



Multi-branched triphenylamine–rhodamine derivatives: Synthesis and fluorescent sensing for Cu^{2+} and Hg^{2+} ions



Yang Yang^{a,b}, Bin Li^{a,*}, Liming Zhang^a, Peng Li^a, Hong Jiang^a

^a State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China

^b University of Chinese Academy of Sciences, Beijing 100039, PR China

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ABSTRACT

Three multi-branched rhodamine based fluorescent probes TPARH1–3 have been designed and synthesized by incorporating the rhodamine fluorophore with triphenylamine. The probe TPARH1 displayed high sensitivity to Cu^{2+} in aqueous CH_3CN . The probes TPARH2 and TPARH3 showed high sensitivity towards Hg^{2+} in aqueous EtOH medium as reflected by their signalling responses. The cooperative effects of multi-branched structures towards metal ions were carried out by UV–vis absorption titrations and time scanning fluorescence spectroscopic. In addition, the binding mode was proposed based on the job's plot. The absorption of probes 1–3 at 558 nm went through a maximum at a molar fraction of 0.5, indicating a 1:1 stoichiometry of the Hg^{2+} to 1, 2 and 3 in the complex, respectively.

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1. Introduction

The specific detection of transition metal ions is an active field of research because of their important roles in biological, industrial and environmental processes [1,2]. Among them, Cu^{2+} is of particular interest due to its essential role in various physiological processes. Abnormal Cu^{2+} levels in human body are toxic and can lead to major health concerns, especially in oxidative stress and neurological disorders [3]. As an environmental contaminant, Hg^{2+} is considered to be dangerous as it can accumulate in human body and causes serious damage to the central nervous and endocrine systems even in a low concentration [4]. Therefore, it is of utmost interest to develop highly sensitive and selective optical chemosensors for Hg^{2+} and Cu^{2+} ions [5,6].

Since the pioneer work of Czarnik's group regarding a rhodamine-based Cu^{2+} fluorescent chemodosimeter [7], rhodamine derivatives have attracted much attention in the construction of small-molecule fluorescence probes for the detection of heavy metal ions and protons in aqueous solutions [8,9]. These probes which are based on rhodamine derivatives can be potentially applied to biological and environmental materials [10]. However, the cooperative effect of multi-branched rhodamine

derivatives in the presence of heavy metal ions has rarely been reported [11].

As the continuation of our study on the sensing of cations and anions of biological significance [12,13], we have synthesized three multi-branched triphenylamine–rhodamine probes 1–3, which can selectively recognize Cu^{2+} and/or Hg^{2+} in a mixed aqueous organic environment.

2. Experimental

2.1. Reagents and chemicals

Most of the metal salts were purchased from Sinopharm Chemicals Ltd. and used as received. Rhodamine B and triphenylamine were procured from Sinopharm Chemicals Ltd. and used without further purifications. Ethanol and acetonitrile (AR grade) were purchased from Beijing Chemical Reagent Plant and purified before use. Water used for the experiment was double distilled. Stock solutions of metal ions (1.0×10^{-2} mol/L) were prepared by dissolving 0.1 mmol of nitrate salts the following compounds in 10 mL of double distilled water. High concentration of the stock solutions TPARH1–3 (1.0×10^{-4} M) were prepared in CH_3CN and EtOH. Before spectroscopic measurements, the solution was freshly prepared by diluting the high concentration stock solution to the corresponding solution.

* Corresponding author. Tel.: +86 431 86176935; fax: +86 431 86176935.
E-mail address: libinteacher@163.com (B. Li)

2.2. Instruments

^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer using tetramethylsilane as the internal standard. IR spectra were recorded in diffuse reflection with a Magna 560 FT-IR spectrophotometer. Mass spectra were obtained from Bruker micro TOF-Q mass spectrometer. Fluorescence spectra were taken on a Hitachi F-4500 and Hitachi F-7000 fluorescence spectrophotometer. The UV/vis spectra were recorded on a Shimadzu UV-3101 spectrophotometer.

2.3. Synthesis of probe TPARH1

To a stirring solution of rhodamine B hydrazide (0.456 g, 1.0 mmol) in EtOH (30 mL), 4-(diphenylamino)benzaldehyde (0.273 g, 1.0 mmol) was added and the reaction mixture was heated to reflux for 12 h. When the reaction was finished the mixture was cooled to room temperature, poured into ice water and then the precipitate was collected through filtration. CH_2Cl_2 (50 mL) was added to the precipitate and washed thoroughly with water (300 mL). The organic phase was dried over MgSO_4 , concentrated and column chromatographed on silica-gel (elution with petroleum ether: CH_2Cl_2 =5:1) to obtain 1 as a yellow powder in 75% yield: ^1H NMR (300 MHz, CDCl_3) δ 8.70 (s, ^1H), 7.97 (dd, J =5.6, 3.2 Hz, ^1H), 7.47 (dd, J =8.9, 5.5 Hz, ^2H), 7.39 (d, J =8.6 Hz, ^2H), 7.21 (dd, J =6.8, 1.6 Hz, ^3H), 7.11 (dd, J =5.6, 2.9 Hz, ^2H), 7.07–6.97 (m, 6H), 6.91 (d, J =8.7 Hz, ^2H), 6.52 (d, J =8.8 Hz, ^2H), 6.41 (d, J =2.3 Hz, ^2H), 6.29–6.19 (m, ^2H), 3.31 (q, J =7.0 Hz, ^8H), 1.15 (t, J =7.0 Hz, ^{12}H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.59, 153.30, 149.25, 149.08, 147.89, 147.29, 132.98, 129.96, 129.28, 128.46, 128.18, 128.06, 124.90, 123.84, 123.30, 122.27, 108.08, 106.61, 98.08, 66.16, 44.32, 12.64; IR (KBr, cm^{-1}): ν =2965, 2925, 1714, 1589, 1547, 1512, 1489, 1306, 1267, 1115, 822, 754, 695. ESI-MS: m/z =710.3.

2.4. Synthesis of probe TPARH2

To a stirring solution of rhodamine B hydrazide (0.456 g, 1.0 mmol) and 4,4'-(phenylazanediyldibenzaldehyde (0.150 g, 0.5 mmol) were used in accordance with the general procedure given above. The product 2 was obtained as a yellow powder in 62% yield: ^1H NMR (300 MHz, CDCl_3) δ 8.65 (s, ^2H), 7.97 (d, J =6.3 Hz, ^2H), 7.46 (s, 4H), 7.38 (d, J =8.2 Hz, ^4H), 7.08 (ddd,

J =24.0, 22.2, 8.0 Hz, ^8H), 6.89 (d, J =8.2 Hz, ^4H), 6.51 (d, J =8.7 Hz, ^4H), 6.41 (s, ^4H), 6.24 (d, J =7.8 Hz, ^4H), 3.32 (dd, J =13.6, 6.7 Hz, ^{16}H), 1.15 (t, J =6.7 Hz, ^{24}H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.62, 153.28, 148.94, 148.60, 146.81, 133.06, 129.98, 129.40, 129.08, 127.47, 125.51, 123.94, 123.19, 108.12, 98.11, 66.15, 44.36, 12.62; IR (KBr, cm^{-1}): ν =2967, 1684, 1617, 1549, 1512, 1462, 1367, 1309, 1268, 1225, 1116, 821, 790, 689. ESI-MS: m/z =1178.8.

2.5. Synthesis of probe TPARH3

Rhodamine B hydrazide (0.456 g, 1.0 mmol) and 4,4'-nitrotribenzaldehyde (0.110 g, 0.33 mmol) were used in accordance with the general procedure given above. The product 3 was obtained as a yellow powder in 57% yield: ^1H NMR (300 MHz, CDCl_3) δ 8.65 (s, ^3H), 8.01–7.90 (m, ^3H), 7.51–7.41 (m, ^7H), 7.37 (d, J =8.7 Hz, ^6H), 7.24–7.15 (m, ^4H), 7.15–7.07 (m, ^4H), 7.06–6.95 (m, ^6H), 6.88 (d, J =8.7 Hz, ^5H), 6.51 (d, J =8.8 Hz, ^6H), 6.40 (d, J =2.4 Hz, ^6H), 6.24 (d, J =8.9 Hz, ^6H), 3.31 (dd, J =14.2, 7.1 Hz, ^{24}H), 1.14 (t, J =7.0 Hz, 36H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.52, 153.37, 153.30, 151.66, 147.08, 133.27, 133.17, 131.66, 131.23, 129.00, 128.74, 128.27, 128.03, 126.11, 125.20, 123.89, 123.28, 123.18, 121.27, 108.11, 98.10, 66.17, 44.29, 12.55; IR (KBr, cm^{-1}): ν =2906, 2676, 1793, 1694, 1613, 1590, 1510, 1376, 1307, 1218, 1147, 1074, 821, 689. ESI-MS: m/z =1644.8.

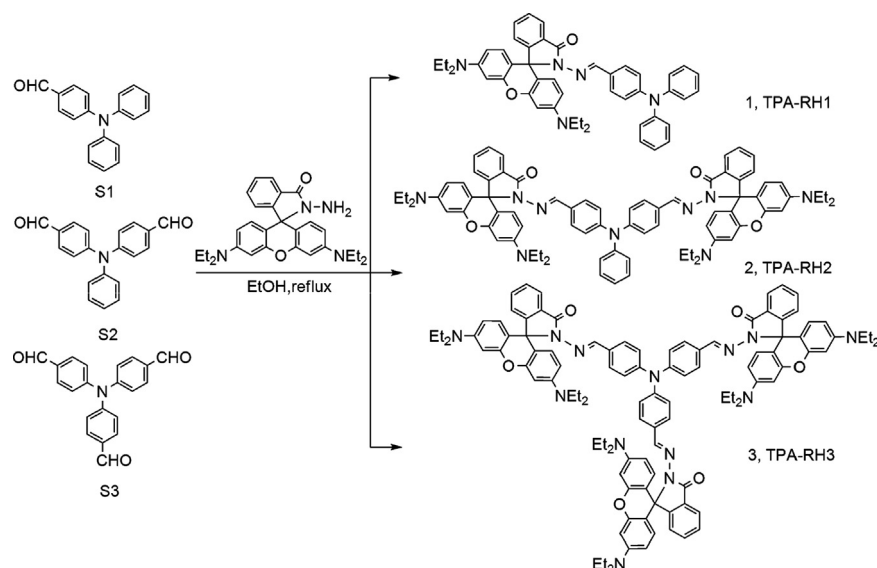
3. Results and discussion

3.1. Synthesis

The synthesized compounds (TPARHn, $n=1, 2, 3$) had triphenylamine (TPA) as the core and rhodamine hydrazide as branch substitutes. Probes 1–3 were facilely synthesized from rhodamine B hydrazide and substituted triphenylamine aldehyde (S1–S3) on the basis of the route shown in Scheme 1.

3.2. Fluorescence and absorbance spectra

In order to investigate the metal ion induced signaling responses in these probes, various metal ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ and Pb^{2+} (taken as their nitrate salts) were investigated in CH_3CN and EtOH solutions. In contrast, when water was added to organic



Scheme 1. Synthesis of rhodamine based probes TPARH1–3.

solvents, especially in 80% aqueous solutions, the fluorescence signal reached its maximum value. These results indicated that 80% aqueous CH_3CN and EtOH media is favorable for fluorescent measurement (Fig. S1). In the presence of 10 equiv excess of metal ions, the fluorescence intensity at 580 nm for most metal ions was found to be almost the same in magnitude and there was no distinguishable difference. In the case of Cu^{2+} and Hg^{2+} , however, a nonstructured emission at 580 nm increased to a significant extent [14].

The UV–vis spectra of 1–3 solutions each exhibited only a very weak band above 558 nm, which was ascribed to the spirolactam form of molecule TPARH1–3. Upon adding 10 equiv of Cu^{2+} and Hg^{2+} , the absorption intensity at 558 nm was significantly enhanced, which induced a clear and gradual change from colorless to pink. This suggested the formation of the ring-opened amide form of TPARH1–3 upon binding. Compared with $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, the absorption enhancement impelled by Hg^{2+} was more obvious in EtOH/ H_2O solution. The addition of Fe^{3+} into the solution of probes 1–3, under the same conditions, could induce a small but significant enhancement of the absorption at 558 nm (Fig. 1).

We first decided to examine the selectivity of the probes 1–3 in mixed aqueous–organic environment. For all the following titration experiments, absorption spectra were recorded 5 min after the addition of Cu^{2+} to ensure the equilibrium of sensing procedure. As shown in Fig. 2a, probes 1–3 displayed only minimal absorption response to Cu^{2+} within 2 equiv in aqueous acetonitrile. By contrast, gradually increasing addition of Cu^{2+} elicited intense absorption within 2 equiv in ethanol–water (Fig. 2b). The absorption of probes 1–3 remarkably increased to their maximum values within 5 min. The significant absorption change in Fig. 2a and b was assigned to the chemical reaction between Cu^{2+} and the spirolactam ring in aqueous ethanol and the complexation equilibrium took place in aqueous acetonitrile [15].

The absorption behavior of probes 1–3 towards Cu^{2+} in ethanol was different from that towards Hg^{2+} in the mixed aqueous media. In Fig. 2b, the Cu^{2+} titration of the absorption intensities increased and reached the maximum values at about 5 equiv of Cu^{2+} ions with the order: $3 < 2 < 1$. While addition of Hg^{2+} ions within 10 equiv, the intensity of absorption band at 558 nm was in the order of $3 < 2 < 1$, but when the concentration of Hg^{2+} ions increased more than 10 equiv the intensity of absorption band shifted to $3 > 2 > 1$ (Fig. 2c).

Furthermore, the time scanning absorption and fluorescence spectrum of probes 1–3 were evaluated in the presence of 10 equiv

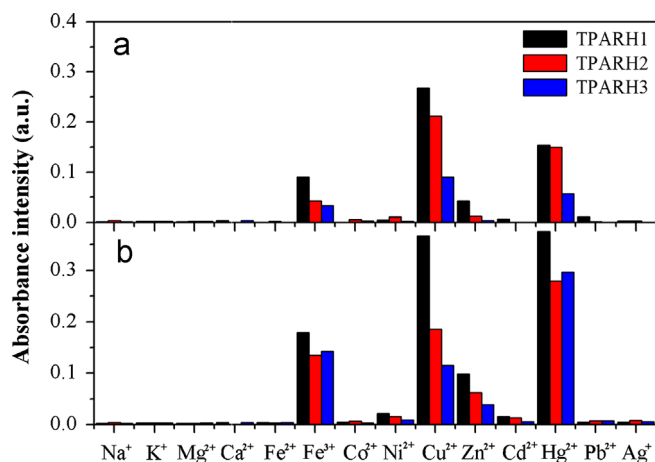


Fig. 1. Change in the absorption at 558 nm of 1–3 (10 μM) in presence of 10 equiv of various metal ions in (a) $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and (b) EtOH/ H_2O (8:2, v/v). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

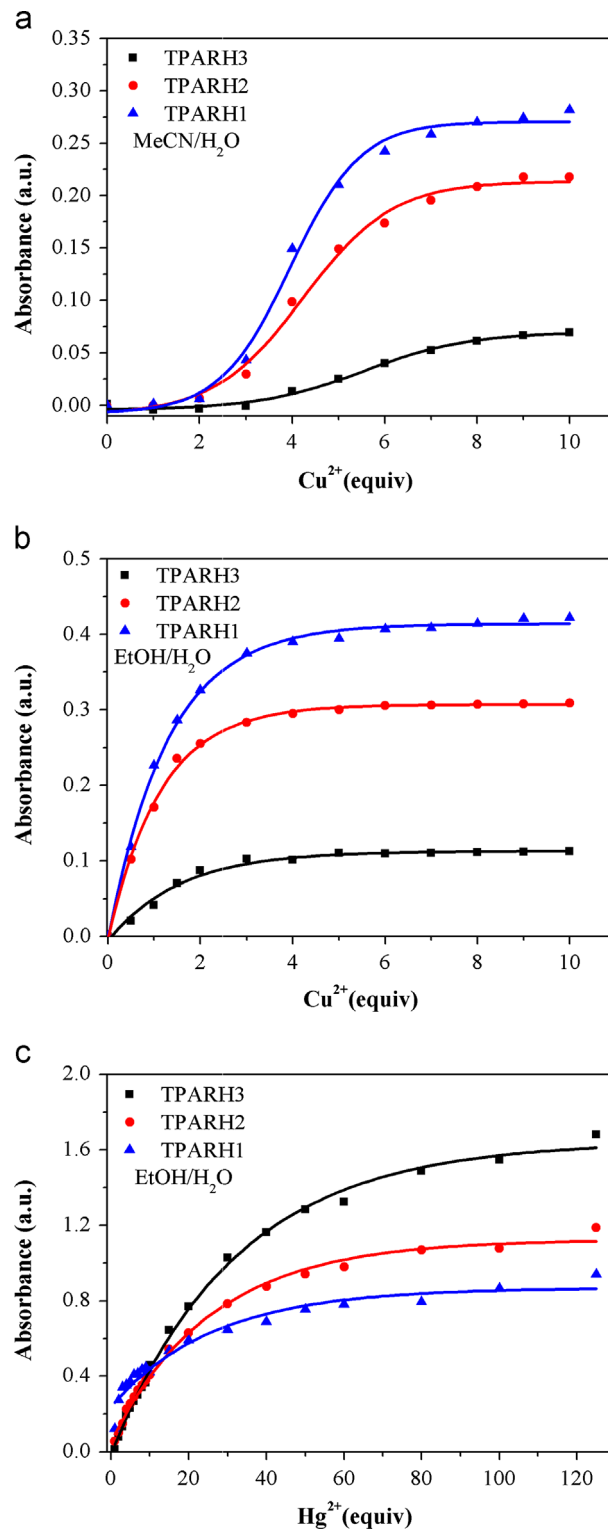


Fig. 2. Change in absorption spectra (558 nm) of 1–3 (10 μM) upon addition of different amounts of Cu^{2+} and Hg^{2+} in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and EtOH/ H_2O (8:2, v/v) solutions.

concentrations of Hg^{2+} ions. In Fig. 3a, there was a linear relationship between the absorption intensity at 558 nm and the reaction time. The gradients of 1–3 were corresponded to 0.00692, 0.01116 and 0.00616 in the order of $1 < 3 < 2$. By the way, the graphs in Fig. 3a also seem curved, when the reaction time prolonged more than 1 h. The maximum fluorescence emission enhancement at 580 nm was observed after the addition of 10 equiv of Hg^{2+} ions which clearly indicated the highly reactive nature of the Hg^{2+}

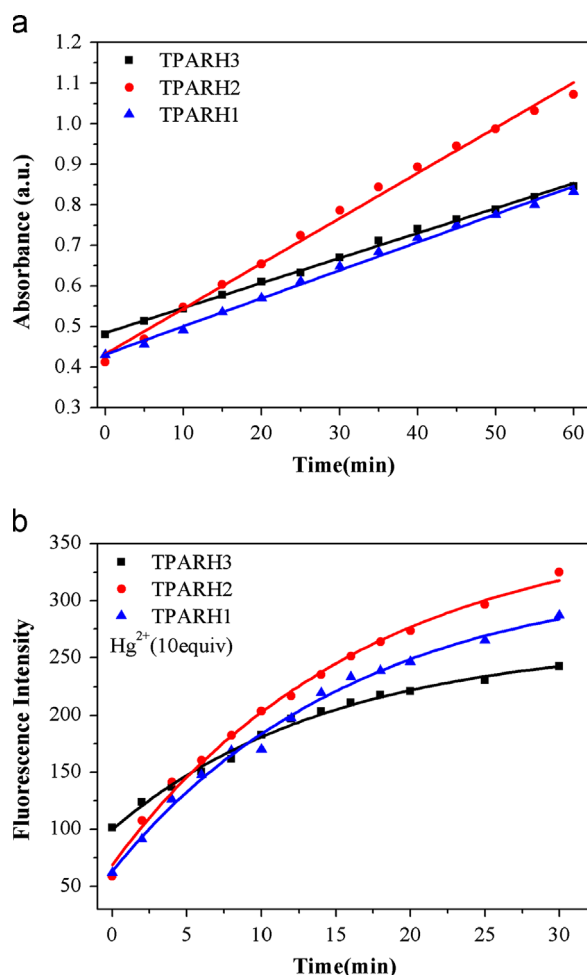


Fig. 3. Time scanning increase of absorption (558 nm) and fluorescence intensity (580 nm) of probes 1–3 to Hg^{2+} (10 equiv) in ethanol–water (8:2, v/v), $\lambda_{\text{ex}}=552$ nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mediated hydrolysis of the spirolactam ring of the rhodamine moiety. The fluorescence intensity at 580 nm increased as the reaction time was prolonged with the order of $3 < 1 < 2$. Careful scrutiny showed the intensity of the pink colours arising from adding Cu^{2+} and Hg^{2+} ions was a little different. It was mentionable that $\text{Cu}(\text{NO}_3)_2$ instead of $\text{Hg}(\text{NO}_3)_2$ opened the spirolactam ring weakly as confirmed from the appearance of the faint pink colour of the solution as well as a weakly intense emission peak at 580 nm [16].

3.3. Sensing mechanism

To find out the stoichiometry of the Cu^{2+} and Hg^{2+} -ligand complex, Job's method for absorption measurement was applied [17]. The absorption of 1–3 in the absence (A_0) and presence (A) of Cu^{2+} and Hg^{2+} were determined at about 558 nm in 5 min (Fig. S5). A plot of $(A-A_0)$ versus the molar fraction of Hg^{2+} was provided in Fig. 4. It showed that the $(A-A_0)$ value went through a maximum at a molar fraction of 0.5, indicating a 1:1 stoichiometry of the Hg^{2+} to 1, 2 and 3 in the complex, respectively. More direct evidence was obtained by comparing the ESI mass spectra of Cu^{2+} and Hg^{2+} complex with chemosensors TPARH1–3. The signal at m/z 1296 corresponded to $[\text{TPARH2}+\text{Cu}^{2+}+3\text{H}_2\text{O}]^+$ and the signal at m/z 1891 corresponding to $[\text{TPARH3}+\text{Hg}^{2+}+3\text{H}_2\text{O}]^+$ was clearly observed. These results indicated a 1:1 binding ratio between TPARH1–3 and $\text{Cu}^{2+}/\text{Hg}^{2+}$ existed in solvent.

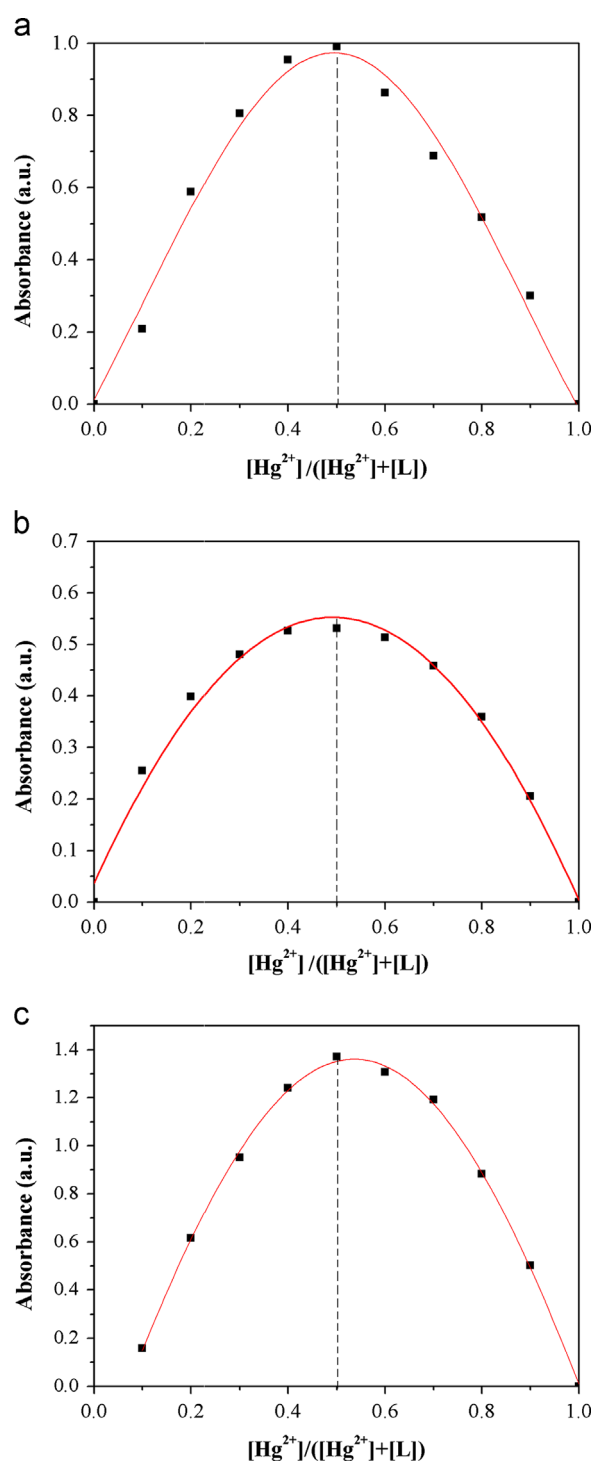
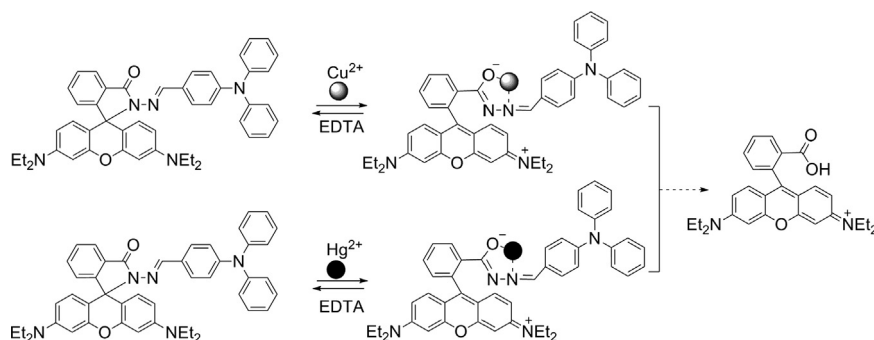


Fig. 4. The Job's plot analysis between probes 1–3 and Hg^{2+} in EtOH–H₂O (8:2, v/v) at room temperature. The total concentration of probes 1–3 and Hg^{2+} was kept constant at 100 μM . The wavelength of absorbance was 558 nm.

Considering the behaviors of fluorescence and absorption spectra, the turn-on response of probes 1–3 may be explained by the spirocycle open–close mechanism [18,19]. It was concluded that the free probes are in the spirocyclic form, which is colorless and non fluorescent, whereas the coordination of Cu^{2+} or Hg^{2+} induced the N atom of spirolactam to attack the C atom of carbonyl, and thus a ring opening of the spirolactam of rhodamine took place (Scheme 2). This reaction procedure was not complete quickly like Cu^{2+} , as the absorption and fluorescence intensity increased until the reaction time prolonged over 5 h. The



Scheme 2. Proposed mechanism for the fluorescence enhancement of TPARH1 upon the addition of Cu^{2+} and Hg^{2+} .

observation inferred a process between metal and ligand interaction and metal mediated hydrolysis of the spirolactam ring at the same time [20]. However, the mechanistic approach for understanding this process properly in rhodamine based signaling probes remains elusive.

4. Conclusion

In summary, we have successfully synthesized three multi-branched TPARH1, TPARH2 and TPARH3 compounds containing triphenylamine core and rhodamine hydrazone arms. The excellent colorimetric and fluorescent response to Cu^{2+} in aqueous CH_3CN can be conveniently detected even by the naked eye, which provides a facile method for visual detection of Cu^{2+} . In addition, the mixed aqueous EtOH medium had shown here to promote Hg^{2+} selectivity in these probes as reflected by their signaling responses. For fluorescent sensory rhodamine derivatives, the cooperative effects of multi-branched structures could amplify the signal compared with its monobranched counterparts.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2013.06.041>.

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