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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.

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,[25–37,6,38,39] 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.[40,41] 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.[42,43] 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.[16,44,45] It plays a key role in the thyroid gland function and in normal human growth.[46] 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.[25–37,6,38,39] 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.

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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.

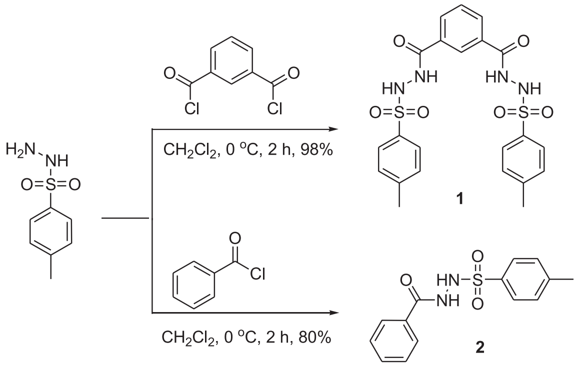
Photophysical studies of receptor **1** were performed in water (10 mM HEPES, pH 7.5). The absorbance spectrum of receptor **1** (10 μM) showed absorbance maxima at 226 nm. Further binding studies of receptor **1** were conducted with various metal ions (Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Mg^{2+}, Ag^{+}, Co^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Na^{+}, and K^{+}), as per Fig. 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 Fig. 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 (Fig. 3). The emission spectrum of receptor **1** was also recorded in the presence of various cations (excitation at $\lambda_{max} = 226$ nm) (Fig. 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 (Fig. 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.

Titration experiments were performed to understand the photophysical behavior of receptor **1** for the recognition of Ag^{+} ions (Fig. 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) × 10^3 M^{-1} with the Benesi-Hildebrand plot (Fig. S3).[47]

To evaluate the stoichiometry of complex formation, a Job's plot was constructed (Fig. S4).[48] 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** (Fig. S5) with that of the complex (Fig. 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 (Fig. S7). It showed $m/z = 663.1517$, which corresponded to ($\mathbf{1} + Ag + 3H_2O$) (calcd: 663.0349). The detection limit of receptor **1** for the estimation of Ag^{+} was determined as 2.43 μM (Fig. S8).[49]

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 Fig. 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.

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



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

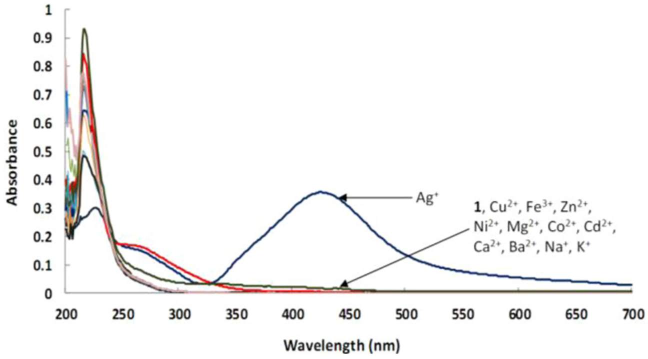


Fig. 1. UV–vis absorbance of receptor **1** (10 μM) upon addition of particular metal (5 equiv) in water (10 mM HEPES, pH 7.5).

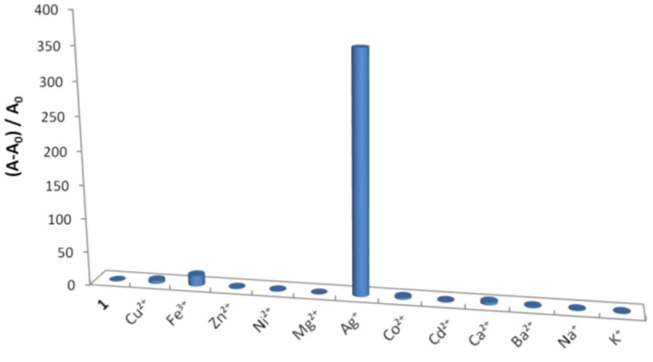


Fig. 2. UV–vis absorbance of receptor **1** (10 μM) upon addition of particular metal (5 equiv) in water (10 mM HEPES, pH 7.5) at 426 nm.