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Cite this: New J. Chem., 2021, 45, 5049 The preparation of novel triphenylamine-based AIE-effect fluorescent probe for selectively detecting mercury(II) ion in aqueous solution[†]

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A TPA-ME fluorescent probe, based on triphenylamine derivative TPA-CHO, has been designed, synthesized and characterized by different spectroscopic methods successfully. TPA-ME and TPA-CHO present similar aggregation-induced emission (AIE) effects under same conditions. Due to the deprotection reaction of mercaptal promoted by mercury ions (Hg²⁺), TPA-ME exhibits excellent selectivity and anti-inference properties over other tested ions in the DMF/H₂O (f_w 70%, pH 6.8) medium. Upon increasing Hg²⁺, the fluorescence of the TPA-ME probe shows an obvious red-shift from blue to green. The fluorescence intensity has a good linearity toward Hg²⁺, with the limit of detection (LOD) below 1.23 × 10⁻⁷ mol L⁻¹. A theoretical calculation was carried out to understand the difference between TPA-ME and TPA-CHO, and experimental results have been met with simulation calculations. Along with the result of the fluorescence change, Hg²⁺ can be easily tested through a conveniently prepared test paper.

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1. Introduction

Mercury, also known as the incarnation of metals in alchemy during middle ages, is a highly hazardous and ubiquitous heavy metal of global pollution. Human activities, including oil refining, mining, and the burning of fossil fuels, are the main causes of mercury spread.¹ Not only do aquatic food chains intentionally increase exposure to Hg²⁺ in human beings,² but inorganic mercury also eventually generates highly toxic organic mercury through high bioaccumulation and the metabolism of organisms.^{3,4} Hg²⁺ has such a horrible effect to our endocrine system, nervous system and other systems even at an extremely low level of concentration.⁵ Recently, various analytical media have been developed in leaps and bounds, such as the electrochemical test,⁶ optical test,⁷ and hyperspectral remote sensing.⁸ Although many of these methods are reliable and mature, they still have disadvantages, including expensive, complex pretreatment, and reliance on large instruments. To meet the modern technological development, it is necessary to establish a reliable detection method for Hg²⁺ with fast response, low-cost, convenience and efficiency, especially via fluorescent probes.

Recently, some kinds of fluorescent probes have been developed for detecting mercury, based on specificity coordination or reactions, in water and in vivo.9 Attributed to the specific recognition group, the reaction-type probes can display excellent sensitivity and selectivity, such as mercury-included facile desulfurization-lactonization reaction,¹⁰⁻¹² displacement reaction of arylboronic acid,^{13,14} mercuration of dichlorofluorescein derivatives,15 mercury-promoted hydrolysis for olefin and alkynes,16 and others. In 2001, Tang et al. found that some organic molecules have an aggregation-induced emission (AIE) effect.¹⁷ That means that these amazing ones can oppose the aggregation-caused quenching (ACQ) effect,¹⁸ which is widely found in traditional fluorescent materials, wherein the increase of the aggregation of the material will lead to the decrease or disappearance of its fluorescence intensity. Since then, many kinds of molecules with the AIE effect have been synthesized; for instance, tetraphenylethylene derivatives,^{19,20} tetraphenylsilane derivatives,²¹ and part of the polycyclic aromatic hydrocarbons.^{22,23} By these means, the fluorescent probes for Hg²⁺ detection with various fluorescent properties have been obtained, and their application range can be further expanded.^{24,25} The triphenylamine-based fluorescent probe has received widespread attention due to its different properties, which could be affected by the disperse systems and/or functional groups.²⁶ Its derivatives presented a completely different fluorescent phenomenon when the groups change from aromatic hydrocarbons and heterocycles to electron-withdrawing groups27 and tautomeric systems.28 Some of the triphenylamine derivatives exhibit the ACQ effect,²⁹ while the

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others display the AIE effect at high concentrations.³⁰ The mercury ion is a desulfurizer from the mercaptal group to aldehyde group in aqueous solution. Fluorescent molecules containing mercaptal groups are most likely to be used to detect or identify mercury ions.

Based on the above, we successfully designed and synthesized a triphenylamine-based fluorescent molecule, 4'-(1,3dithiolan-2-yl)-N,N-diphenyl-[1,1'-biphenyl]-4-amine (TPA-ME), applied as the reaction-type fluorescent probe for detecting the mercury ion. The TPA-ME is synthesized via two steps. The fluorophore intermediate, 4'-(diphenylamino)-[1,1'-biphenyl]-4carbaldehyde (TPA-CHO), is prepared through the Suzuki-Miyaura reaction. Then, TPA-ME is obtained via thioacetal reaction at room temperature. The AIE properties of TPA-ME were studied in a dimethyl formamide (DMF)/H2O (PBS buffer, pH 6.8) mixed medium. The Hg²⁺ caused an obvious fluorescent red shift of the TPA-ME probe from blue to green, and the fluorescent intensity of the probe presents a good linear relationship with the concentration of Hg²⁺. The TPA-ME probe also shows excellent selectivity over a variety of cations and anions. The sensing mechanism of the TPA-ME probe was investigated with the analysis of the fluorescent spectra of TPA-CHO/TPA-ME under the same conditions by studying the Job's plot, LC-MS spectra of the reaction mixture of TPA-ME and Hg²⁺, and the simulation calculations based on the density functional theory (DFT). It reveals that the change of the molecular structure causes the enhancement of the ICT effect, which leads to the decrease of the excitation energy and the red shift of the absorption wavelength. Based on this obvious fluorescence change, test papers for the detection of Hg^{2+} have been prepared. After that, this may provide a new idea for the synthesis of reaction-type fluorescent probes.

2. Material and methods

2.1 Materials and apparatus

All raw materials and solvents, including 4-bromotriphenylamine, (4-formylphenyl) boronic acid, $Pd(PPh_3)_4$, enthronement, $Hg(NO_3)_2$ and various other salts, were purchased through commercial channels, unless otherwise mentioned.

¹HNMR and ¹³CNMR spectra were recorded by a nuclear magnetic resonance spectrometer (AV-400, Bruker, Germany). The UV-Vis spectra and fluorescence spectra were monitored *via* a UV-Vis spectrophotometer (UV-3900, Hitachi, Japan) and fluorescence spectrometer (FL-7000, Hitachi, Japan). The LC-MS data of the sample were obtained by a liquid chromatography-mass spectrometer (LCMS-2020, Shimadzu Co., Japan). The fluorescence phenomena of the samples were primarily detected by a three-purpose ultraviolet spectrometer (ZF-I, Sinopharm Group, China).

2.2 Spectroscopic detections

The concentration of TPA-ME was set at $1 \times 10^{-5} \text{ mol L}^{-1}$ in the typical fluorescence detection system. It was prepared by the followed procedures. First, TPA-ME was dispersed into DMF to prepare $1 \times 10^{-3} \text{ mol L}^{-1}$ stock solution. Second, a series of $1 \times 10^{-3} \text{ mol L}^{-1}$ ionic stock solutions were obtained *via* ions

dissolved into deionized water. Third, 0.1 mL TPA-ME stock solution and 2.9 mL DMF were dropped into the 10 ml volumetric flask, then several ion stock solutions were added into the flask. Finally, the 10 ml constant volume probe detecting system was obtained by adding 0.01 mol L^{-1} of a phosphate buffer solution (PBS) with given pH at 6.8. The fluorescence emission spectra of all detection systems were recorded in the wavelength range from 300 to 800 nm under 277 nm excitation.

2.3 Computational details

The construct optical properties of the TPA-ME and TPA-CHO molecules were simulated by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) carried out in the Gaussian 09 software package. The geometries of TPA-ME and TPA-CHO were optimized by the B3LYP/6-31g(d) level in the DFT framework. Their transition energies were calculated with the B3LYP/6-31g(d) level of the time-dependent density functional theory.

2.4. Synthesis of TPA-ME

Preparation the fluorophore intermediate, TPA-CHO. The fluorophore intermediate, 4'-(diphenylamino)-[1,1'-biphenyl]-4carbaldehyde (TPA-CHO), was prepared through the Suzuki-Miyaura reaction. According to the literature method,³¹ the typical procedures are presented in Scheme 1, and briefly described as follows: firstly, 4-bromotriphenylamine (1.29 g, 3.98 mmol) and (4-formylphenyl) boronic acid (0.66 g, 4.38 mmol) were fully dissolved into 40 mL dry tetrahydrofuran (THF), and then 10 mL K₂CO₃ (9.95 mmol) aqueous solution was added. After the mixture was stirred for 30 minutes at room temperature, 150 mg of Pd(PPh₃)₄ was added into the system, and the mixed system was heated to continually reflux for 16 h under nitrogen. Finally, when the system was cooled to room temperature, the reaction was quenched by adding 30 mL of water, and the product was extracted with CH_2Cl_2 (3 \times 50 mL). The crude TPA-CHO product was obtained when CH₂Cl₂ was removed from the organic phase by a rotary evaporation device. The crude product was further purified by silica gel column with petroleum ether/CH₂Cl₂ (2:1) as the eluent. TPA-CHO was yielded as a yellow-green amorphous solid



Scheme 1 Synthetic route for TPA-ME

(0.92 g, 66%). ¹H NMR (400 MHz, chloroform-d) δ 10.15 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.40 (q, *J* = 6.7, 5.7 Hz, 6H), 7.28 (s, 4H), 7.19 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (101 MHz, chloroform-d) δ 191.99, 148.55, 147.46, 146.74, 134.80, 132.90, 130.47, 129.54, 128.15, 127.02, 125.01, 123.61, 123.23. MS: C₂₅H₁₉NO [M + 1]⁺ calculated value 350.43, detected value 350.3 (Fig. S1–S3, ESI⁺).

Preparation of the target substance, TPA-ME. The target substance, 4'-(1,3-dithiolan-2-yl)-N,N-diphenyl-[1,1'-biphenyl]-4-amine (TPA-ME) was synthesized by a convenient thialdehyde reaction, a common aldehyde protection reaction.³² The reaction process is presented in Scheme 1, and the typical synthetic procedure is as follows: TPA-CHO (0.15 g, 0.43 mmol) and 1,2ethanedithiol (44 µL, 0.52 mmol) are dissolved in 10 mL trichloromethane (CHCl₃), before iodide is added. The mixture is stirred continuously for 30 minutes by magnetic stirrer at room temperature, and then 10 mL Na₂S₂O₃ (0.1 mol L^{-1}) is quickly added to the system for quenching the reaction. The reaction solution is extracted with $CHCl_3$ (3 \times 30 mL). After that, the organic phase only remained in the end. The crude TPA-ME product is obtained when CHCl₃ is removed from the organic phase by a rotary evaporation device. The crude product is further purified by silica gel column with petroleum ether/ CH_2Cl_2 (3:1) as the eluent. TPA-ME is yielded as a white amorphous solid. (0.12 g, 66%) ¹H NMR (400 MHz, DMSO-d₆) δ 7.57 (d, I = 8.5 Hz, 6H), 7.31 (t, I = 7.9 Hz, 4H), 7.05 (q, I = 8.7Hz, 8H), 5.77 (s, 1H), 3.60–3.45 (m, 2H), 3.40–3.34 (m, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 147.00, 146.80, 139.47, 139.14, 133.50, 129.59, 128.40, 127.58, 126.13, 124.16, 123.25, 54.72,

39.80. MS: $C_{27}H_{23}NS_2$ [M + H]⁺ calculated value: 426.61, detected value: 426.1 (Fig. S4–S6, ESI⁺).

3. Results and discussion

3.1 Photophysical properties of TPA-CHO and TPA-ME

Since TPA-CHO can be reobtained from TPA-ME through the mercaptal deprotection reaction promoted by Hg²⁺, we investigated the optical properties of TPA-CHO and TPA-ME in the same solvents. Five common solvents were tested with different polarities in order to select a suitable disperser, and their relative images obtained in sunlight or UV-light are shown in Fig. 1. In Fig. 1a, in the sunlight, the color of TPA-CHO changes from colorless in THF to cvan-yellow in DMF, DMSO, MeCN, MeOH. However, under 365 nm UV-light, the fluorescence properties of TPA-CHO in the above solvents showed a significant difference: TPA-CHO exhibits a strong cyan-green fluorescence in THF solvent, medium strong yellow or orange fluorescence in DMSO and DMF, weak yellow fluorescence in MeCN, and very weak blue vellow fluorescence in MeOH. However, TPA-ME appears colorless under sunlight and blue fluorescence under 365 nm UV-light, and hardly changes with a different solvent (Fig. 1b). Fig. 1c further presents that the fluorescence properties of TPA-CHO change with the above five kinds of solvents. It clearly exhibits that the fluorescent band of TPA-CHO may shift beyond 100 nm with the change of solvent. Meanwhile, only a slight red-shift phenomenon appeared in TPA-ME (Fig. 1d). These results should be attributed to the difference of the molecular polarity between



Fig. 1 The photographs of TPA-CHO (a) and TPA-ME (b) in different solvents under 365 nm UV-light and sunlight, respectively. The fluorescence emission spectra of TPA-CHO (1×10^{-3} mol L⁻¹, (c) and TPA-ME (1×10^{-3} mol L⁻¹, (d), measured at their maximum excitation wavelength.

Paper

TPA-CHO and TPA-ME, and different interactions between TPA-CHO and solvents. The UV-Vis absorption spectroscopies of the two fluorophores in these solvents are shown in Fig. S8 (ESI[†]). It indicates that the solvent polarity has little effect on the UV-Vis absorption of TPA-ME, for they have similar absorption bands in the UV region with the maximum absorption peak at about 340 nm. However, the absorption spectra of TPA-CHO are more affected by the solvents. This is because they have two similar absorption bands in the range of 270–320 nm and 325–400, but the maximum absorption peaks slightly vary with the type of solvents.

These distinct differences between TPA-CHO and TPA-ME can be attributed to the aldehyde group in TPA-CHO, which brings about a large rigid plane by the large π -conjugation of the molecule with strong polarity. The aldehyde group attracts the electronic cloud within the molecule, and generates the ICT effect due to the strong electron-withdrawing ability. Thus, the fluorescent band of TPA-CHO is red-shifted by about 100 nm compared to that of TPA-ME. Although the order of polarity of the five solvents is as follows: DMSO > MeOH > DMF > MeCN > THF, they may exhibit different types of combinations with TPA-CHO, resulting in their fluorescence properties not being consistent with the polarity of the solvents. In the DMSO, DMF and THF solvents, the interaction between TPA-CHO and the solvent increases with the polarity of solvents, leading to the fluorescence red-shift and the decrease of its intensity. Compared with the THF solvent, in the methanol solvent, TPA-CHO may react with methanol to form a hemiacetal structure. This leads to the destruction of the large conjugated system, the weakening of the ICT effect of the aldehyde group, and the fluorescence blue-shift phenomenon. The weakest fluorescence intensity is attributed to the strong solvent effect of methanol. In the MeCN solvent, TPA-CHO may strongly interact with MeCN because of its small molecular size and the presence of the -CN group, causing a fluorescent red-shift with weak fluorescence intensity.³³ The environmental factor decreases the excitation energies and increases the molecular dipole moment, resulting in a red shift.³⁴ However, the fluorescent properties of the TPA-ME molecule are less affected by the solvent, except for its intensity compared with that of TPA-CHO. This result should be attributed to the mercaptal group, which destroys the formation of a large π -conjugation and significantly decreases the polarity of the molecule. It not only leads to the interaction between the solvent and TPA-CHO, but also results in the lower fluorescent red shift of TPA-ME in different solvents with various polarities.

Although TPA-CHO and TPA-ME have good solubility in the above organic solvents, they are almost insoluble in water. The effect of the water content (f_w) was investigated based on their fluorescent properties in DMF/H₂O (pH 6.8) medium at the same concentration of 1×10^{-5} mol L⁻¹. As shown in Fig. 2a, all samples with various f_w values were a colorless and transparent solution in sunlight, but they presented diverse colors from yellow to violet to green under 365 nm UV-light. The fluorescence spectra of TPA-CHO are shown in Fig. 2c with diverse water content under 277 nm UV-light, and their relative intensity changes are shown in Fig. S7(a) (ESI⁺). Compared to the yellow fluorescence at 561 nm of TPA-CHO in pure DMF, the fluorescent band is quickly shifted to 428 nm when a slight amount of water is added to the system, and with its intensity gradually decaying with the f_w value increasing from 0 to 60%. However, when the water content is beyond 60%, a new green fluorescent band appears around 482 nm, and its fluorescent intensity was enhanced with the increase of the f_w value until it



Fig. 2 The photographs of TPA-CHO (a) and TPA-ME (b) in various DMF/H₂O (pH 6.8) media under 365 nm UV-light irradiation, respectively. The fluorescence emission spectra of TPA-CHO (c) and TPA-ME (d) excited by 277 nm.

reaches 95%. These results are consistent with the photographs listed in Fig. 2a. Compared with the pure DMF solvent, the H_2O molecules may strongly act with TPA-CHO by hydrogen bond or hemiacetal structure, similar with TPA-CHO dispersed into the MeOH solvent, leading to the blue-shift of the fluorescence emission band of TPA-CHO. However, when the water content is beyond 60%, due to the poor dissolubility in water, the TPA-CHO molecules are aggregated *via* intermolecular interaction, and results in aggregation-induced fluorescence.

For another thing, it was found that the fluorescence properties of TPA-ME also change with the water content, except for the change of the color not being more obvious (Fig. 2b). It was further proved by the fluorescence spectra obtained at 277 nm, shown in Fig. 2d and Fig. S7(b) (ESI†). The fluorescence intensity of TPA-ME decays at 425 nm with a f_w value change from 0 to 50%. When the water content increases from 50% to 80%, the new fluorescence peak of the system presents and reaches the strongest intensity around 451 nm. Compared to TPA-CHO, TPA-ME does not exhibit a significant fluorescent band shift with the change of the water content. It should be due to the mercaptal group with weak polarity and steric hindrance, which weakly acts with H₂O and interacts among the TPA-ME molecules. The above investigation obviously reveals that TPA-CHO and TPA-ME possess the aggregation-induced emission characterization. According to the abnormal phenomenon of TPA-CHO in methanol and DMF/H2O medium, it suggests that TPA-CHO can be used as a potential fluorescent probe for detecting methanol and water at given conditions.

3.2 Fluorescence response to Hg²⁺

The fluorescence responsive behavior of TPA-ME toward Hg^{2+} was investigated in DMF/H₂O (f_w 70%, pH 6.8) medium. As shown in Fig. 3, TPA-ME exhibited the unique emission peak at 451 nm. When Hg^{2+} was added into the system, the fluorescence band was obviously red-shifted from blue to green. Meanwhile, the fluorescence intensity changes with Hg^{2+} increased from 0.1 to 1.5 equiv., and their relationship curves

are listed in Fig. 3b. In general, the fluorescence intensity of the system decreases with the increase of the mercury ion concentration. In addition, the fluorescence intensity at 462 nm has a reliable linear relationship with the mercury ion concentration within a certain concentration range from 1×10^{-6} mol L⁻¹ to 8×10^{-6} mol L⁻¹ (0.1–0.8 equiv.).

Compared to Fig. 2c, it is speculated that the TPA-CHO molecules have the best aggregation to produce the maximum fluorescence intensity. With the addition of Hg^{2+} , the TPA-CHO molecules are formed and tend to pile up with each other due to its large π -conjugation rigid structure. At the low level of Hg^{2+} (from 0.5×10^{-6} mol L⁻¹ to 1×10^{-6} mol L⁻¹, 0.05 equiv. to 0.1 equiv.), the TPA-CHO molecules are quickly aggregated. They reach the best aggregation for the highest fluorescent intensity at the given 70% water content. After that, with the increase of Hg^{2+} , more TPA-CHO molecules are aggregated and result in the gradual decay of the fluorescence intensity. As the concentration of Hg^{2+} surpasses 1.0×10^{-5} mol L⁻¹, TPA-ME is completely converted to TPA-CHO, and its degree of aggregation is not increased, so the fluorescent intensity of the system is not obviously decay.

The decrease in the distance between the molecules, and the radiation transition produced by the molecules after they absorb the photons is disturbed. In this way, most of the energy is dissipated in the form of non-radiative transitions, which leads to a decrease in the fluorescence intensity. In addition, the fluorescence intensity at 462 nm showed an excellent linear relationship with the concentration of Hg²⁺. According to the detection limit formula "DL = $3\sigma/k$ ", the detection limit of the probe TPA-ME for Hg²⁺ can be calculated as $1.23 \times 10^{-7} \text{ mol L}^{-1}$, which is lower than some reported probes.^{35–37}

3.3 Selectivity and anti-interference capacity of the TPA-ME probe

Selectivity is an important indicator to measure whether the fluorescent probes can be applied in actual situations. The concentration of all interfering ions is twice $(2 \times 10^{-5} \text{ mol L}^{-1})$



Fig. 3 (a) Fluorescence emission spectra of TPA-ME excited at 277 nm changed with Hg^{2+} from 0 to 1.5×10^{-5} mol L⁻¹. Inset: The change of the fluorescence with the addition of Hg^{2+} under 365 nm UV-light irradiation. (b) The linear matching curve of the fluorescence intensity with the concentration of Hg^{2+} at 462 nm.



Fig. 4 (a) The photographs of TPA-ME in the presence of 2×10^{-5} mol L⁻¹ of the interfering ions and 1×10^{-5} mol L⁻¹ of Hg²⁺ in DMF/H₂O (f_w 70%, pH 6.8) under 365 nm UV-light irradiation. (b) Fluorescence emission spectra of TPA-ME with different ions excited by 277 nm.

that of Hg²⁺. As shown in Fig. 4a, the change of the fluorescence emission peak occurs when Hg²⁺ ($1 \times 10^{-5} \text{ mol L}^{-1}$) is added, while the existence of various interfering ions (Pb²⁺, Mn²⁺, Ag⁺, Co²⁺, Ba²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Cu²⁺, Ca²⁺, Cr³⁺, Fe³⁺, Fe²⁺, Mg²⁺, Cl⁻, SO₄²⁻, NO₃⁻, CO₃²⁻ and CH₃COO⁻) only exhibit a negligible response. According to R. G. Pearson's soft and hard acidbase theory, Hg²⁺ and S²⁻ are soft particles because they have a lower charge density and a larger ionic radius. Therefore, Hg²⁺ combines easily with mercaptals,³⁸ and only the fluorescence of the TPA-ME solution containing Hg²⁺ has changes from blue to green (Fig. 4b). These interfering ions cannot induce the deprotection reaction of the mercaptal, and the probe TPA-ME has a good selectivity toward Hg²⁺.

In actual production applications, the real environment is often full of various uncertainties. For fluorescent probes, the anti-interference capacity is another important indicator. The anti-interference of the probe TPA-ME was carried out upon the addition of 2.0 equiv. of various interfering ions in DMF/H₂O (f_w 70%, pH 6.8). For comparison, the fluorescence

intensity of TPA-ME containing these interfering ions and Hg^{2+} was also measured in turn. It can be obtained from the data in Fig. 5 that these different interfering ions do not cause an obvious interference toward the detection of Hg^{2+} . Compared with the blank one, the samples with both Hg^{2+} and different interfering ions exhibited a red shift from 451 nm to 482 nm, which is attributed to the reaction between Hg^{2+} and mercaptals. Based on the above two experiments, the probe TPA-ME has excellent specific detection ability for Hg^{2+} .

3.4 Mechanism of the sensing process for Hg²⁺

Mercaptals are commonly used as aldehyde protecting groups in organic synthesis. Hg^{2+} is a mercaptal deprotection reagent because of its strong sulfur–absorbing property. Based on this characteristic, the reaction mechanism of the probe TPA-ME with Hg^{2+} is shown in Scheme 2.

To further verify our conjecture, we compared four fluorescence data, including TPA-CHO, TPA-ME, TPA-ME with Hg²⁺ (1:1 equiv.), and TPA-ME with Hg²⁺ (1:1.5 equiv.), in Fig. 6a. With the addition of Hg²⁺, the fluorescence emission peak presents an obvious red-shift from 451 nm to 482 nm. The fluorescence emission peak of TPA-CHO coincided with the spectra of TPA-ME with the Hg²⁺ system. In addition, the Job's plot curve assumed the 1:1 reacting stoichiometry for TPA-ME toward Hg²⁺ (Fig. 6b). This suggests that the mercaptal group in TPA-ME is hydrolyzed under the influence of Hg²⁺, and TPA-ME in the system is gradually reduced and converted to TPA-CHO. Besides, comparing the retention time of the reaction mixture (TPA-ME and Hg²⁺, Fig. S9, ESI[†]) to pure TPA-CHO and TPA-ME (Fig. S3 and S6, ESI⁺), the LC-MS spectra of the reaction mixture show that TPA-ME turned into TPA-CHO with the addition of Hg^{2+} , which is consistent with our above conjecture.

In order to reveal the fluorescence emission of TPA-ME and TPA-CHO, the relative theoretical calculations were performed *via* a Gaussian software package based on the density functional theory. Their structure and transition energies are first optimized through the density functional theory (DFT) and time-dependent



Fig. 5 (a) Fluorescence emission spectra of TPA-ME ($1 \times 10^{-5} \text{ mol L}^{-1}$) in DMF/H₂O (f_w 70%, pH 6.8) with the presence of other interfering ions ($2 \times 10^{-5} \text{ mol L}^{-1}$) and Hg²⁺ ($1 \times 10^{-5} \text{ mol L}^{-1}$). (b) Fluorescence intensity of TPA-ME ($1 \times 10^{-5} \text{ mol L}^{-1}$) in the presence of $2 \times 10^{-5} \text{ mol L}^{-1}$ of other ions at 451 nm with Hg²⁺ ($2 \times 10^{-5} \text{ mol L}^{-1}$) or not (1. only Hg²⁺, $2. \text{ Pb}^{2+}$, $3. \text{ Mn}^{2+}$, $4. \text{ Ag}^+$, $5. \text{ Co}^{2+}$, $6. \text{ Ba}^{2+}$, $7. \text{ Ni}^{2+}$, $8. \text{ Zn}^{2+}$, $9. \text{ Cd}^{2+}$, $10. \text{ Cu}^{2+}$, $11. \text{ Ca}^{2+}$, $12. \text{ Cr}^{3+}$, $13. \text{ Fe}^{3+}$, $14. \text{ Fe}^{2+}$, $15. \text{ Mg}^{2+}$, $16. \text{ Cl}^-$, $17. \text{ SO}_4^{2-}$, $18. \text{ NO}_3^{-}$, $19. \text{ CO}_3^{-2}$ and $20. \text{ CH}_3\text{COO}^{-}$).



 $\label{eq:scheme 2} Scheme 2 \quad Sensing \mbox{ process for TPA-ME toward } Hg^{2+}.$



Fig. 6 (a) The fluorescence emission spectra of TPA-ME with a typical concentration of Hg^{2+} and TPA-CHO in DMF/H₂O (f_w 70%, pH 6.8), excited by 277 nm UV-light. (b) The Job's plot between TPA-ME and Hg^{2+} , with a total concentration of ([Hg^{2+}] + [TPA-ME]) = 2 × 10⁻⁵ mol L⁻¹.

density functional theory (TD-DFT) using the Gaussian 09, Revision-D.01 program and visualized using the Gauss view 6.0.16 program.³⁹ Their optimized molecular geometries and transition energies are carried out under the calculation level of B3LYP/ 6-31g(d). The calculated values are in good agreement with the experimental results shown in Fig. 7. From the calculation of the electronic excitation contribution by Multiwfn,40 the charge of TPA-CHO and TPA-ME are excited from the ground states (HOMOs) to the excited states (LUMOs) by suitable UV-light. From their simulated electronic cloud distribution image, it shows that their electronic clouds are uniformly distributed throughout triphenylamine at the ground state. However, in the excited states, there are significant differences in the distribution of the electron cloud between them. In the TPA-CHO molecule, the electron cloud is mainly concentrated on the phenyl-aldehyde group, while in the TPA-ME molecule, the electron cloud is mainly compiled in the biphenyl group. The main reason for this difference is due to the aldehyde group and mercaptal group. In the TPA-ME molecule, mercaptal cannot attract electrons strongly as a weak electronwithdrawing group, while the diphenyl group has a strong conjugation effect, leading to the low distribution of the electron cloud on the mercaptal group in the excited state. However, in

the TPA-CHO molecules, the aldehyde group presents strong electron-absorbing ability and larger π -conjugation with the diphenyl group, causing the electron cloud to shift almost entirely in favor of the aldehyde group, showing the ICT effect. This suggests that the substituents play a critical role in the fluorescence properties of the molecules under the same fluorophore. Compared with TPA-ME, the fluorescence emission band of TPA-CHO is red-shifted due to the strong intramolecular conjugation. It is further proved by the energy gap of their HOMO–LUMO listed in Fig. 7a.

According to Koopmans theorem, the HOMO–LUMO gap can be approximately equivalent to a fundamental gap and optical gap. The energy between HOMO and LUMO can be used to roughly describe some properties of the organic molecules, such as the difference of the reaction activity and excitation energy.⁴¹ The HOMO–LUMO gap of TPA-ME and TPA-CHO can be calculated, which are 3.9118 eV and 3.1733 eV, respectively. This indicates that the mercaptal and aldehyde group directly affect the π -conjugation and polarity of the molecule. Compared to TPA-ME, TPA-CHO exhibits a significant reduction in the HOMO–LUMO gap, leading to a decrease in the excitation energy and red shift in the UV-Vis absorption spectrum. It indicates that TPA-CHO has a larger dipole moment due to the

NJC



Fig. 7 (a) HOMO, LUMO, optimized molecular geometries for TPA-ME and TPA-CHO. (b) The UV-Vis absorbance for TPA-ME and TPA-CHO in different solvents with PBS solution (*f*_w 70%, pH 6.8).

aldehyde group. This result is further indicated by the UV-Vis absorption spectra shown in Fig. 7b of different solvent systems containing 70% water. Due to the strong polar interaction between the aldehyde group and water, the UV-visible absorption band of the organic solvent is red-shifted. When the polar organic solvent and water form a mixed solvent, the interaction between the solvent and aldehyde group causes the solvent effect of UV absorption, which leads to the decrease of the absorption intensity. Compared with the energy of the ground state (HOMOS), TPA-ME (-5.0234 eV) is higher than TPA-CHO (-5.0941 eV), which suggests that TPA-ME easily converts into TPA-CHO. These results further confirm that TPA-ME may be used as a reaction-type fluorescent probe for Hg²⁺.

3.5 Test paper application

To explore the practical application of the fluorescent testing paper, the TPA-ME test paper was prepared to detect Hg^{2+} in water. The filter paper was first placed on a clean slide, and then immersed in a storage solution of 1×10^{-3} mol L⁻¹ TPA-ME for 5 minutes. The solvent was removed and dried in an oven. Finally, a drop of Hg^{2+} (1×10^{-3} mol L⁻¹) aqueous solution was added to the dry TPA-ME test paper. For comparison, a drop of Zn^{2+} (2×10^{-3} mol L⁻¹) and a drop of Cd^{2+} (2×10^{-3} mol L⁻¹) aqueous solution were added to other two identical test papers. Samples

were observed under the irradiation of 365 nm UV-lamp after they were dried completely. As shown in Fig. 8, the fluorescence of the blank TPA-ME test sample is blue, similar to TPA-ME in solution. When Hg^{2+} is dropped on it, the test paper shows an obviously yellow-green fluorescence. Meanwhile, the fluorescent color of the test paper does not obviously change upon adding Zn^{2+} and Cd^{2+} , although their concentration is twice that of Hg^{2+} . These results indicate that the TPA-ME test paper can react with Hg^{2+} to form TPA-CHO. The test paper further shows that TPA-ME and TPA-CHO have different AIE fluorescent properties due to the difference of the molecular structure. This test paper experiment shows that the probe TPA-ME has the ability to detect Hg^{2+} in practice.



Fig. 8 The photographs of the TPA-ME based test paper under sunlight and 365 nm UV-light irradiation.

Paper

4. Conclusions

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In summary, based on the fluorescent group from the triphenylamino derivatives and the recognition group of mercaptal, the TPA-ME molecule was first prepared and applied to detect Hg²⁺ in aqueous solution successfully. Through the investigation of five kinds of organic solvents, a probe solution was constructed with DMF as the solvent. With the increase of the water content, the fluorescence of TPA-ME shows the characteristics of the first inhibition and then increased, with a redshift of the luminescence band. This indicated that TPA-ME may exhibit ACO or AIE characterization in suitable water content. In the DMF/H₂O system with 70% water content, the TPA-ME probe shows good selectivity, anti-interference and linear correlation with the LOD at about 1.23×10^{-7} mol L⁻¹. Through DFT and TD-DFT simulation calculation, it was further proved that the aldehyde group and mercaptal group have an important influence on the properties of the fluorescent molecules. The TPA-ME test strip provides a convenient and qualitative way to detect mercury ions. In the future, we will apply other groups to modify triphenylamine and prepare more diverse functional fluorescent materials, further exploring the fluorescent properties of the TPA-CHO probe for detecting hydroxyl compounds and their photoluminescence mechanism of these kinds of fluorescent molecules.

Conflicts of interest

The authors declare no conflicts of interest.

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