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A new ratiometric Ag^+ fluorescent sensor based on aggregation-induced emission

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ABSTRACT

The novel tetraphenylethylene(TPE)-based sensor **1** bearing bis(2-pyridin-2-ylmethyl)amine (BPA) units linked with triazole moieties could be obtained by click reaction efficiently. The results show that **1** can demonstrate a Ag^+-specific emission shift and highly sensitive fluorescent enhancement with a 1:2 binding ratio based on the aggregation-induced emission mechanism. Compound **1** is shown to behave as a ratiometric sensor.

Introduction

The design and synthesis of highly sensitive and selective fluorescent chemosensors used for detection in the presence of heavy and transition metal (HTM) ions continues to grow at an unabated pace due to their important functions or produce toxic effects in environmental chemistry and biology.[1] Among the important precious metal ions, silver(I) (Ag^+) has received considerable attention due to its toxic effects and bioaccumulation. For instance, silver ions inactivate sulfhydryl enzymes and combine with amine, imidazole, and carboxyl groups of various metabolites. Thus, the development of sensitive methods for the determination of trace amounts of silver ion in various media is of considerable importance for environmental protection and human health.[2]

The traditional analytical methods, such as atomic absorption spectroscopy, inductively coupled plasma mass spectroscopy and electrochemical analysis, have been reported for the trace-quantity determination of Ag^+. But, most of those methods are expensive and time-consuming in practice. In comparison, fluorescence spectroscopy is widely used because of its high sensitivity and facile operation. More importantly, most fluorescent sensors are ready for in vivo and in vitro cellular imaging to make the fluorescence approach superior to other analytical methods. Therefore, much effort has been devoted to design various fluorescent sensors for the detection of Ag^+.[3–5] Nevertheless, most of the reported fluorescent chemosensor for Ag^+ are based on quenching mechanism.[4] Recently, the fluorescence 'turn on' chemosensors for Ag^+, based on photoinduced electron transfer (PET) mechanism, internal charge transfer (ICT) mechanism, metal chelation enhancement and excimer/exciplex, are attracting increasing attention.[2g,4–7] In addition, various strategies have been adopted for the design of ratiometric fluorescent chemosensors because of such a ratiometric fluorescent sensor would offer an advantage over the intensity-based probes such as less sensitivity to the errors associated with the sensor concentration, photobleaching, instrument's sensitivity, and environmental effects. However, ratiometric fluorescent chemosensors for the detection of Ag^+ have remained rare up to now, due to the scarcity of suitable fluorophore prototypes displaying silver chelation-induced emission/excitation. [4,6–11] Thus, it is highly desirable to propose a novel sensor with ratiometric module for silver ions. To our best knowledge, ratiometric fluorescent sensor for Ag^+, especially with fluorescent enhancement technique based on aggregation-induced emission (AIE) mechanism still remains rare.[4a,12–14] It is well known that the fluorogen in tetraphenylethylene (TPE) derivatives is nonemissive when dissolved but becomes highly emissive when aggregated due to its intramolecular rotations by the aggregate formation, thereby showing a novel effect of AIE.[15] Herein, inspired by the 'abnormal' AIE behavior of TPEs, we reported the synthesis via click reaction and the fluorescent properties of a new ratiometric fluorescence 'turn on' chemosensor **1** for Ag^+ by making use of AIE feature of tetraphenylethylene motif with bis(2-pyridin-2-ylmethyl)amine (BPA).

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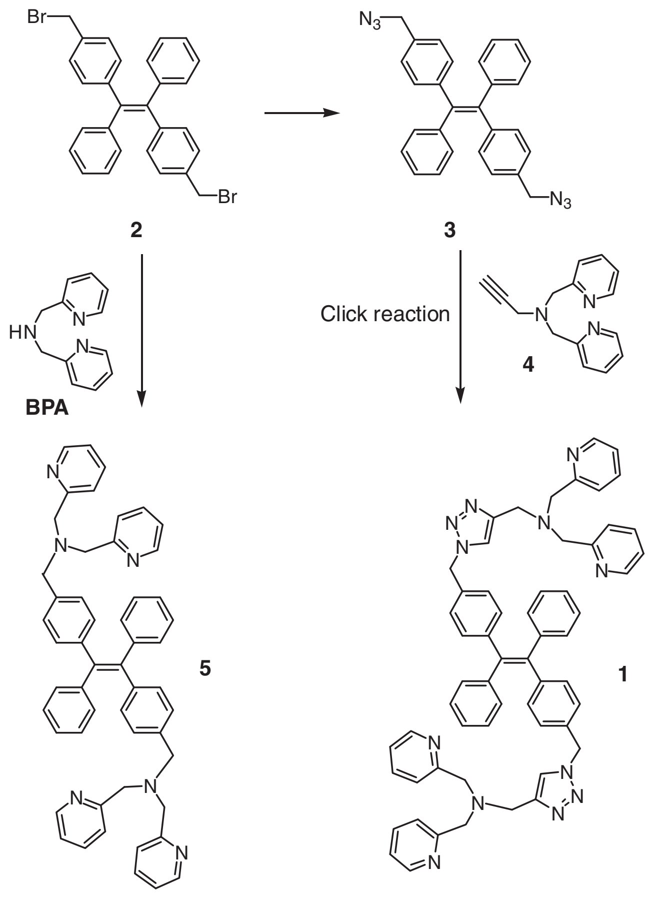
Results and discussion

The synthesis route of **1** is shown on Scheme 1. Initially, tetraphenylethylene derivate **2** was chosen as the starting material which was converted to dibromo **3** by reaction with NBS in the presence of catalytic amount of benzoyl peroxide (BPO) under reflux in CCl_4. The target compound **1** was obtained from the further reaction of dibromo **3** with NaN_3 followed by the click reaction with BPA derivate **4**. Similarly, another tetraphenylethylene derivate **5** with BPA unit was also prepared similarly (Scheme 1). The chemical structures of these new compounds were established by spectroscopic and elemental analysis data.

First, we attempted to determine the selective fluoroionophoric properties of **1** toward representative alkali (Li$^+$, Na$^+$, K$^+$), alkaline earth (Mg^{2+}, Ca^{2+}), and transition-metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Ag$^+$, Cd^{2+}). After systematically looking for selective signaling toward a specific target metal ion, we found that aqueous THF solutions are relatively well optimized sensing media. Therefore, all the fluorescence measurements were carried out in THF:H_2O (1:2,v/v) solvent ([**1**] = 1.0×10^{-5} mol/L, [**M**] = 4.0×10^{-5} mol/L), where the most pronounced selectivity toward Ag$^+$ ion was realized (Fig. 1). Figure 2 shows the fluorescence spectrum of compound **1** and those in the presence of different amounts of Ag$^+$ in THF/H_2O. Free compound **1** shows rather weak emission at 435 nm. However, after addition of Ag$^+$, the emission band at 485 nm emerged and its intensity increased gradually when the ratio of [Ag$^+$]$_{total}$/[**1**] is below or equal to 2:1. Moreover, the fluorescence intensity of **1** at 485 nm increases linearly with the concentration of Ag$^+$ as shown in the inset of Figure 2, where a nearly linear plot of I_{485nm} versus the concentration of Ag$^+$ in the range of 0.2–2.0 μM was displayed (with an enhancement factor of about fourfold, linear dependency coefficient $\gamma = 0.997$). The detection limit of this Ag$^+$ assay can reach 0.2 μM. When the ratio reached 2:1, higher [Ag$^+$]$_{total}$ did not lead to any further emission enhancement. The enhancement of emission intensity in Ag$^+$-binding titration saturated at the addition of two equivalent of Ag$^+$ suggested that **1** forms a 1:2 complex with Ag$^+$ in THF:H_2O (1:2, v/v). Furthermore, the Job plot measurement was carried out by varying the concentration of **1** and the Ag$^+$ ion (see Supplementary data Fig. S1). The maximum point appears at the mole fraction of 0.67, close to the typical ligand mole fraction (0.66), indicated the 2:1 stoichiometry between Ag$^+$ and **1**. The remarkable bathochromic shift made compound **1** a potential ratiometric sensor for Ag$^+$. Similar fluorescence enhancement was observed for **1** after the addition of Ag$^+$ salts with different counteranions (NO_2^-, F$^-$, BF_4^- and OAc$^-$) (Supplementary data Fig. S2). In contrast, the titration result indicates that compound **5** reveals no fluorescent detective behavior toward Ag$^+$ and other metal ions (see Supplementary data Fig. S3).



Scheme 1. Synthesis of **1**.

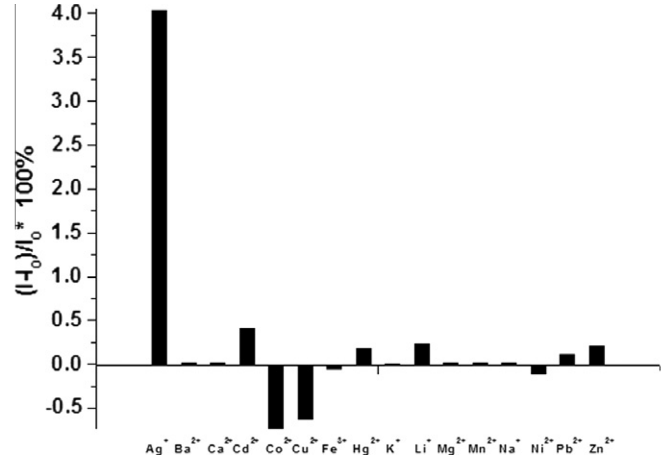


Figure 1. Variation of the fluorescence intensity at 485 nm (λ_{ex} = 320 nm) of compound 1 (1.0×10^{-5} M) in THF/H_2O (1:2, v/v) in the presence of 4.0 equiv of the respective metal ions.

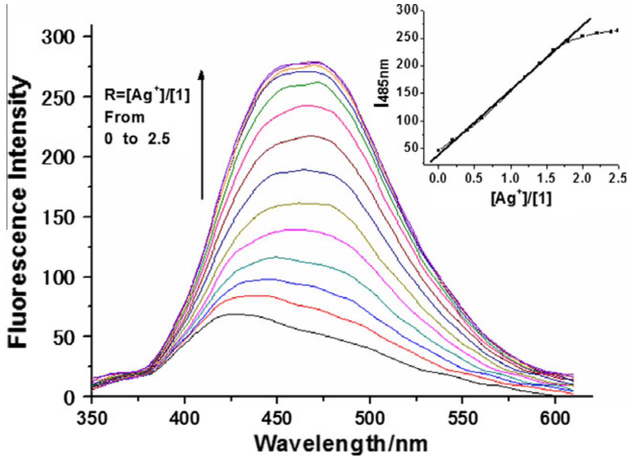


Figure 2. Fluorescence titration spectra of compound **1** (1.0×10^{-5} M) in the presence of different concentrations of Ag$^+$ in THF/H_2O (1:2, v/v), [Ag$^+$]/[**1**] = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.5. Inset the plot of the fluorescence intensity at 485 nm (λ_{ex} = 320 nm) vs the concentration of Ag$^+$.

Such fluorescence enhancement observed for **1** in the presence of Ag$^+$ is attributed to the coordination of BPA moieties of **1** with Ag$^+$ ions leading to the formation of coordination complexes which may further aggregate due to the low solubility; as a result, the fluorescence due to the tetraphenylethylene unit of **1** in-