Letter

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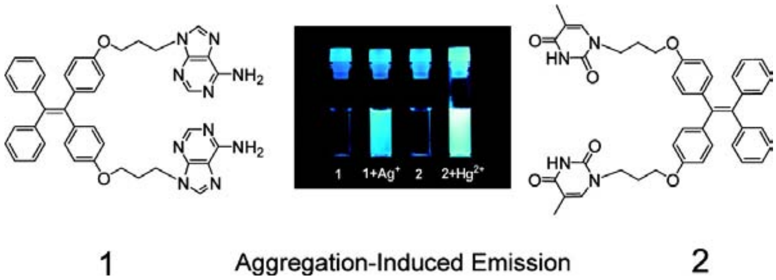

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Fluorescence "Turn On" Chemosensors for Ag^+ and Hg^{2+} Based on Tetraphenylethylene Motif Featuring Adenine and Thymine Moieties

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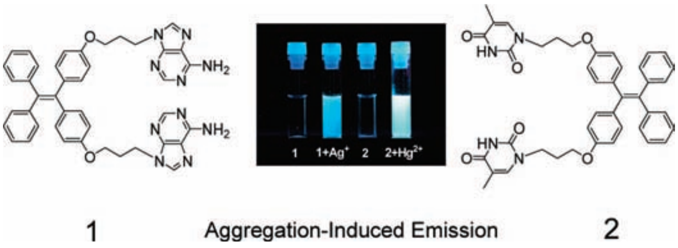
ABSTRACT



Two new tetraphenylethylene (TPE) compounds 1 and 2 bearing adenine and thymine moieties, respectively, were found to be fluorescence "turn on" chemosensors for Ag^+ and Hg^{2+} by making use of the AIE feature of TPE motif and the specific binding of adenine/thymine with Ag^+/Hg^{2+}.

Mercury ions act as severe environmental pollutants, and several diseases are known to be associated with mercury contamination.[1] Silver ions also have adverse biological effects, and there are are many reports on silver bioaccumulation and toxicity.[2] For instance, silver ions inactivate sulfhydryl enzymes and combine with amine, imidazole, and carboxyl groups of various metabolites. Thus, development of sensitive and selective chemosensors for Ag^+ and Hg^{2+} in various media is of considerable importance for environmental protection and human health.

Traditional quantitative approaches of Ag^+ and Hg^{2+} are expensive and time-consuming in practice. For instance, atomic absorption spectroscopy, inductively coupled plasma-mass spectroscopy, and potentiometric methods based on ion-selective electrodes have been described for the trace-quantity (down to ppb range) determination of Ag^+ and Hg^{2+}.[3,4a] In comparison, sensitive and selective optical sensors for Ag^+ and Hg^{2+} with simple instrumental implementation and easy operation have received a lot of attention. But, both Ag^+ and Hg^{2+} are heavy transition-metal ions (HTM) which are known as fluorescence quenchers. Most of the reported fluorescent chemosensors for Ag^+ and Hg^{2+} are based on a

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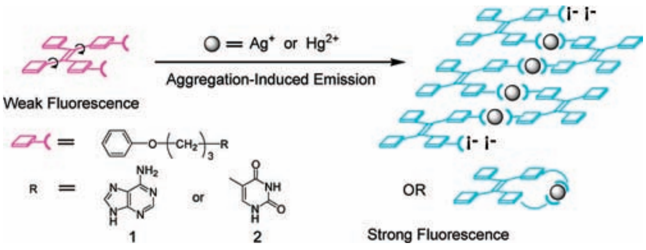
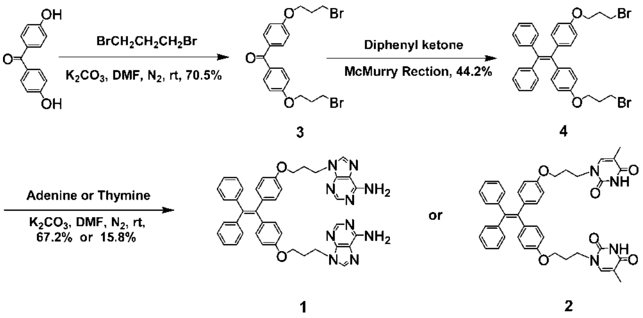
fluorescence quenching mechanism.[4] By now, only a few fluorescence "turn on" chemosensors for Ag$^+$ and Hg^{2+} have been described.[4a,5] Herein, we report fluorescence "turn on" chemosensors for Ag$^+$ and Hg^{2+} by making use of the unique aggregation-induced emission (AIE) feature of tetraphenylethylene motif and the selective binding abilities of adenine (with Ag$^+$) and thymine (with Hg^{2+}).[6]

The design rationale for these Ag$^+$ and Hg^{2+} chemosensors is schematically illustrated in Scheme 1 and explained as follows: (1) tetraphenylethylene (TPE) derivatives show weak fluorescence in solution, but they become strong emission after aggregation. In fact, new detection methods based on this AIE feature of TPE for protein and DNA have been described recently;[7] for example, a quaternized tetraphenylethylene salt has been successfully used as a fluorescent probe for G-quadruplex formation and real-time monitoring of DNA folding;[7d] (2) it is known that adenine and thymine can selectively bind with Ag$^+$ and Hg^{2+}, respectively.[6] For TPE compounds **1** and **2** (Scheme 2), aggregation would occur in the presence of Ag$^+$ and Hg^{2+}, respectively, leading to fluorescence enhancement. Therefore, it is anticipated that selective fluorescence "turn on" chemosensors for Ag$^+$ and Hg^{2+} can be established with TPE compounds **1** and **2**, respectively. The intramolecular coordination may also occur within **1** or **2** (see Scheme 1), and accordingly, the intramolecular rotations would be also restricted, leading to fluorescence enhancement.

Scheme 1. Design Rationale for the Ag$^+$ and Hg^{2+} Chemosensors



Scheme 2. Synthetic Approach for Compounds **1** and **2**



In this paper, we will describe the synthesis and spectral variation of **1** and **2** after addition of Ag$^+$ and Hg^{2+}. The results show that the fluorescence intensities of **1** and **2** are remarkably enhanced after introducing Ag$^+$ and Hg^{2+}; thus, compounds **1** and **2** can function as fluorescence "turn on" chemosensors for Ag$^+$ and Hg^{2+}.

The synthesis of compounds **1** and **2** started from 4,4′-dihydroxybenzophenone which was converted to dibromo **3** by reaction with 1,3-dibromopropane. Compound **4** was yielded through a McMurry reaction between compound **3** and diphenyl ketone. Further reactions of dibromotetraphenylethylene **4** with adenine and thymine in the presence of K_2CO_3 led to compounds **1** and **2**, respectively, in acceptable yields. The chemical structures of these new compounds were established by spectroscopic and elemental analysis data.

Figure 1 shows the fluorescence spectrum of compound **1** and those in the presence of different amounts of $AgClO_4$ in H_2O/THF (5:1, v/v). Compound **1** shows rather weak emission at this concentration (see Figure S1-1 of the Supporting Information). However, after addition of $AgClO_4$, the emission band at 470 nm emerged and its intensity increased gradually as displayed in Figure 1. Actually, the fluorescence difference for the solution of **1** before and after addition of Ag$^+$ can be distinguished by the naked eye as displayed in the inset of Figure 1. Moreover, the fluorescence intensity of **1** at 470 nm increases linearly with the

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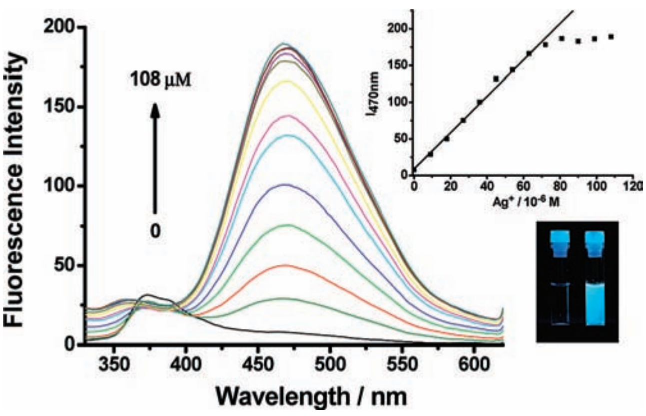

Figure 1. Fluorescence spectra of compound **1** (5.60×10^{-5} M) in H_2O/THF (5:1, v/v) in the presence of increasing amounts of $AgClO_4$ (from 0 to 108 μM); $\lambda_{ex.} = 319$ nm. Inset: (1) the plot of the fluorescence intensity (I_{470nm}) vs the concentration of $AgClO_4$; (2) the photos of the solution of **1** before and after additon of 1.0 equiv of $AgClO_4$ under UV light illumination (365 nm).

concentration of $AgClO_4$ as shown in the inset of Figure 1, where a nearly linear plot of I_{470nm} vs the concentration of Ag^+ in the range of 0−75 μM was displayed ($I_{470nm} = 2.48 [Ag^+] + 8.86$, $r = 0.996$, $n = 9$). The detection limit of this Ag^+ assay can reach 0.34 μM ($K = 2$). Similar fluorescence enhancement was observed for **1** after the addition of Ag^+ salts with different counteranions (NO_3^-, NO_2^-, PF_6^-, $CF_3SO_3^-$, AsF_6^-, and BF_4^-) (see Figure S5 of the Supporting Information).

Such fluorescence enhancement observed for **1** in the presence of Ag^+ is attributed to the coordination of adenine moieties of **1** with Ag^+ ions leading to formation of coordination complexes which may further aggregate due to the low solubility (see Scheme 1); as a result, the fluorescence due to the tetraphenylethylene unit of **1** increases. The following experimental facts support this assumption: (1) Figure 2 shows the variation of the absorption spectrum of **1** after addition of Ag^+. The absorption band around 256 nm became weak and the absorption intensity of that around 317 nm increased gradually in the presence of Ag^+, leading to an isobestic point at 242 and 274 nm. Furthermore, an absorption tail above 400 nm was detected. These absorption spectral changes are in agreement with the aggregation of **1** after addition of Ag^+. (2) Variation of ^1H NMR spectra of **1** in the presence of Ag^+ also indicates the aggregation of **1**. As shown in Figure S3 (Supporting Information), the signals around 6.55−8.25 ppm due to the aromatic protons of **1** were upfield shifted and became weak after the gradual addition of Ag^+. These ^1H NMR spectral changes are likely due to the "shielding effect" of neighboring molecules of **1** in the aggregation state. (3) TEM analysis with the solution of **1** containing 1.0 equiv of Ag^+ indicates the formation of aggregates with fiber-like structure (see Figure S8 of the Supporting Information). But, obvious fluorescence enhancement was not oberserved upon addition of Ag^+ when the concentration of **1** was reduced to 1.0×10^{-5} M. This result implies that the intramolecular coordination of **1** with Ag^+ may not contribute to the fluorescence enhancement of **1** after addition of Ag^+.

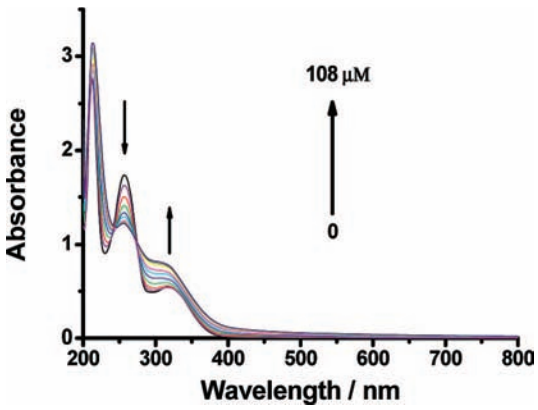

Figure 2. Absorption spectra of compound **1** (5.60×10^{-5} M) in H_2O/THF (5:1, v/v) in the presence of increasing amounts of $AgClO_4$ (from 0 to 108 μM).

The fluorescence spectrum of **1** was also measured in the presence of other metal ions including Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} Zn^{2+}, Cs^+, and K^+ under identical conditions. As shown in Figure 3, variation of the fluorescence intensity of **1** at 470 nm was rather small (compared to that in the presence of Ag^+) after addition of 1.0 equiv of the respective metal ions, except for that in the presence of Hg^{2+} which caused a little interference. Cross-contamination tests were also performed (see Figure S1-4 of the Supporting Information). These results clearly indicate that compound **1** shows good selectivity toward Ag^+, and other competitive metal ions such as Pb^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+} induce a rather low interference effect on this fluorescence assay for Ag^+.

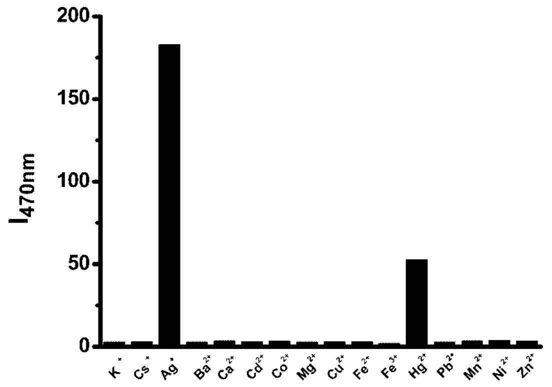

Figure 3. Variation of the fluorescence intensity at 470 nm (I_{470nm}) of compound **1** (5.60×10^{-5} M) in H_2O/THF (5:1, v/v) in the presence of 1.0 equiv of the respective metal ions.

Figure 4 shows the fluorescence spectrum of compound **2** and those in the presence of different amounts of $Hg(ClO_4)_2$ in H_2O/CH_3CN (2:1, v/v). Compound **2** shows rather weak

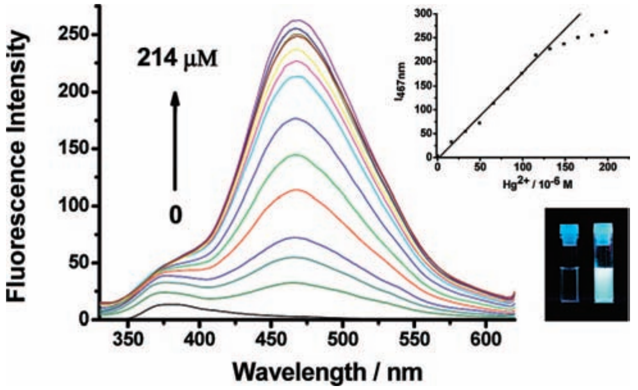

Figure 4. Fluorescence spectra of compound **2** (1.34×10^{-4} M in H_2O/CH_3CN (2:1, v/v) in the presence of increasing amounts of $Hg(ClO_4)_2$ (from 0 to 214 μM); $\lambda_{ex} = 319$ nm. Inset: (1) the plot of the fluorescence intensity (I_{467nm}) vs the concentration of $Hg(ClO_4)_2$; (2) the photos of the solution of **2** before and after additon of 1.0 equiv of $Hg(ClO_4)_2$ under UV light illumination (365 nm).

emission at this concentration. But, after addition of $Hg(ClO_4)_2$, the emission band around 467 nm emerged and its intensity increased gradually. Moreover, the fluorescence intensity at 467 nm increased linearly with the concentration of Hg^{2+} in the range of 0−125 μM as displayed ($I_{467nm} = 1.81\,[Hg^{2+}] - 2.99$, $r = 0.995$, $n = 8$) in the inset of Figure 4. Thus, Hg^{2+} with concentration as low as 0.37 μM ($K = 2$) can be detected with compound **2**. Similar fluorescence enhancement was observed for **2** after addition of Hg^{2+} salts with different counteranions (Cl^-, Br^-, CNS^- and CH_3COO^-) (see Figure S6 of the Supporting Information).

Similarly, such fluorescence enhancement is due to the aggregation of **2** after addition of Hg^{2+}. It is believed that such aggregation was induced by coordination of thymine units in **2** with Hg^{2+} as schematically shown in Scheme 1. This assumption was supported by the corresponding absorption and ^1H NMR spectral studies as well as TEM analysis: (1) Figure S7 shows the variation of the absorption spectrum of **2** after addition of Hg^{2+}. The absorption band around 256 nm became weak and the absorption intensity in the range of 312−600 nm increased gradually in presence of Hg^{2+}. These absorption spectral changes are in agreement with the aggregation of **2** after addition of Hg^{2+}. (2) Variation of ^1H NMR spectra of **2** in the presence of Hg^{2+} also indicates the aggregation of **2**. As shown in Figure S4, the signals around 7.00−7.80 ppm due to aromatic protons of **2** were upfield shifted and became weak after the gradual addition of Hg^{2+}. These ^1H NMR spectral changes are likely due to the "shielding effect" of neighboring molecules of **2** in the aggregation state. (3) TEM analysis with the solution of **2** containing 1.0 equiv of Hg^{2+} indicates the formation of aggregates with the size up to 200 nm (see Figure S9 of the Supporting Information).

The fluorescence spectrum of **2** was recorded in the presence of other metal ions including Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Ag^+, Cs^+ and K^+ under identical conditions. As shown in Figure 5, variation of the fluorescence intensity at 467 nm (I_{467nm}) was rather small (compared to that in the presence of Hg^{2+}) after addition of 1.0 equiv of the respective metal ions. Cross-contamination tests were also performed (see Figure S2-4 of Supporting Information).The results clearly indicate that compound **2** shows rather good selectivity toward Hg^{2+}. This is understandable by considering the specific binding of thymine with Hg^{2+}.

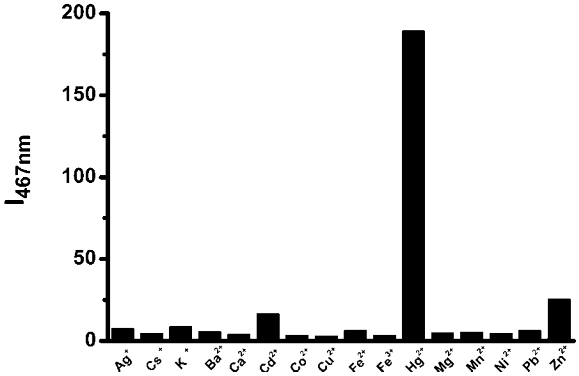

Figure 5. Fluorescence intensity (I_{467nm}) of compound **2** (1.34×10^{-4} M in H_2O/CH_3CN, 2:1, v/v) in the presence of 1.0 equiv of the respective metal ions.

In summary, compounds **1** and **2** were designed and investigated with a view to developing new fluorescent sensors for Ag^+ and Hg^{2+} by making use of the specific binding of adenine with Ag^+ and thymine with Hg^{2+} as well as the AIE feature of TPE motif. Absorption and ^1H NMR spectral studies indicated the aggregation of **1** and **2** in the presence of Ag^+ and Hg^{2+}, respectively; the aggregation was also directly confirmed by TEM analyses. Fluorescent spectral results clearly demonstrate that compound **1** and **2** can be used as fluorescent sensor for Ag^+ and Hg^{2+} with good selectivity and sensitivity. Further studies include the design of new analogues of **1** and **2** with good solubility in water which will enable the practical application of these types of Ag^+ and Hg^{2+} sensors to be implemented.

Acknowledgment. The present research was financially supported by NSFC, Chinese Academy of Sciences, and State Key Basic Research Program.

Supporting Information Available: Synthesis and characterization data; fluorescence and absorption spectra of compound **1** and **2** under different conditions; ^1H NMR spectra and TEM images of **1** and **2** in the presence of Ag^+ and Hg^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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