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A novel Hg²⁺ fluorescence sensor TPE-TSC based on aggregation-induced emission

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Abstract: A fluorescent sensor TPE-TSC with aggregation induced emission (AIE) characteristic is synthesized for detecting Hg^{2+} by attaching thiosemicarbazide (TSC) unit into tetraphenylethylene (TPE) group. TPE-TSC exhibits intense green emission in DMSO/H₂O (V:V=1:9) solution with the formation of the aggregation. TPE-TSC shows outstanding fluorescence quenching toward Hg^{2+} over other metal ions due to the formation of complex TPE-TSC/Hg²⁺ with a 2:1 binding ratio. The detection limit of TPE-TSC for Hg^{2+} is 1×10^{-5} mol·L⁻¹.

Keywords: Hg²⁺; Tetraphenylethylene; Mannich reaction; Aggregation induced emission (AIE).

Introduction

Fluorescence-based sensors have recently attracted considerable attention due to their ability in detecting heavy metal ions¹. Among these heavy metal ions, mercury is regarded as one of the most toxic ones, and even at the ppm level it has a detrimental effect on the cardiovascular system, kidneys, the immune system as well as the central nervous system in humans ^{2, 3}. Compared with most traditional analytical methods, such as inductively coupled plasma mass spectrometry⁴, atomic absorption spectroscopy⁵ and electrochemical analysis⁶, fluorescence sensors for mercury detection can have high sensitivity and facile operation⁷. For these reasons, many fluorescence sensors for detecting mercury in the aqueous medium have been designed, which are based on the photo induced electron transfer⁸, energy transfer⁹, and internal charge transfer¹⁰ mechanisms. However, many of the known fluorescence sensors show low sensitivity to mercury in high concentration or aggregation due to the aggregation-caused quenching (ACQ)¹¹. In addition, fluorescent sensors based on the aggregation induced emission (AIE) are rarely designed and applied for mercury detection ¹².

Herein, we report the design and synthesis of a new fluorescent sensor TPE-TSC for the highly selective detection of Hg^{2+} , where the AIE-active tetraphenylethylene (TPE) group is modified with the thiosemicarbazide (TSC) unit based on the Mannich reaction. TPE-TSC can aggregate and emit intense green radiation in the DMSO/H₂O (V:V=1:9) solution. In the presence of Hg^{2+} , the fluorescence emission intensity of TPE-TSC decreases gradually and is eventually quenches by increasing the ion concentration. Meanwhile, TPE-TSC responds highly selectively and sensitively toward Hg^{2+} in aqueous medium. Thus, we provide an alternative approach for the design and construction of a new type of ion-fluorescence probe.

Results and discussion

The synthesis of TPE-TSC is outlined in Scheme 1. 4-(1, 2, 2-triphenylvinyl) benzaldehyde (compound 1 is first prepared from the reaction between bromo-triphenylethylene and 4-formylphenylboronic acid in the presence of a catalytic amount of $Pd(PPh_3)_4$ under the reflux in toluene. TPE-TSC is then efficiently synthesized from compound 1 and thiosemicarbazide (TSC) through the Mannich reaction. The chemical structures of these as-synthesized compounds are confirmed by ¹H-NMR, ¹³C-NMR and HRMS spectroscopic methods.



Figure 1 TPE-TSC (1×10^{-4} mol·L⁻¹ in DMSO) with different fractions of water.

TPE-TSC is soluble in DMSO but not in water. The AIE characteristics of TPE-TSC was investigated in the DMSO-H₂O mixture with varying water fraction. As shown in Figure 1, when the water fraction in the DMSO-H₂O mixture increases from 10% to 80%, TPE-TSC shows almost no fluorescence emission. However, TPE-TSC shows strong fluorescence emission when the water fraction is above 90%. Based on the above AIE behavior of TPE-TSC, further fluorescence experiments were carried out in the DMSO/H₂O (V:V=1:9) mixture as the solvent.



Figure 2 Fluorescence spectra of TPE-TSC $(1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1})$ in DMSO/H₂O (V:V=1:9) in the presence of Hg²⁺ (from 0 to 0.7 equiv). The plot of the fluorescence intensity at 492 nm ($\lambda_{ex} = 364$ nm) vs the concentration of Hg²⁺.

Figure 2 shows the change in the fluorescence spectrum of TPE-TSC upon titration with the Hg^{2+} ion. TPE-TSC shows strong emission at 492 nm in the DMSO/H₂O (V:V=1:9) mixture. However, intensity of the fluorescence emission of TPE-TSC gradually decreases with the increasing concentration of Hg^{2+} . In fact, the fluorescence emission intensity of the mixture decreases almost linearly with the relavite coefficient (R²) of ~0.973 when the concentration of Hg^{2+} change from 0 to 2.5×10^{-5} mol·L⁻¹. When the ion concentration is beyond 3×10^{-5} mol·L⁻¹, the fluorescence quenching phenonema of the mixed system was observed because of hardly detected fluorescence emission. This should be attributed to the formation of complex TPE-TSC/Hg²⁺ with fluorescence quenching in mixtures solvent. In addition ,TPE-TSC responses toward Hg²⁺ at as low as 1×10^{-5} mol·L⁻¹.



Figure 3 The fluorescence responses of TPE-TSC $(1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1})$ upon addition of various metal ions $(1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}, 10 \text{ equiv})$ in the absence and presence of Hg²⁺ (2×10⁻⁴ mol·L⁻¹, 2 equiv) in DMSO/H₂O (V:V=1:9). (Black bars: TPE-TSC with other metals, red bars: TPE-TSC with other metals and Hg²⁺ ($\lambda_{ex} = 364 \text{ nm}$).



Figure 4 Fluorescent intensity of 1 in DMSO/H₂O (1:9, v/v) in the presence of 10.0 equiv of different anions.

TPE-TSC shows selective fluorescence properties toward Hg^{2+} over other metal ions. As shown in Figure 3. For better comparison, fourteen metal ions at the same concentration were added into the TPE-TSC and DMSO/H₂O (V:V=1:9) mixed media, and the fluorescence intensity of these TPE-TSC media show different features. When other metal ions such as Na⁺, Cr³⁺, Ni²⁺, Pb²⁺, Zn²⁺, Ba²⁺, Co²⁺, Fe³⁺, Cd²⁺, Ca²⁺, Fe²⁺, Mg^{2+} , Mn^{2+} and Hg^{2+} were added to the aqueous solution of TPE-TSC, the fluorescence of the media was not quenched, whereas Na⁺, Cr³⁺ and Fe³⁺ can enhance the fluorescence intensity. Pb^{2+} and Fe^{2+} ions slightly weakens the fluorescence of TPE-TSC. On the other hand, TPE-TSC significantly quenches the fluorescence response to Hg^{2+} . Competitative experiments was performed by adding Hg^{2+} into the solution of TPE-TSC in DMSO/H₂O (V:V=1:9) in the presence of other metal ions. The result is shown in Figure. 3. As expected, other metal ions have almost no effect on the fluorescence intensity in the presence of Hg^{2+} suggesting the exclusive selectivity of TPE-TSC toward Hg²⁺. Meanwhile, some other anions were investigated and found to have nearly no influence on the fluorescence intensity as shown in Figure 4. Thus, our experimental results show that the as-prepared TPE-TSC can be used as highly selective and sensitive fluorescence sensor for the Hg²⁺ ion in the DMSO/H₂O (V:V=1:9) media.



Scheme 2 Proposed binding mode of TPE-TSC with Hg²⁺



Figure 5 Partial ¹H-NMR spectra (400 MHz) of TPE-TSC ($1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) in DMSO-d₆/D₂O (1:9, v/v) in the presence of increasing amounts of Ag⁺: 0; 0.1; 0.2; 0.3; 0.4; 0.5 equiv [from (1) to (6)].



Figure 6 HR-MS spectrum of the complex TPE-TSC/Hg²⁺

For determining the exact binding sites between TPE-TSC and Hg^{2+} , ¹H-NMR titration of TPE-TSC with Hg^{2+} was carried out in the DMSO-d₆/D₂O (V:V=1:9) media. As shown in Figure 5, When adding Hg^{2+} (from 0 to 0.5 equiv) to the TPE-TSC solution, the chemical shifts of thiosemicarbazide protons H_a and H_b and the aldehyde proton H_c exhibit an upfield shift. Moreover, The signals of the H_b and H_c protons are gradually upfield-shifted from 8.14 ppm to 7.91 ppm and 11.37ppm to 11.23 ppm when increasing the amount of Hg^{2+} from 0 to 0.5 equiv, respectively. The signal of the H_a proton becomes weaker after the gradual addition of Hg^{2+} . The chemical shifts of all the protons show that their chemical environments are changed upon coordination of TPE-TSC with Hg^{2+} . The change in the fluoresence signals illustrate that the N atom connected to the aldehyde unit and the atom on the

thiosemicarbazide unit are bound to Hg^{2+} . Based on these results, the coordination structure of TPE-TSC with Hg^{2+} is proposed as shown in Scheme 2. Furthermore, the structure of this complex was further studied by high resolution mass spectrometry. As shown in Figure 6, the complex TPE-TSC/Hg²⁺ (m/z=1068) gives a molecular ion peak[M-1] at 1067, which confirms the coordination type in Scheme 2.

Conclusions

In conclusion, a novel Hg^{2+} fluorescent sensor TPE-TSC was synthesized by attaching a thiosemicarbazide unit into the tetraphenylethylene group. TPE-TSC shows the aggregation induced emission characteristic in the DMSO-H₂O media. TPE-TSC also shows outstanding fluorescence quenching property toward Hg^{2+} over other metal ions due to the formation of the TPE-TSC/Hg²⁺ complex with a 2:1 binding ratio. The detection limit of TPE-TSC for Hg^{2+} was found to be below 1×10^{-5} mol·L⁻¹. The fluorescence properties of TPE-TSC indicate that it has the potential for detecting Hg^{2+} in extremely low concentration in natural drainage system.

Experimental

All chemical reagents was purchased as analytic grade. TPE-TSC and Compound **1** were synthesized as shown below. The stock solutions of metal ions were prepared $(1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}, \text{ H}_2\text{O})$ from NaCl, NaNO₃, Na₂SO₄, AcONa, K₂CO₃, CrCl₃·6H₂O, NiCl₂, (CH₃COO)₂Pb·3H₂O, ZnSO₄·7H₂O, BaCl₂, Co(NO₃)₂·6H₂O, FeCl₃·6H₂O, CdCl₂·5H₂O, Hg(NO₃)₂, CaCO₃, FeSO₄·7H₂O, MgSO₄, and MnCl₂·4H₂O with doubly distilled water. ¹H-NMR and ¹³C-NMR spectra were measured on a Bruker spectrometer (operating at 400 and 100 MHz, respectively) at 298 K using DMSO-d₆ as the solvent. UV-vis spectra were recorded using Shimadzu UV3600. TLC analysis was carried on silica gel plates, and column chromatography was performed over silica gel (mesh 200–300).

Synthesis of 2-(4-(1,2,2-triphenylvinyl)benzylidene)hydrazine-1-carbothioamide (TPE-TSC)

Compound 2 (1.0 g, 2.77 mol) was dissolved in ethanol (20 ml) and thiosemicarbazide (0.28 g, 3.05 mol) in methanol (15 mL) was added, followed by dropwise addition of glacial acetic acid (0.4 mL). The mixture was stirred at 80 °C for 12 h. the solution was cooled and a precipitate was formed. The solid was separated by filtration, washed with ice-cooled water, and dried under reduced pressure to yield 1 (1.1 g, 92%). ¹H-NMR (DMSO-d₆, 400 MHz, ppm): δ 6.97-7.02 (m, 8H), 7.11-7.18 (m, 9H), 7.11-7.18 (m, 17H), 7.55-7.57 (d, J=8.4Hz, 2H), 7.92-7.95 (d, J=12.8Hz, 2H), 8.14 (s, 1H), 11.37 (s, 1H).

¹³C-NMR ((DMSO-d₆, 100 MHz, ppm): δ 127.0, 127.1, 127.2, 128.2, 128.3, 128.4, 131.0, 131.1, 131.2, 131.5, 132.8, 140.5, 141.7, 142.3, 143.3, 143.4, 143.5, 145.2. HR-MS: [M-H]⁻. Cal.:433.57, found: 432.2072.

Synthesis of 4-(1, 2, 2-triphenylvinyl) benzaldehyde (compound 1)

4-formylphenylboronic acid (1.35 g, 9 mmol), bromotriphenylethylene (2.01 g, 6 mmol), TBAB (0.19 g, 0.6 mmol) and 1.2 M potassium carbonate aqueous solution (40 mL) were added to a solution of toluene (40 mL). <AQ Authors to check this

previous senstence at proofing as the language was not clear </AQ> The mixture was stirred at room temperature for 30 min under N₂ gas followed by the addition of Pd(PPh₃)₄ (60 mg, 5.3×10^{-3} mmol). After that the mixture was heated to 90 °C for 24 h. The solution was poured into water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by column chromatography with CH₂Cl₂/n-hexane (v/v = 1:3) as an eluent to afford yellow powder with a yield of 90.1%. ¹H-NMR ((DMSO-d₆, 400 MHz, ppm): δ 6.98-7.02 (m, 6H), 7.14-7.17 (m, 9H), 7.18-7.20 (d, J=7.9Hz, 2H), 7.67-7.69 (d, J=8.2Hz, 2H), 9.89 (s, 1H).

¹³C-NMR ((DMSO-d₆, 100 MHz, ppm): δ 127.3, 127.5, 128.3, 128.4, 128.5, 129.5, 131.0, 131.1, 131.9, 134.6, 140.1, 142.8, 142.9, 134.0, 143.1, 150.1, 192.87. ESI-MS: [M+H]⁺. Cal.: 361.15, found: 361.3.

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