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A NOVEL TETRAPHENYLETHENE-BASED FLUORESCENCE PROBE BASED ON THE Hg²⁺-PROMOTED DEPROTECTION OF THIOACETAL

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Abstract – A novel tetraphenylethene-based fluorescence probe compound **1** bearing 1,2-ethanedithiol units linked with tetraphenylethene moiety is synthesized efficiently. Compound **1** exhibit sensitively and selectively to Hg²⁺ over other metal ions in DMF/H₂O solution based on aggregation induced emission (AIE) mechanism. The results show that compound **1** demonstrates an Hg²⁺-specific bathochromic shift and fluorescent enhancement with a 1:2 reacting stoichiometry. The detection limit of compound **1** for Hg²⁺ is 2×10^{-6} mol·L⁻¹.

INTRODUCTION

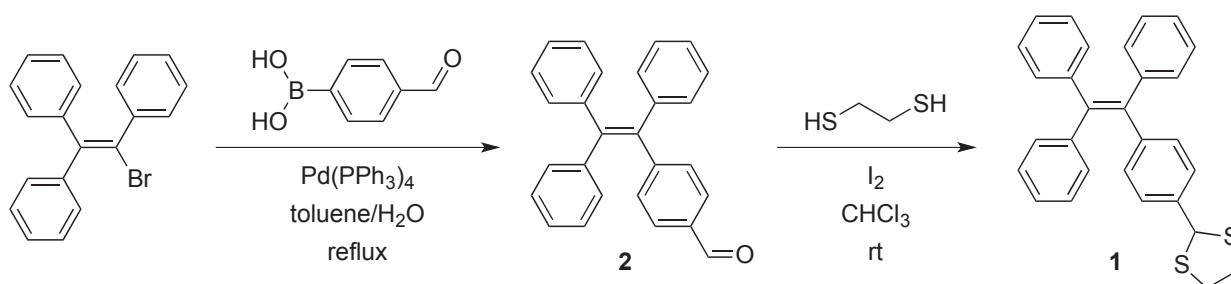
The development of the fluorescent probe with highly selective and sensitive recognition of metal ions has attracted considerable attention in recent years, due to their significance in the fields of biology, environment and chemistry, etc.¹ Among heavy metal ions, mercury is regarded as one of the most toxic metal ions, which has a negative effect on cardiovascular, kidneys, immune system as well as central nervous system in humans even at mercury concentration of ppm levels.² For this reason, the design and synthesis of highly selective and sensitive fluorescence probes for mercury are important to human health. Compared with the most traditional analytical methods, such as inductively coupled plasma mass spectrometry,³ atomic absorption spectroscopy⁴ and electrochemical analysis,⁵ fluorescence probes for mercury demonstrate high sensitivity and facile operation. Recently, many fluorescence probes for mercury in aqueous medium based on the coordination⁶ or chemical reaction between them⁷ have been exploited. In these methods, reaction-based fluorescent probes has attracted considerable interest, because their emission intensities could be measured at two different wavelengths, avoiding environmental effects and increasing the dynamic range of fluorescence measurement. Reaction-based fluorescent probes have been designed, including Hg²⁺-promoted desulfurization,⁸ Hg²⁺-promoted cycloaddition of thiourea substrates,⁹ mercuration¹⁰ and Hg²⁺-promoted hydrolysis,¹¹ for the detection of Hg²⁺ in aqueous solution.

As we all know, the thioacetals are severed by Hg^{2+} ,¹² which induces the formation of low polarity compound, making remarkable aggregation induced emission (AIE).¹³ Various kinds of fluorescence probe for mercury have been designed based on aggregation induced emission (AIE) mechanism. However, many of these fluorescence probes show significant challenges for practical application.

In this paper, a novel tetraphenylethene-based compound **1** is designed and synthesized for mercury based on the Hg^{2+} -promoted deprotection of thioacetal.¹⁴ The thioacetals are severed by Hg^{2+} , which induces the formation of low polar aggregates of compound **2** with a strong fluorescence signal. This induces bathochromic shift and fluorescent enhancement of compound **2**. As a result, compound **1** shows highly selective and sensitive response toward mercury in aqueous medium. Hence, we report the synthesis, characterization, and fluorescence properties of compound **1** in detail.

RESULTS AND DISCUSSION

The synthetic pathway of compound **1** is outlined in Scheme 1. Initially, 4-(1,2,2-triphenylvinyl)-benzaldehyde (compound **2**), as the starting material, is obtained from interaction between bromo-triphenylethylene and 4-formylphenylboronic acid in the presence of catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ under reflux in toluene. Compound **1** is synthesized from the compound **2** and 1,2-ethanedithiol through thioacetalization with iodine catalyst efficiently (Scheme 1). The chemical structures of these new compounds are confirmed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopic methods.



Scheme 1. The structure and synthetic of compound **1**

Figure 1 shows the fluorescence spectrum change of compound **1** upon titration with Hg^{2+} ion. As anticipated, with addition of Hg^{2+} , the weak fluorescence emission aqueous solution of compound **1** becomes more and more strongly emissive. In fact, the fluorescence emission intensity of the mixture system almost linearly increases at 490 nm with the concentration of Hg^{2+} in the range from $2 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ to $10 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ and $12 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ to $20 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. This is associated with the formation of low polar aggregates of compound **2** with a strong fluorescence signal based on aggregation induced emission (AIE) mechanism. Compound **1** has response toward Hg^{2+} at as low as $2 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. In

addition, the remarkable bathochromic shift indicates that compound **1** can be used as a potential ratiometric fluorescent probe for Hg^{2+} .

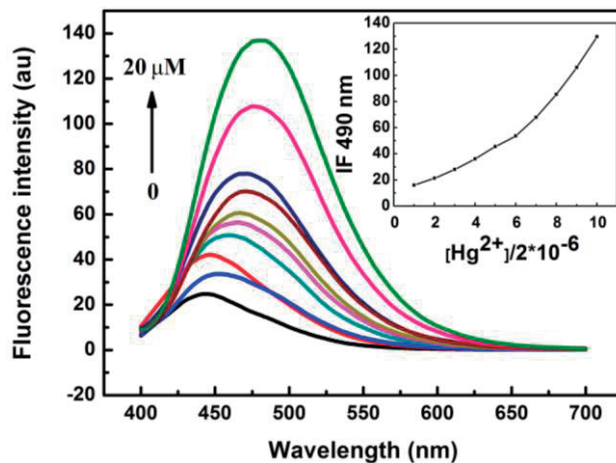


Figure 1. Fluorescence spectra of compound **1** ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in DMF-water (5:95) in the presence of Hg^{2+} (from 0 to 2 equiv). The plot of the fluorescence intensity at 490 nm ($\lambda_{\text{ex}} = 380 \text{ nm}$) vs the concentration of Hg^{2+}



Figure 2. Digital photographs of compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) upon addition of different metal ions (4 equiv) in DMF-water (5:95) mixtures solvent with a UV lamp ($\lambda_{\text{ex}} = 365 \text{ nm}$)

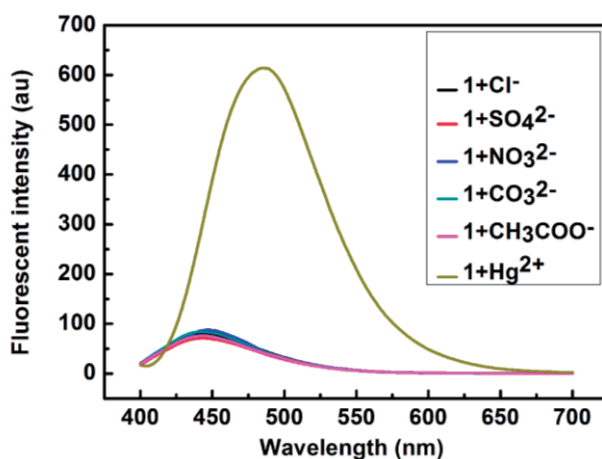


Figure 3. Fluorescent intensity of compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in DMF-water (5:95) mixtures solvent in the presence of 10 equiv of different anions

When Hg^{2+} is added to compound **1** in DMF-water (5:95) mixtures solvent, the significant color changes are observed with a UV lamp ($\lambda = 365 \text{ nm}$) (as shown in Figure 2), which shows that compound **1** has a potential for practical application. In addition, the effects of some anions have also been investigated and relative results are shown in Figure 3, the experimental results indicate that the anions do not almost influence the fluorescence intensity of the detecting system. Above results show that the as-prepared compound **1** can be excellent selective and sensitive fluorescence sensor for Hg^{2+} ion in DMF-water media.

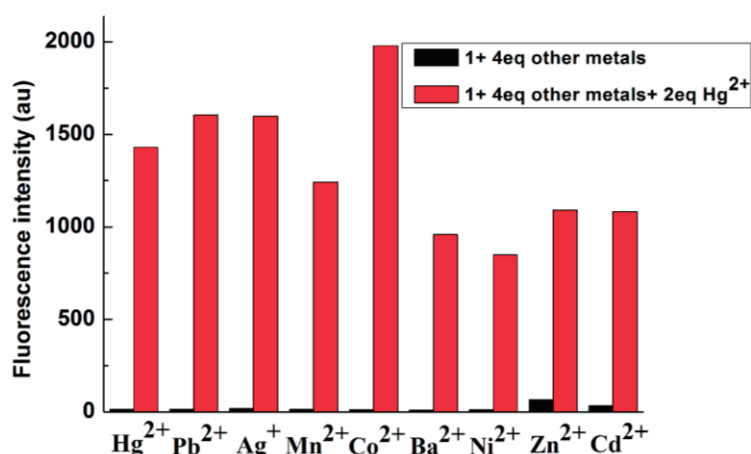


Figure 4. The fluorescence responses of compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) upon addition of various metal ions ($2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, 4 equiv) in the absence and presence of Hg^{2+} ($1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, 2 equiv) in DMF-water (5:95, v/v) (Black bars: compound **1** with other metals, red bars: compound **1** with other metals and Hg^{2+} ($\lambda_{\text{ex}} = 380 \text{ nm}$))

Compound **1** shows good selectivity fluorescence properties toward Hg^{2+} over other metal ions, as shown in Figure 4. In order to better comparison, nine kinds of metal ions with the same concentration are added into compound **1** / DMF/ H_2O media (5:95), respectively, and the fluorescence intensity of compound **1** media show different feature. When other metal ions including Pb^{2+} , Ag^+ , Mn^{2+} , Co^{2+} , Ba^{2+} , Ni^{2+} and Cd^{2+} ions are added to the aqueous solution of compound **1**, the fluorescence of the media do not obviously enhance, except that Zn^{2+} ion causes a slight fluorescence enhancing of the media. However, the media show significant fluorescence enhancing toward Hg^{2+} . The competition experiment also is executed by adding Hg^{2+} to the solution of compound **1** in DMF-water (5:95) in the presence of other metal ions. The result is shown in Figure 4. As is expected, compared with single Hg^{2+} ion, the fluorescence intensity of the media have hardly been effected by other metal ions presented in the system, this result suggest the compound **1** possess excellent selectivity toward Hg^{2+} ion.

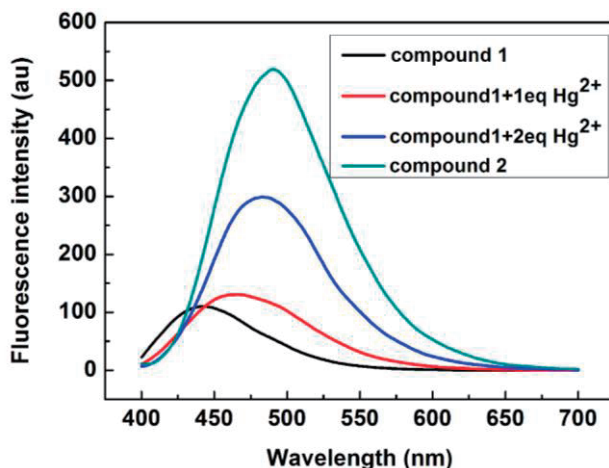


Figure 5. The bathochromic shifted fluorescence emission of compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) upon addition of different Hg^{2+} (from 0 to 2 equiv) in DMF-water (5:95) mixtures solvent

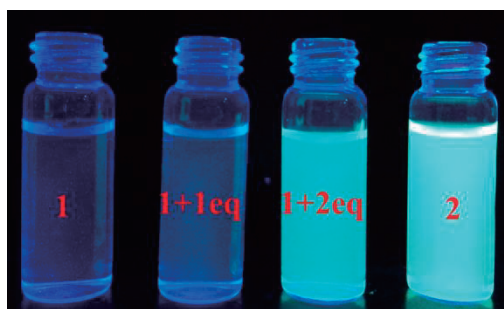
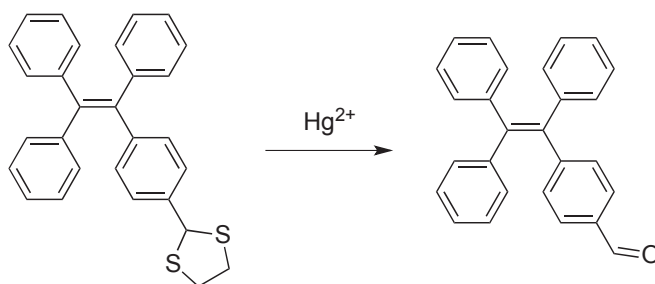


Figure 6. Digital photographs of compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$), compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) + Hg^{2+} ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$), compound **1** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) + Hg^{2+} ($1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$), compound **2** ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in DMF-water (5:95) mixtures solvent with a UV lamp ($\lambda_{\text{ex}} = 365 \text{ nm}$)



Scheme 2. Schematic illustration of the reaction between compound **1** and Hg^{2+} ions

An obvious bathochromic phenomenon is appeared in the system consisted of compound **1** and DMF-water (5:95) mixtures solvent as shown in Figure 5. The maximum emission is shifted from 450 nm to 490 nm with Hg^{2+} ion is added from 0 to 2 equiv. The maximum fluorescence intensity of the detecting system is obtained with emission wavelength at 490 nm, which is in accordance with the result obtained via the system made up of compound **2** and DMF-water (5:95) mixtures. This result indicates

that the reacting ratio might be 1:2 (mol/mol) between compound **1** and Hg^{2+} . The compound **2** is produced via reaction between compound **1** and Hg^{2+} ion. The obvious color change of experiment sample images are further clearly demonstrated above conjecture shown in Figure 6. As shown in Scheme 2, compound **1** is severed by Hg^{2+} ions on the basis of Hg^{2+} -promoted deprotection of thioacetal. The formation of aggregates of compound **2** shows a strong turn-on fluorescence signal, accompanied with obvious color change from colorless to blue.

CONCLUSION

In conclusion, a novel tetraphenylethene-based compound **1** bearing 1,2-ethanedithiol units linked with tetraphenylethene moiety is synthesized. Compound **1** demonstrates an Hg^{2+} -specific bathochromic shift and fluorescent enhancement based on aggregation induced emission (AIE) mechanism. The fluorescent spectra results indicate that compound **1** is a potential ratiometric fluorescent probe for Hg^{2+} with a detection limit of $2 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$.

EXPERIMENTAL

All chemical reagents were purchased as analytic grade. Compound **1** and **2** were synthesized according to the reported procedures. The stock solutions of metal ions were prepared ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, H_2O) from NaCl, NaNO_3 , Na_2SO_4 , AcONa, K_2CO_3 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, AgNO_3 , NiCl_2 , $(\text{AcO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, BaCl_2 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2$ with doubly distilled water. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured on a Bruker spectrometer (operating at 400 MHz and 100 MHz, respectively) at 298 K using $\text{DMSO-}d_6$ as 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 compound **1**

To a solution of the 4-(1,2,2-triphenylvinyl)benzaldehyde (compound **2**) (1.0 g, 2.77 mmol) and 1,2-ethanedithiol (0.3 mL, 3.33 mmol) in CHCl_3 (25 mL) was added iodine (0.14 g, 0.55 mmol), and the resulting mixture was stirred at room temperature for 15 min. After completion of the reaction, the reaction was quenched with aqueous solutions of $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 M, 25 mL) and NaOH (10%, 25 mL), respectively. The resulting reaction mixture was extracted with CHCl_3 (30 mL \times 3), dried via anhydrous Na_2SO_4 , concentrated in vacuo and purified by column chromatography on silica gel (hexane: CH_2Cl_2 , 1:3). The 2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3-dithiolane (compound **1**) was obtained (1.1 g, 91%). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 400 MHz, ppm): δ 3.28–3.32 (m, 2H), 3.44–3.48 (m, 2H), 5.64 (s, 1H), 6.91–6.93 (d, $J=8.2$ Hz, 2H), 6.95–7.00 (m, 6H), 7.09–7.18 (m, 9H), 7.26–7.28 (d, $J=8.2$ Hz, 2H); $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, 100 MHz, ppm): δ 37.39, 55.14, 127.02, 127.76, 128.25, 128.32, 131.06, 139.43, 140.57, 141.23, 143.13,

143.54.

Synthesis of compound 2

Bromotriphenylethylene (2.01 g, 6 mmol), 4-formylphenylboronic acid (1.35 g, 9 mmol), TBAB (0.19 g, 0.6 mmol) and 1.2 M potassium carbonate aqueous solution (10 mL) were dissolved in toluene (40 mL) in turn. The mixture was stirred at room temperature for 30 min under N₂ gas followed by addition of Pd(PPh₃)₄ (60 mg, 5.3×10⁻³ mmol). The mixture was heated to 90 °C for 24 h. The solution was poured into water and extracted with EtOAc. 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. The 4-(1,2,2-triphenylvinyl)benzaldehyde (compound 2) was obtained (1.22 g, 90.1%). ¹H-NMR (DMSO-*d*₆, 400 MHz, ppm): δ 6.98-7.02 (m, 6H), 7.14-7.17 (m, 9H), 7.18-7.20 (d, *J*=7.9 Hz, 2H), 7.67-7.69 (d, *J*=8.2 Hz, 2H), 9.89 (s, 1H); ¹³C-NMR (DMSO-*d*₆, 100 MHz, ppm): δ 127.33, 127.48, 128.32, 128.46, 128.48, 129.50, 131.07, 131.15, 131.89, 134.64, 140.08, 142.80, 142.94, 143.08, 143.13, 150.14, 192.87.

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