lit.[53] 114.5-115.5 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H, -CH_3), 7.33 (d, J = 10 Hz, 2H, Ar), 7.37-7.43 (m, 3H, Ar), 7.58-7.64 (m, 2H, Ar), 7.79 (s, 2H, Ar), 7.89 (s, 1H, CONH), 7.91 (s, 1H, $NHSO_2$).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org.

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Highlights

- Receptor **1** could be used as a colorimetric sensor for the sensing of Ag^+ ions in water.
- The resultant **1**-Ag complex was capable of sensing iodide.
- Receptor **1**'s binding mode involving Ag^+ and I^- ions is presented.