A novel self-assembled supramolecular sensor based on thiophene-functionalized imidazophenazine for dual-channel detection of Ag\(^{+}\) in an aqueous solution†

Hai-Xiong Shi, Wen-Ting Li, Qiao Li, Hai-Li Zhang, You-Ming Zhang, Tai-Bao Wei, Qi Lin and Hong Yao

Herein, a novel self-assembled supramolecular sensor (S1) based on thiophene-functionalized imidazophenazine for Ag\(^{+}\) was designed and synthesized. It showed dual-channel detection properties for Ag\(^{+}\) based on the competitive mechanism of supramolecular self-assembly with high sensitivity and selectivity even in the presence of other metal ions. Its detection limit for Ag\(^{+}\) is \(8.18 \times 10^{-9}\) M. Upon the addition of Ag\(^{+}\), the solution changes from yellow to light purple and the fluorescence is quenched. Furthermore, the sensing mechanism between Ag\(^{+}\) and S1 is investigated via IR and \(^{1}H\) NMR spectroscopy, mass spectrometry, and density functional theory calculations.

Introduction

With the development of modern industry, increasing industrial emissions containing metal ions have caused serious water pollution, which affects food and agriculture and further threatens human health and the environment.\(^1\) Among the important metal ions, silver has attracted extensive attention due to its wide applications in the fields of electricity, photography, imaging, and pharmacy.\(^2\) In fact, trace amounts of silver ions can control bacteria breeding or rehabilitate and reconstruct essential human tissue.\(^3\) However, as is well known, excess silver ions can inactivate sulfhydryl enzymes; on the other hand, silver ions can combine with amine, imidazole, and carboxyl groups of various metabolites, such as high molecular weight protein and metallothionein, in the tissue of the cytosol fraction, resulting in harmful effects to humans.\(^4\) Thus, the maximum bearable concentration of Ag\((i)\) issued by the World Health Organization (WHO) is 0.5 \(\mu\)M in drinking water.\(^5\)

Considering the importance of Ag\((i)\) in industrial production and in daily life, the development of techniques for sensing and monitoring Ag\((i)\) is in great demand. There are various available methods to monitor Ag\(^{+}\), such as electrothermal atomic absorption spectrometry (ETAAS), voltammetry, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and potentiometry.\(^6\) However, most of them are expensive, time-consuming, or unsuitable for on-site and real-time monitoring. Therefore, the development of fast, efficient, sensitive, and selective methods for the detection of Ag\(^{+}\) is necessary for both the environment and human health.\(^7\) In comparison, fluorescence techniques exhibit attractive advantages, such as high selectivity and sensitivity, real-time detection, practical-simple sample preparation, and great potential in high throughput detection of Ag\(^{+}\) on-site. However, some of these probes suffer from serious drawbacks such as complicated synthesis procedures and poor solubility, sensitivity, and selectivity in aqueous media.\(^8\) Due to the efforts of researchers, numerous Ag\(^{+}\) sensors with good properties have been reported. However, most of them exhibit ultraviolet or fluorescent single channel recognition or are less selective.\(^9\) Moreover, it is worthwhile to note that sensors for the detection of Ag\(^{+}\) in aqueous systems are relatively scarce although Ag\(^{+}\) usually exists in water or sewerage. Consequently, the design and synthesis of colorimetric and fluorescent chemosensors with high sensitivity and selectivity for the quantification of Ag\(^{+}\) in aqueous media via a simple reaction is still an intriguing area of research.\(^10\)

In view of this and based on our previous research in host-guest chemistry,\(^11\) we designed and synthesized a sensor molecule IM (Scheme 1) based on thiophene-functionalized imidazophenazine via a simple reaction; this sensor could self-assemble into a supramolecular system and form a supramolecular chemosensor S1. This sensor combines the phenazine fluorescent signaling subunit, which has attracted extensive attention due to its excellent photophysical properties. In addition, among the different fluorogens, it is very sensitive to...
conformational changes.\textsuperscript{22} Consequently, phenazines are ideal platforms for the development of cation, anion, and neutral molecule recognition platforms. Moreover, there are only a few reports on ion recognition in host–guest chemistry. Compared to some Ag\textsuperscript{+} sensors reported in previous studies, the Ag\textsuperscript{+} sensor reported herein is a self-assembled supramolecular sensor (S1). The Ag\textsuperscript{+} sensing mechanism is based on a competition between self-assembly of the sensor molecules and Ag\textsuperscript{+} coordination with the sensor molecules. This novel competitive mechanism provides the S1 sensor with better Ag\textsuperscript{+} detection sensitivity. The detection limit of S1 for Ag\textsuperscript{+} is 8.18 \times 10^{-9} M, which is lower than that reported in some previous studies.\textsuperscript{4} Therefore, S1 is utilized as a supramolecular self-assembled sensor to study the recognition performance of Ag\textsuperscript{+}.

Results and discussion

To investigate the Ag\textsuperscript{+} recognition abilities of the S1 sensor in an aqueous solution, we performed a series of host–guest recognition experiments. The recognition profiles of the chemosensor S1 towards various metal ions, including Fe\textsuperscript{3+}, Hg\textsuperscript{2+}, Ag\textsuperscript{+}, Ca\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+}, Zn\textsuperscript{2+}, Cr\textsuperscript{3+}, and Mg\textsuperscript{2+}, were primarily investigated using UV-vis spectroscopy and fluorescence spectroscopy in a DMSO/water (v:v = 1:1) solution.

As shown in Fig. 1, the sensor immediately responded with obvious color changes (from yellow to light purple) when Ag\textsuperscript{+} was added to the S1 solution at room temperature. In the corresponding UV-vis spectra, the strength of the absorption peak at 413 nm decreased, and the peak red-shifted to 376 nm (Fig. S1\textsuperscript{†}). However, yellow fluorescence with one emission band centered at 547 nm appeared when the S1 sensor solution was excited at 400 nm. The fluorescence intensity of the peak at 547 nm sharply decreased with the addition of the Ag\textsuperscript{+} solution. No significant UV-vis or fluorescence spectra changes were observed when solutions of other cations (such as Fe\textsuperscript{3+}, Hg\textsuperscript{2+}, Ca\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+}, Zn\textsuperscript{2+}, Cr\textsuperscript{3+}, and Mg\textsuperscript{2+}) were added to the S1 sensor solution.

Subsequently, we further investigated the supramolecular sensor S1 recognition for Pd\textsuperscript{2+}, as shown in Fig. S2 and S3; however, S1 could not sense Pd\textsuperscript{2+}. These results confirmed that the self-assembly supramolecular sensor S1 could sense Ag\textsuperscript{+} with high sensitivity and selectivity.

The specific selectivity of a sensor towards an analyte in the presence of other competitive species is important. To explore the utility of the S1 sensor as an ion-selective chemosensor for Ag\textsuperscript{+}, competitive experiments were carried out in the presence of 10 equiv. of Ag\textsuperscript{+} and 10 equiv. of Fe\textsuperscript{3+}, Hg\textsuperscript{2+}, Ca\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+}, Zn\textsuperscript{2+}, Cr\textsuperscript{3+}, and Mg\textsuperscript{2+} metal ions in DMSO/water (v:v = 1:1, buffered with HEPES pH = 7.2) binary solutions (Fig. 2 and S4\textsuperscript{†}). From the bar diagram, it was observed that none of these ions induced any significant change in the fluorescence and UV-vis absorbance spectrum of the sensor. Therefore, it is clear that the interference of other ions is negligible during the detection of Ag\textsuperscript{+}. These results further suggested that S1 could be used as a sensor for Ag\textsuperscript{+} over a wide range of cations. Thus, S1 could selectively and instantly (dual-channel) detect Ag\textsuperscript{+} in DMSO/water (v:v = 1:1, buffered with HEPES pH = 7.2).

To evaluate the Ag\textsuperscript{+}-responsive nature of S1, fluorescence and UV-vis absorbance titrations with Ag\textsuperscript{+} at varying concentrations were conducted. As shown in Fig. 3, upon the addition of Ag\textsuperscript{+} to the S1 sensor, the emission peak at 547 nm gradually diminished, and the fluorescence of S1 was almost quenched by 18.0 equiv. of Ag\textsuperscript{+} ions. In the UV-vis spectra (Fig. 4), the initial absorption peak at 413 nm gradually decreased, and simultaneously, a broad shoulder peak appeared at 530 nm and an isosbestic point at 495 nm was clearly observed. This should be attributed to the damage of intramolecular hydrogen-bonding...
interactions in the sensor and confirms the coordination of the sensor and Ag⁺. Based on the equation LOD = \frac{K}{\delta}, the detection limits obtained from the UV-vis and the fluorescence spectra were 8.75 × 10⁻⁷ M and 8.18 × 10⁻⁹ M for silver ions, respectively. This data indicates that the sensor can detect Ag⁺ at very low concentrations in the environment with high selectivity and sensitivity. This result also shows that S₁ has higher sensitivity for silver ions as compared to other reported Ag⁺ sensors (Table S₁†). Therefore, S₁ can be used as a potential colorimetric and fluorescent sensor for Ag⁺ recognition.

Since the pH value of the environment around a chemosensor usually influences its detection toward target metal ions due to the protonation or deprotonation reaction of the sensor, the influence of pH value on the absorbance and emission bands of S₁ in a DMSO/water (1 : 1, v:v, buffered with HEPES pH = 7.2) solution has been investigated. As shown in Fig. 5 and S7, when the pH increased from 5 to 10, the absorbance and emission values remained almost unchanged. These results indicated that Ag⁺ could be clearly detected via UV-vis and fluorescence spectral measurement using S₁ over a wide pH range.

The self-assembly and Ag⁺ recognition mechanism of the S₁ sensor were investigated using concentration titration, ESI-MS, ¹H NMR titration, and DFT methods. To establish the supramolecular self-assembly mechanism, we performed the concentration titration in the absence and presence of different concentrations of S₁. As shown in Fig. 6, the fluorescence intensity of the peak at 547 nm sharply increased with the addition of S₁; this suggested that with the gradual increase in the concentration of S₁, the self-assembled system was formed by π–π stacking and H-bonding in the aqueous solution. Moreover, the XRD spectra (Fig. S₈†) support the
ion mode) (Fig. S15). As shown in Fig. S16, the addition of Ag⁺ and I⁻ was absent, and an obvious enhancement was observed for the S1 sensor. Based on all the abovementioned tests, we confirmed that IM self-assembly formed S1 via π–π stacking and H-bonding in the aqueous solution.

The reversibility of the sensor function was tested by the addition of I⁻ to the S1–Ag complex. With the alternative addition of Ag⁺ and I⁻ to the aqueous solution of the self-assembled S1 sensor, the fluorescence emission of the tested solution exhibited alternating quenching and reactivation processes (Fig. S9†). This off–on switching process was repeated several times. Therefore, the S1 sensor can be considered a good ON–OFF fluorescence switch.

The 2:1 stoichiometry of the S1 and Ag⁺ complex was further confirmed by the results of the ESI-MS studies. The free probe shows a main peak at m/z = 301.09, corresponding to [IM – H⁺]− (ESI-MS negative ion mode) (Fig. S14†), and the complex is confirmed by the appearance of a peak at m/z = 731.12, assignable to [2IM + Ag⁺ + H₂O + H⁺]− (ESI-MS positive ion mode) (Fig. S15†). The Job plot between S1 and Ag⁺ was implemented, demonstrating a 2:1 stoichiometry for S1 and Ag⁺, as shown in Fig. S16†.

The FTIR spectra of the receptor IM and its complex with Ag⁺ were obtained to examine the binding sites (Fig. S10†). In the FTIR spectrum of the free probe IM, the characteristic absorption band of S1–Ag⁺ for N–H (3428 cm⁻¹) of the imidazole group was absent, and an obvious enhancement was observed for the C–N absorption bands from 1322 to 1421 cm⁻¹; this confirmed the binding of S1 with silver.

To gain more information about the complexation between S1 and Ag⁺, we performed an ¹H NMR titration in the absence and presence of different concentrations of Ag⁺. As shown in Fig. S11†, the ¹H NMR titration of S1 in DMSO-d₆ (10 mmol) with Ag⁺ in D₂O (1 mol) established the stoichiometry and binding site towards the sensor response. Most interestingly, the N–H peak (H₁) of the imidazole group in IM disappeared after the addition of 2.0 equiv. of Ag⁺ to D₂O;¹ this proved that S1 was strongly bound with Ag⁺. Moreover, the signal of the hydrogen atoms in the phenazine (H₄, H₄, H₅, H₇, and H₈) and thiazole (H₄, H₉, and H₉) rings showed a significant downfield shift; this suggested that the intermolecular π–π stacking was destroyed after the addition of Ag⁺, and it further caused the deshielding for the hydrogen protons and resulted in downfield shifts.

To further investigate the binding behavior of S1 with Ag⁺ ions, we optimized the structure of IM and IM–Ag⁺ complex by applying the B3LYP/6-31G(d, p) method in the gas phase using the Gaussian-09 computational code.¹⁶ The optimized structures of IM and IM–Ag⁺ are shown in Fig. S12 and S13,+ respectively. The short N34–H49–N23 distance of 2.041 Å indicates the presence of an intramolecular hydrogen bond in IM. Additionally, some of the relevant optimized geometric parameters are presented in Tables S2–S5.† The relevant occupied molecular orbital HOMO (−0.295 a.u.) of IM was localized mainly to the thiophene groups, whereas the unoccupied orbital LUMO (−0.227 a.u.) was localized over the phenazine and imidazole groups. The HOMO–LUMO energy gap (DE) for IM was found to be 0.068 a.u. (Fig. 7). On the other hand, upon interaction with Ag⁺, the HOMO (−0.291 a.u.) and LUMO (−0.279 a.u.) were almost localized on the entire molecule, where the electron density was polarized toward the whole molecule. The HOMO–LUMO energy (DE) for IM with Ag⁺ was found to be 0.012 a.u. These results suggested that the fluorescence quenching was most probably attributed to the prevention of IM intramolecular charge transfer (ICT) by Ag⁺ (Scheme 1).

To investigate the practical application of the chemosensor S1, test strips were prepared by immersing filter paper in a DMSO/water (v:v = 1:1, buffered with HEPES pH = 7.2) solution of S1 and then drying them in air. The test strips containing S1 were utilized to sense Ag⁺ and other metal ions. As shown in Fig. 8, when Ag⁺ and other ions were added to the test kits, an obvious color change was only observed for the Ag⁺ solution under a 365 nm UV-lamp. The potential competitive

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**Fig. 6** Fluorescence spectra in the presence of different concentrations of S1 (0–2.86 × 10⁻⁵ M) in the DMSO/H₂O (v:v = 1:1, buffered with HEPES pH = 7.2) solution.

**Fig. 7** DFT-optimized Frontier molecular orbitals and HOMO–LUMO energy gaps for S1 (left) and S1–Ag⁺ (right).
ions did not influence the detection of Ag$^+$ by the test strips. Therefore, the test strips could conveniently detect Ag$^+$ in the solution.

Conclusions

In summary, we developed a novel self-assembled supramolecular sensor S1 that could recognize Ag$^+$ over other metal ions with significant UV-vis absorption and fluorescence quenching changes with highly selective and sensitive properties based on the competitive mechanism of supramolecular self-assembly. The obvious color changes and pronounced ON-OFF-type fluorescence signaling behavior can be seen by the naked eyes. The limit of detection for Ag$^+$ was as low as 8.18 × 10^{-9} M in an aqueous solution, which was lower than that in some previously reported research. We believe that the sensor will be regarded as an environmentally friendly material that can sense Ag$^+$ in an aqueous solution and make a great contribution to the development of silver ion sensors.

Conflicts of interest

There are no conflicts to declare.

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