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A thiophene-derived hexaazatriphenylene (HAT) fluorescent sensor for the selective detection of Ag^+ ion

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ABSTRACT

Herein, by symmetrically merging six thiophene units into the hexaazatriphenylene (HAT) core, a HAT-based sensor (**1**) was designed and synthesized, which was found capable of exhibiting selective recognition of Ag^+ with detection limit as low as 1.79×10^{-6} M in chloroform featuring with significant fluorescence "turn-off" property. Through the systematical investigation with UV–Vis absorption, fluorescence spectroscopy and the naked-eye experiments, as well as the ^1H NMR titration and the Job's plot, it was revealed that sensor **1** could complex with Ag^+ in a stoichiometric ratio of 2:3. We envisage the construction of such a thiophene-derived HAT molecule is conducive to exploring new type of Ag^+ sensors, and it also will bring potential application in environmental detection.

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Introduction

The design and construction of chemosensors targeting cations [1-5] or anions [6-10] of biological, chemical and environmental importance is one of vibrant areas in supramolecular chemistry. Silver ion (Ag^+), on one hand, plays an indispensable role in a wide range of fields such as pharmacy,[11] catalysis,[12,13] and supramolecular self-assembly.[14-16] On the other hand, the utilization of silver compounds causes unavoidable negative impact on the environment, and long-term and excess intake of Ag^+ will lead to healthy problem such as stomach distress, skin irritation, disruptive renal and neurological functions.[17-19] Owing to the duplicitous effects of Ag^+ ion, the development of new chemosensors for the excellently selective, instantly responsive and efficient detection of Ag^+ is highly desirable.

Traditional approaches such as atomic absorption spectrometry, [20] inductively-coupled plasma emission mass spectrometry [21] and electrochemical method [22] have been utilized to monitor the existence of Ag^+. However, these strategies commonly suffer from disadvantages of high-cost, time-consuming and labour-intensity. Comparatively speaking, fluorescent probes featuring with easy operation, high selectivity and sensitivity are more preferable tools. In this context, a vast number of Ag^+ sensors with conjugated aromatic structures such as fluorescein, [23] rhodamine, [24] rhodanine, [25] boron-dipyrromethene,[26,27] 1, 8-naphthalimide, [28,29] coumarin,[30] anthracene,[31] isoquinoline,[32] phenazine,[33,34] as well as polymers[35] have been extensively explored, benefiting from the distinctive characteristics of extensive π-electron delocalization and strong fluorescent emission.

Hexaazatriphenylene (HAT),[36] which is a rigid planar conjugated motif with the feature of easy derivatization and plentiful *N*-containing coordinative sites, has been extensively explored not only to fabricate self-assembly systems but also as fluorescent probes for ion recognition. In our previous work, a series of HAT-based derivatives were developed to achieve the selective detection of F^-,[37] Cu^{2+},[38] and even proton-anion ion-pair.[39] Moreover, Bu and co-workers have showed that pyridine-derived HAT molecules could be applied as Cd^{2+} fluorescent sensors.[40,41] However, the HAT-based molecules have rarely been used as selective fluorescent probes for Ag^+ so far. Aiming to enrich the structural diversity of Ag^+ chemosensors and expand the application scope of HAT-based derivatives, we here report a unique HAT-based sensor (compound **1** in Scheme 1) containing six symmetrically substituted thiophene units, the introduction of which was found to enable **1** to selectively recognize Ag^+ ion with significant "turn-off" of emission. The Job's plot and ^1H MR titration experiments revealed that **1** could complex with Ag^+ in a ratio of 2:3 with

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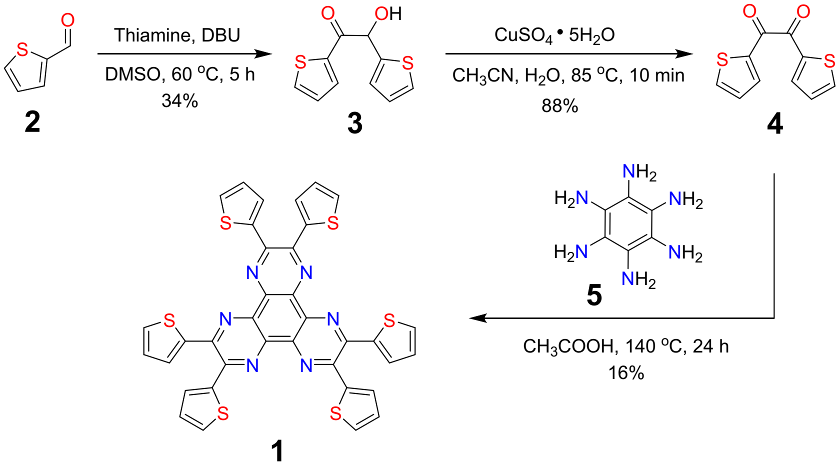

Scheme 1. The synthesis of sensor **1**.

an apparent association constant of 3.98 × 10^7 M^{-1}, and the limit of detection was calculated to be 1.79 × 10^{-6} M.

Results and discussion

Sensor **1** was synthesized through a facile three-step route as showed in Scheme 1. The benzoic condensation of 2-thenaldehyde (**2**) yielded compound **3**, which was further efficiently oxidized by $CuSO_4$ to give diketone **4**. Then, the condensation of **4** with hexaaminobenzene(**5**) [15] afforded the target compound **1**, the chemical structure of which was unambiguously assigned by ^{1}H NMR, ^{13}C NMR as well as HR-MS spectroscopies (see ESI for details).

Naked-eye experiments were first carried out in chloroform under ambient condition and UV-lamp irradiation, respectively. As depicted in Fig. 1, the addition of Ag^+ (4 equiv.) into the solution of **1** led to the development of distinct colour change from light yellow to dark yellow and discernible fluorescence quenching phenomenon. By contrast, both the colour and fluorescence changes were negligible when the same amount of other metal ions were introduced. This result demonstrated that **1** was capable of serving as a colorimetric sensor for Ag^+ with a high selectivity, and the detailed recognition behaviour of **1** over Ag^+ was then investigated.

The spectroscopic property of **1** in chloroform was then revealed by UV–Vis and fluorescent spectroscopic studies. Upon the addition of Ag^+, it was found that the absorption of **1** at 425 nm decreased gradually and a new peak cantered at 450 nm appeared (Fig. 2a), the dramatic spectral change of which could be attributed to the coordination between Ag^+ and **1**.[25] However, the characteristic absorption band of **1** exhibited negligible responses when other metal ions were introduced (Fig. 2b), again suggesting the high selectivity towards Ag^+.

Fluorescent spectroscopic experiments were further carried out to investigate the recognition behaviour of **1** towards Ag^+ ion. As shown in Fig. 3a, upon the addition of 6 equiv. of Ag^+, the fluorescence emission intensity at 475 nm drastically decreased until completely quenched, which could be attributed to the d^{10} configuration of silver.[25,30] However, except for the observation of slight decrease for the emission intensity of **1** at 475 nm after introducing Fe^{3+} and Cu^{2+} ions, the fluorescent spectra of **1** exhibited negligible changes while other metal ions were added to its solution (Fig. 3b). Furthermore, the detection limit could be calculated as 1.79 × 10^{-6} M in $CHCl_3$,[42] which suggested a high recognition sensitivity of **1** for the Ag^+ ion (Fig. S5).

To further reveal the selective recognition behavior of **1** to Ag^+, fluorescent spectra of sensor **1** in the presence of various metal

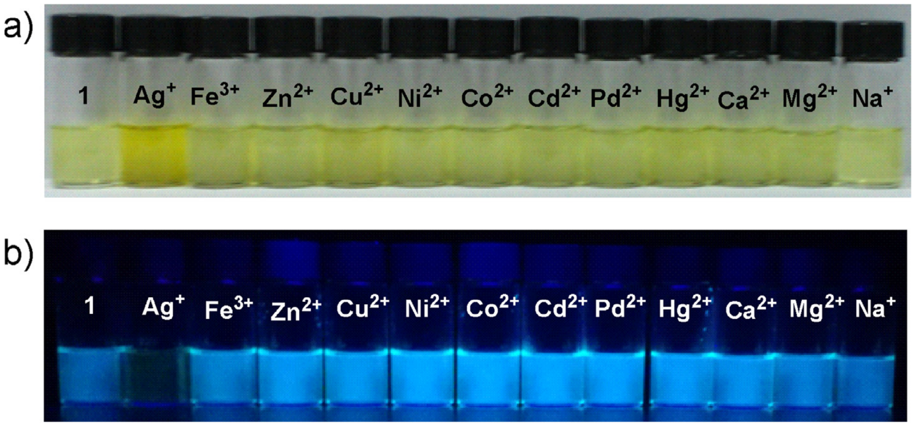

Fig. 1. The solutions of **1** (5 × 10^{-6} M) in chloroform before and after the addition of various metal cations (2 × 10^{-5} M) under (a) visual light and (b) UV lamp (365 nm) irradiation.

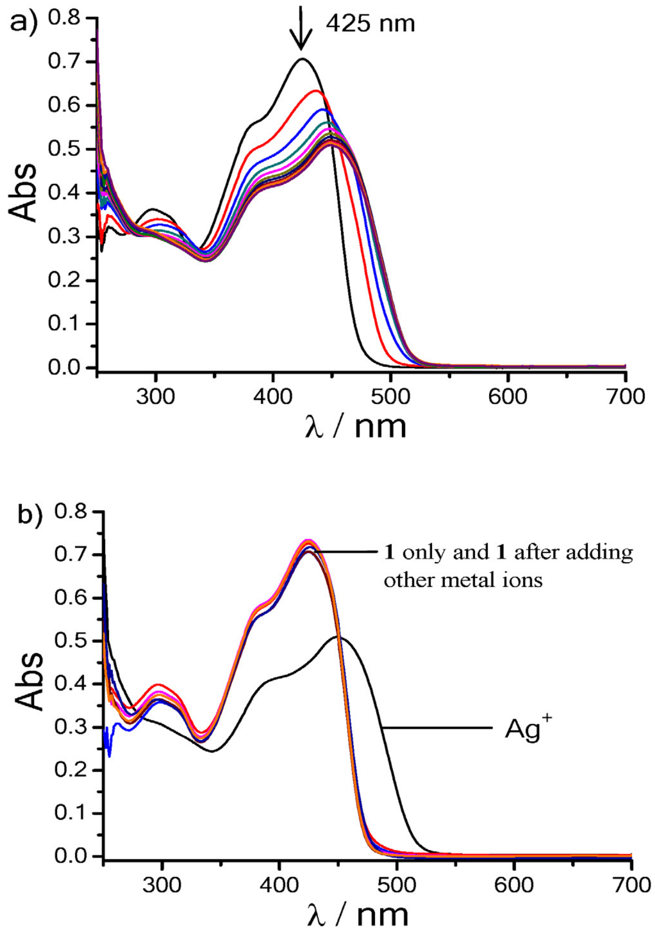

Fig. 2. (a) UV–Vis spectra of sensor **1** (1.25×10^{-5} M, $CHCl_3$) upon the addition of Ag^+ (0 to 6 equiv.), (b) UV–Vis spectra of sensor **1** (1.25×10^{-5} M, $CHCl_3$) upon the addition of 6 equiv. of various metal ions (Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pd^{2+}, Hg^{2+}, Ca^{2+}, Mg^{2+}, and Na^+).

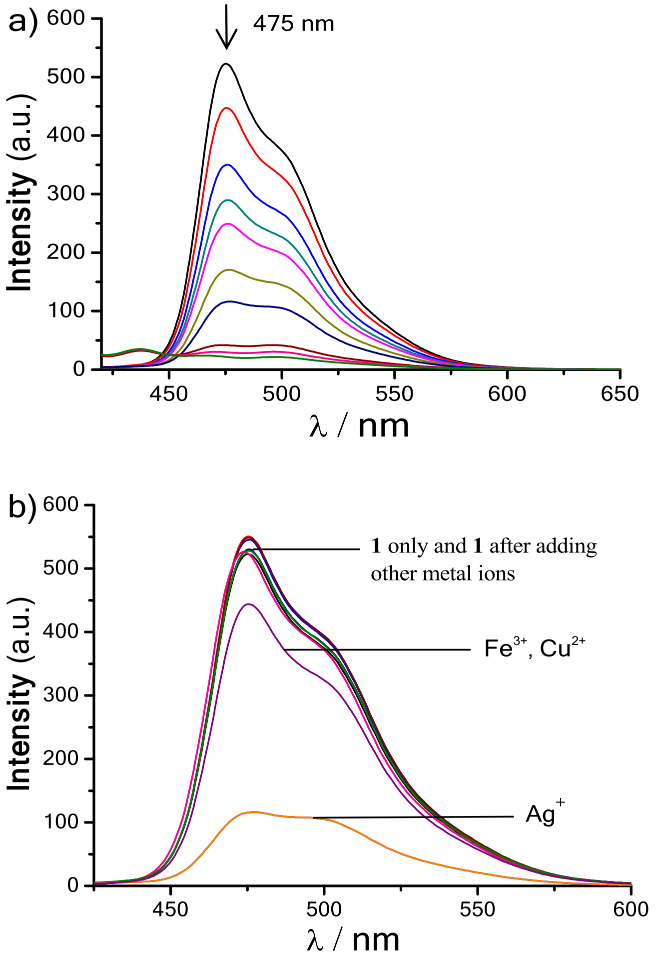

Fig. 3. Fluorescent spectra of **1** (5×10^{-6} M, $CHCl_3$) (a) upon the addition of Ag^+ (0 to 6 equiv.), and (b) upon adding 6 equiv. of various other metal ions (Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pd^{2+}, Hg^{2+}, Ca^{2+}, Mg^{2+}, and Na^+).

ions (Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pd^{2+}, Hg^{2+}, Ca^{2+}, Mg^{2+}, and Na^+) were recorded, and the emission intensity of **1** at 475 nm was further compared with that of after introducing Ag^+ ion. As exhibited in Fig. 4a, no pronounced signal interference was observed for the detection of Ag^+ by **1** in the presence of other metal ions, suggesting that **1** exhibited great potential for discriminating Ag^+ from other competing metal ions, especially Cu^{2+} and Hg^{2+}. In addition, the fluorescent reversibility of **1** was also tested by alternative addition of Ag^+ and EDTA (Fig. 4b), which showed fluorescence quenching with Ag^+ and comparable restoration in fluorescence with EDTA in 6 cycles, accompanied by almost no loss of fluorescent intensity at each cycle. Moreover, the time dependent plot was generated by correlating the fluorescence intensity of **1** to Ag^+ vs. time, from which it was found that the steady complex between **1** and Ag^+ could be formed in less than 40 s (Fig. S6). These results demonstrated that **1** could serve as a quickly responsive Ag^+ sensor.

Job's plot experiments were performed to determine the stoichiometry of **1** and Ag^+. The absorbance value of the mixed solution of **1** and $AgNO_3$ reached a maximum at 0.4 molar fraction of Ag^+, suggesting a 2:3 stoichiometry for **1** and Ag^+ (Fig. S7a). By using the Benesi-Hildebrand method based on titration data [43], the apparent association constant of **1** and Ag^+ was calculated to be 3.98×10^7 M^{-1} (Fig. S7b). In addition, theoretical calculations were performed, which gave an optimized sandwich-like coordination structure of **1**-Ag^+ (2:3) complex (Fig. S8). This further confirmed the complexation behaviour of **1** and Ag^+ revealed by the experimental investigations.

To get more insight of the recognition mechanism between **1** and Ag^+, ^1H NMR titration experiments were further performed. As displayed in Fig. 5, the thiophene protons signals (H_1, H_2 and H_3) of **1** gradually broadened and then completely disappeared during the addition of Ag^+. Meanwhile, as the concentration of Ag^+ increased, the proton signals of the aromatic rings slightly shifted upfield which might be attributed to conformation change of **1** after its complexion with Ag^+. We proposed that the structural rigidification and redistribution of electron density of sensor **1** could be induced upon coordination with Ag^+, which might facilitate the intramolecular photoinduced electron transfer (PET) process,[44] thus causing the fluorescent quench of **1**. It is worthy of mentioning that the heavy metal atom effect of Ag^+ could also be responsible for such impressive fluorescent quenching behavior. [45]

Conclusion

In summary, a unique HAT derivative (sensor **1**) bearing six thiophene substituents was prepared, and its recognition behaviour towards various metal ions was systematically investigated. It was found that **1** could exhibit a naked-eye detection capability

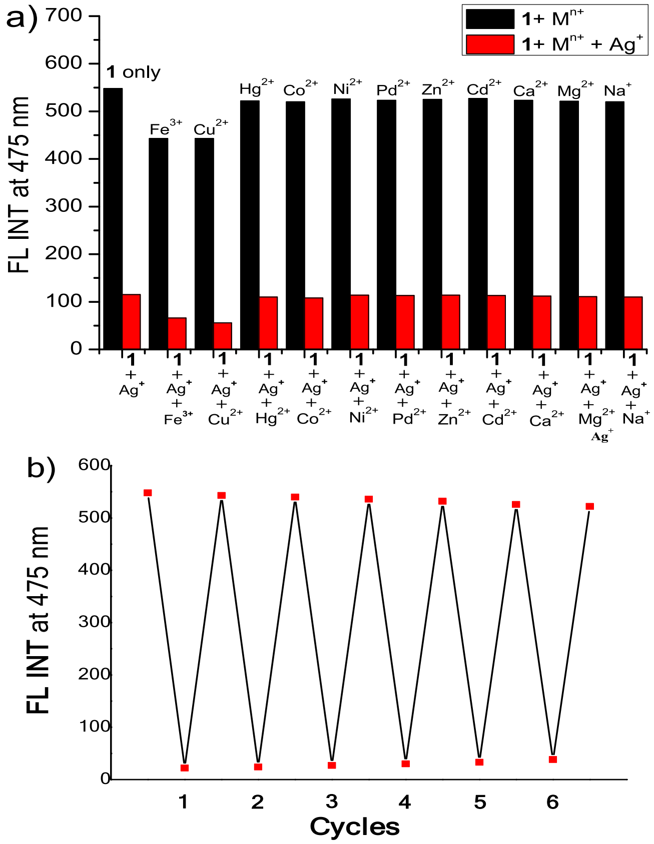

Fig. 4. (a) Fluorescence intensity variations of **1** (5×10^{-6} M, $CHCl_3$) without (black column) and with (red column) the addition of Ag^+ (4 equiv.) at the existence of various other metal ions (4 equiv.), and (b) plot of corresponding fluorescence intensity at λ = 475 nm of **1** (5×10^{-6} M, $CHCl_3$) after alternative addition of Ag^+ (6 equiv.) and EDTA (6 equiv.).

and distinctive "turn-off" fluorescence featuring with excellent selectivity, reversibility and fast-response towards Ag^+. In addition, sensor **1** was found insensitive to the presence of Hg^{2+}, which suggests its unique ability to distinguish Ag^+ without the interference of mercury ions. These features enabled such a thiophene-derived HAT sensor to be capable of serving as a new type of colorimetric and fluorescent chemosensor. More broadly, this work has well-demonstrated that the modification of HAT core by introducing heteroaromatic substitutions might be an efficient approach for the exploration of novel HAT-based chemosensors with unprecedented recognition behavior towards a wider range of guest species.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.152911.

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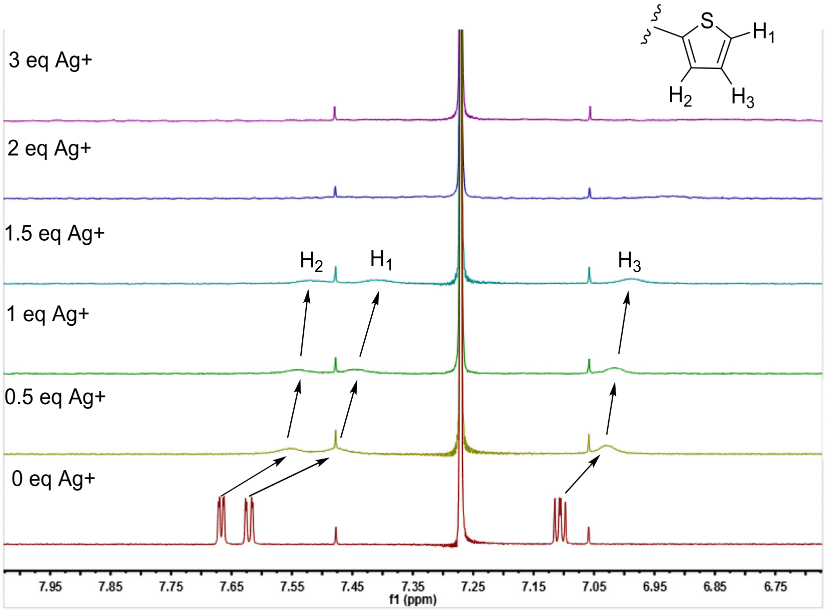

Fig. 5. ^1H NMR titration spectra (400 MHz, $CDCl_3$, 298 K) of sensor **1** (5×10^{-4} M) before and after the addition of 0 to 3 equiv. of $AgNO_3$.

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