Electronic Supplementary Material

A reversible fluorescent chemosensor for the rapid detection of mercury ions (II) in water with high sensitivity and selectivity

YuanRong Zhu, Hui Li, BingBing Shi, WenJuan Qu, YouMing Zhang, Qi Lin, Hong Yao, TaiBao Wei*

E-mail: weitaibao@126.com

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070. P. R. China

CONTENTS

1. General Methods: Fresh double distilled water was used throughout the experiment. All reagents and solvents were commercially available at analytical grade and were used without further purification. ^{1}H NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 150 MHz. Chemical shifts are reported in ppm down field from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X-4 digital melting-point apparatus. Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Mass spectra was recorded on an esquire 6000 MS instrument equipped with an electrospray (ESI) ion source and version 3.4 of Bruker Daltonics Data Analysis as the data collection system.

All fluorescence spectra were recorded on a Shimadzu RF–5301 fluorescence spectrometer after the addition of perchlorate metal salts in water, while keeping the ligand concentration constant (2.0×10^{-5}M). The excitation wavelength was 343 nm. Solutions of metal ions were prepared from the perchlorate salts of Fe^{3+}, Ag^{+}, Hg^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+} and Mg^{2+}.

For ^{1}H NMR titrations, two stock solutions were prepared in

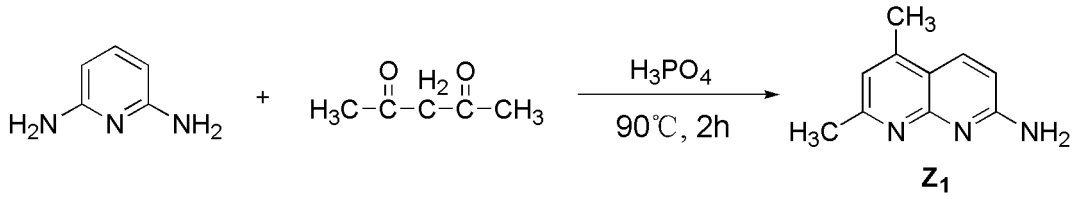
DMSO-d_6, one containing the sensor $\mathbf{Z_1}$ and the second containing an appropriate concentration of the metal ion. Aliquots of the two solutions were mixed directly in NMR tubes.

2. Determination of association constant

The association constants (Ka) were calculated based on\x the fluorescent titration curve of the probes with ions. Association constants were determined by a nonlinear least squares fit of the data with the following equation as referenced elsewhere.[1] Where **x** is $I\text{-}I_o/I_{max}\text{-}I_o$, **y** is the concentration of metal ions, **a** is the association constant, and **b** is the concentration of sample.

$$y = (x/(2\times a\times b\times(1-x)^2) + ((x\times b)/2)$$

3. Synthesis of sensor $\mathbf{Z_1}$



Scheme S1 Synthesis of the sensor molecule $\mathbf{Z_1}$.

A mixture of 2, 4-pentanedione (0.50 mL, 4.85 mmol) and 2, 6-diaminopyridine (0.50 g, 4.58 mmol) in phosphoric acid (2.50 mL) were heated at reflux for 2 hours. After cooling to room temperature, the resulting mixture was neutralized; the solid formed was collected by vacuum filtration, and washed with cool water (3×5mL) and dried in vacuo. The crude product was

recrystallized from ethanol by slow evaporation to give a pale yellow solid. Yield: 0.33g (41%); m.p: 226-227 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 6.87 (s, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 5.00 (s, 2H), 2.58 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.96, 159.68, 156.94, 145.42, 135.08, 120.35, 115.80, 111.97, 25.85, 18.34; IR (KBr, cm^{-1}) *v*: 3398, 3310 (-NH_2), 1641 (C=N); ESI-MS m/z: $(M+H)^+$ Calcd for $C_{10}H_{11}N_3$ 174.0987; Found 174.0970; Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26; Found C 69.27; H, 6.58; N, 24.15.

4. ^{13}C NMR spectra of compound Z_1

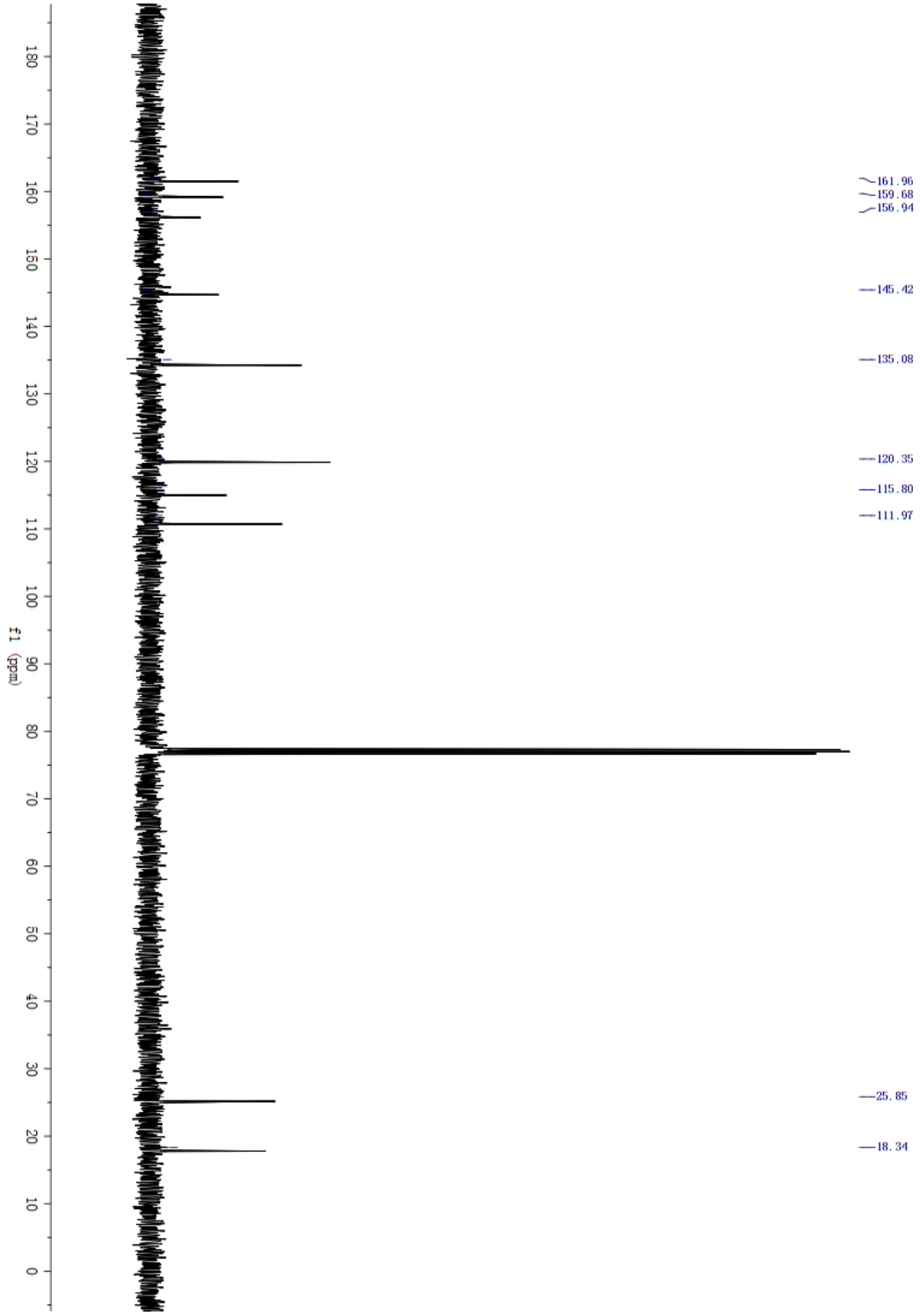


Figure S1 ^{13}C NMR spectra of compound $\mathbf{Z_1}$.

5. The single-crystal structures of the sensor Z_1

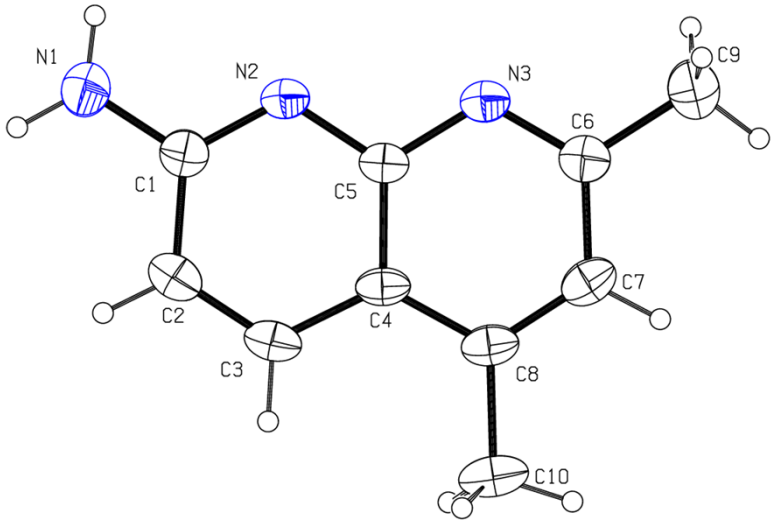


Figure S2 Single-crystal X-ray structure of sensor $\mathbf{Z_1}$.

6. The UV–vis spectroscopy of Z_1 with Hg^{2+}

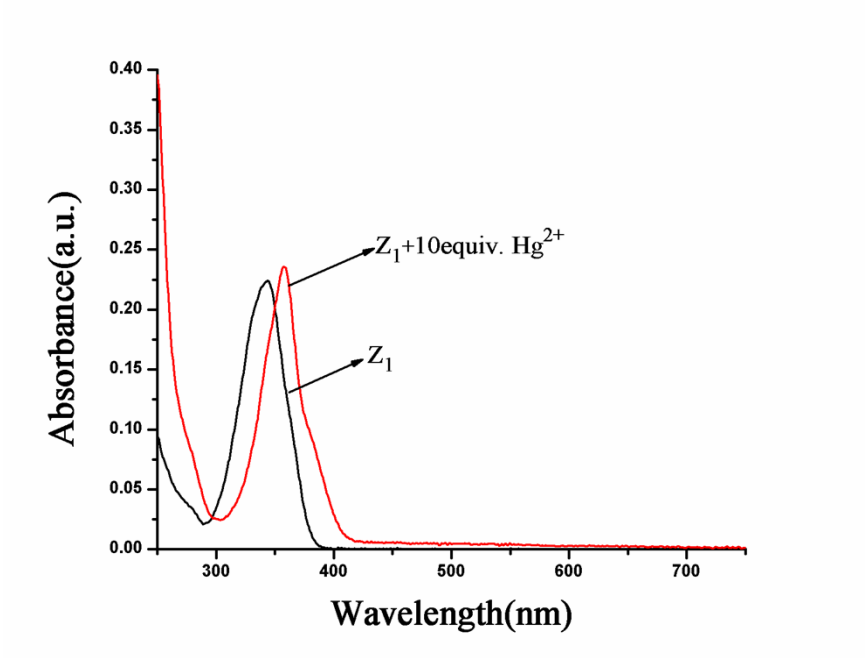


Figure S3 UV-vis spectra of compound $\mathbf{Z_1}$ (20 μM) in water upon addition of 10 equiv. of Hg^{2+}.

7. The Fluorescence Responses of Z_1 with Metal ions

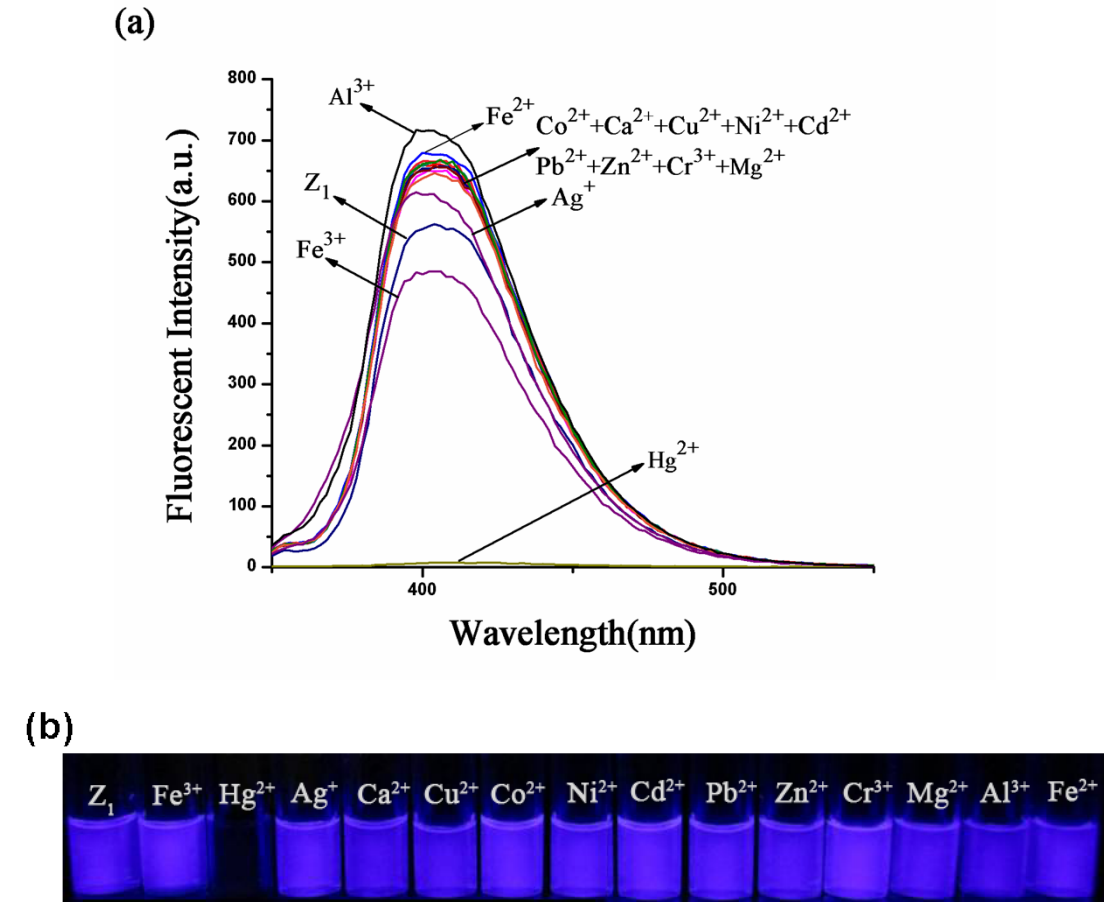


Figure S4 (a) Fluorescence emission data for a 1:10 mixture of $\mathbf{Z_1}$ (20 μM) and different metal ions, as their perchlorate salts, in water. (λ_{ex} = 343 nm). (b) Visual fluorescence emissions of sensor $\mathbf{Z_1}$ after the addition of various metal ions (10 equiv.) in water on excitation at 365 nm using UV lamp.

8. Time-dependent Fluorescence Change of Z_1 with Hg^{2+}

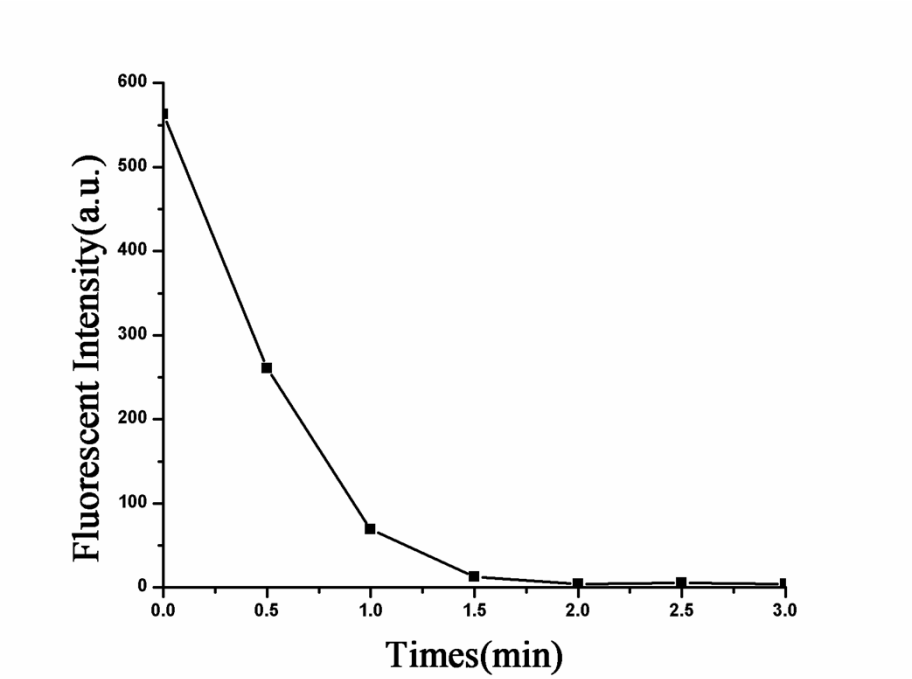


Figure S5 Time-dependent fluorescence change of $\mathbf{Z_1}$ (20 μM) in the presence of 10 equiv. of Hg^{2+} in water. Fluorescence intensity changes: each spectrum was recorded after 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3 minutes.

9. A plot of fluorescence intensity Change of Z_1 with Hg^{2+}

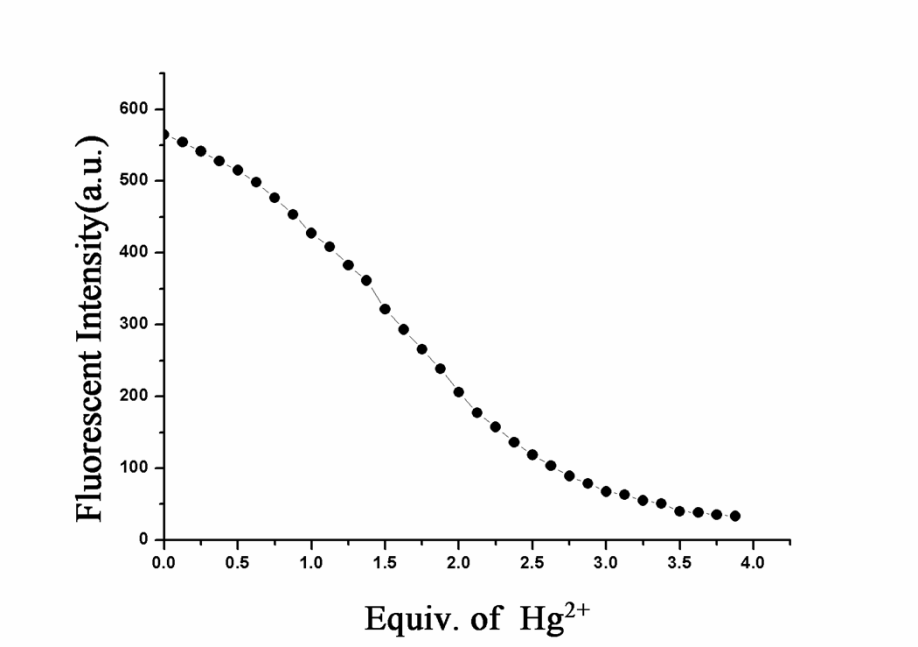


Figure S6 A plot of fluorescence intensity depending on the concentration of Hg^{2+} in the range from 0 to 5.28 equivalents.

10. Fitting curve of emission intensity with concentration

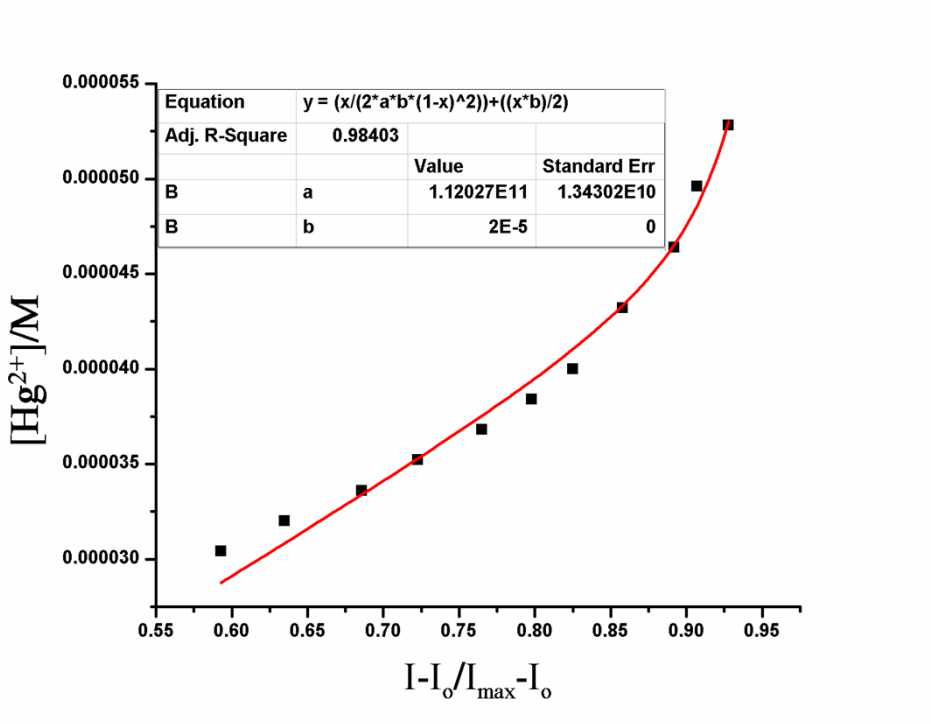


Figure S7 Non-linear least square fitting of intensity vs concentration of Hg^{2+} using 2:1 complex model.

11. Determination of Detection Limit of Hg^{2+}

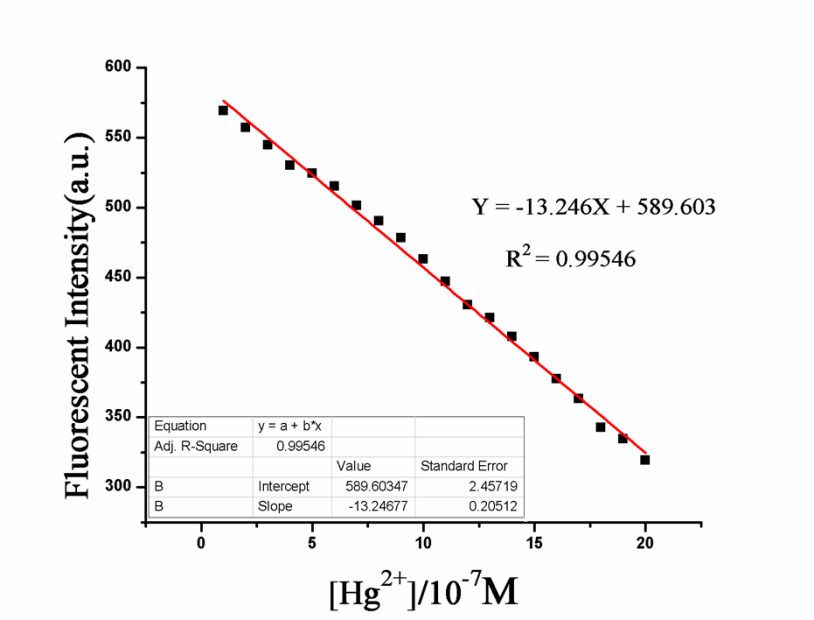


Figure S8 Plot of the intensity at 402 nm for a mixture of $\mathbf{Z_1}$ and Hg^{2+} in water in the range $1.0 \times 10^{-7} – 2.0 \times 10^{-6}$ M (λ_{ex}= 343 nm).

Linear Equation: $Y = -13.246 \times X + 589.603$, $R^2 = 0.99546$

$$K = 3\sqrt{\frac{\sum (F_0 - F_1)^2}{N - 1}}$$

$S = 1.324 \times 10^7$ δ= = 0.391 (N = 10)

$LOD = K \times \delta / S$

$LOD = 8.859 \times 10^{-8}$ M

F_0 is the fluorescence intensity of $\mathbf{Z_1}$; F_1 is the average of the F_0.

12. Influence of pH on Z_1 and Hg^{2+}

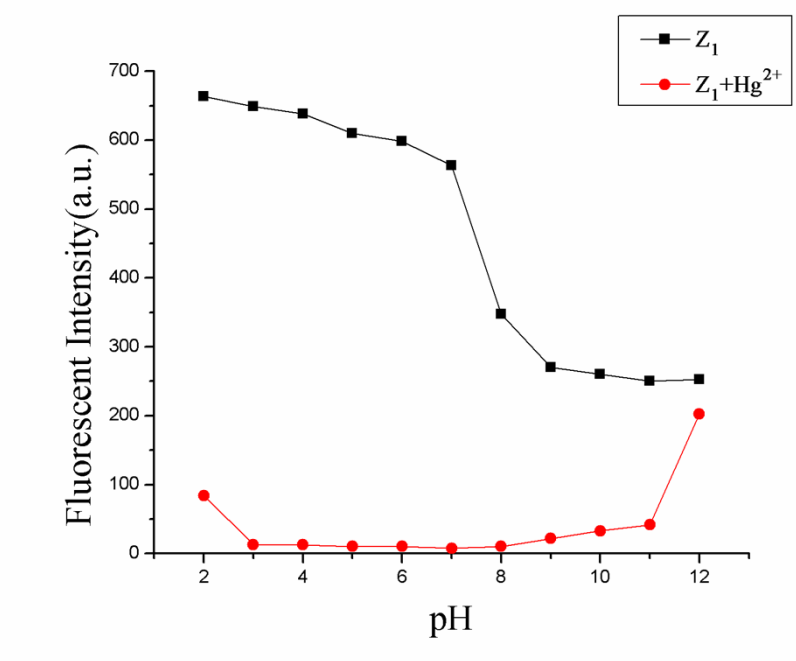


Figure S9 Influence of pH on the fluorescence of $\mathbf{Z_1}$ and $\mathbf{Z_1}$+Hg^{2+}in HEPES buffered solution in water.

13. The response of Z_1 to heavy metal ions in the pH range of 6.0 to 7.0

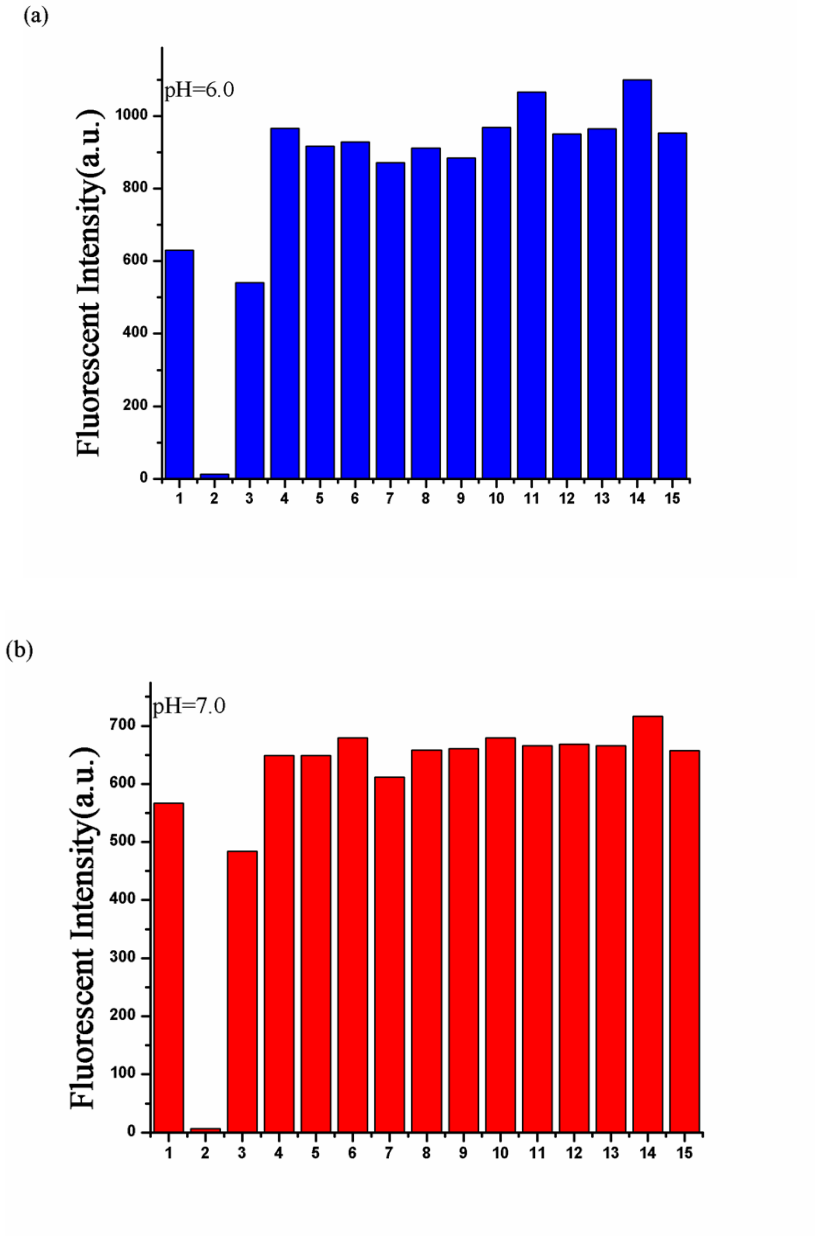


Figure S10 The response of $\mathbf{Z_1}$ to heavy metal ions in the pH range of 6.0 to 7.0. Left to Right: (1)only $\mathbf{Z_1}$, (2)$\mathbf{Z_1}$+Hg^{2+} (3) $\mathbf{Z_1}$+Fe^{3+} (4) $\mathbf{Z_1}$+ Ca^{2+} (5) $\mathbf{Z_1}$+ Cu^{2+} (6) $\mathbf{Z_1}$+ Fe^{2+} (7) $\mathbf{Z_1}$+ Ag^{+} (8) $\mathbf{Z_1}$+ Cd^{2+} (9) $\mathbf{Z_1}$+ Pb^{2+} (10) $\mathbf{Z_1}$+ Zn^{2+} (11) $\mathbf{Z_1}$+ Cr^{3+} (12) $\mathbf{Z_1}$+ Mg^{2+} (13) $\mathbf{Z_1}$+ Co^{2+} (14) $\mathbf{Z_1}$+ Al^{3+} (15) $\mathbf{Z_1}$+ Ni^{2+}.

14. The response of Z_1 to heavy metal ions in the pH range of 8.0 to 9.0

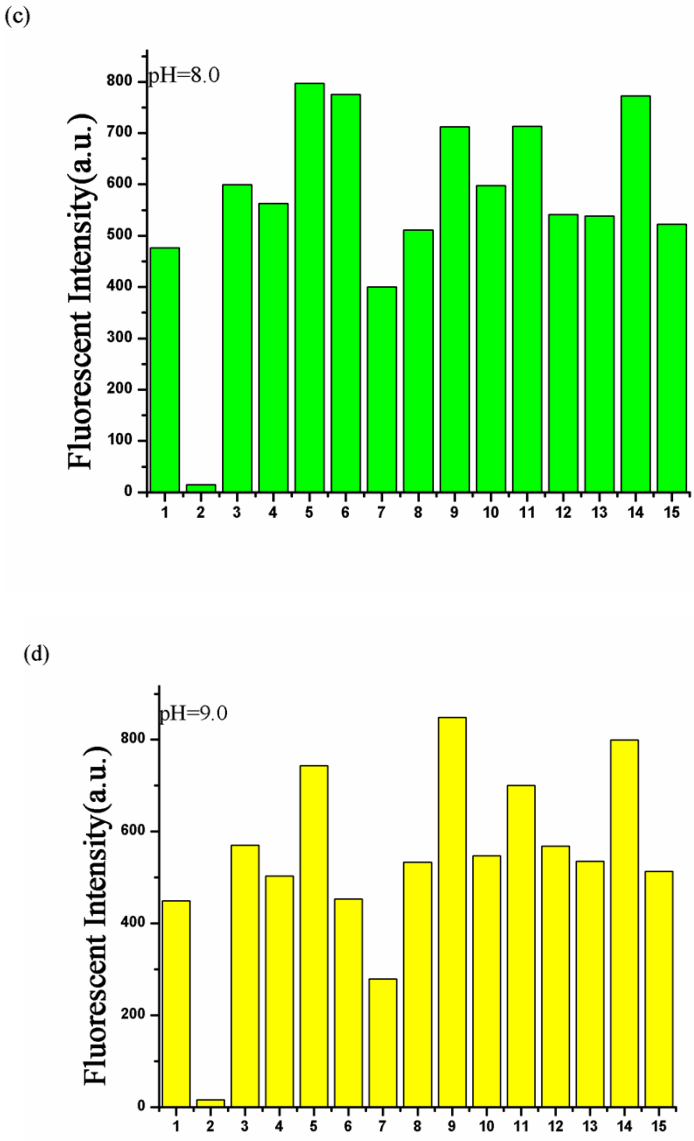


Figure S11 The response of $\mathbf{Z_1}$ to heavy metal ions in the pH range of 8.0 to 9.0. Left to Right: (1)only $\mathbf{Z_1}$, (2)$\mathbf{Z_1}$+Hg^{2+} (3) $\mathbf{Z_1}$+Fe^{3+} (4) $\mathbf{Z_1}$+ Ca^{2+} (5) $\mathbf{Z_1}$+ Cu^{2+} (6) $\mathbf{Z_1}$+ Fe^{2+} (7) $\mathbf{Z_1}$+ Ag^{+} (8) $\mathbf{Z_1}$+ Cd^{2+} (9) $\mathbf{Z_1}$+ Pb^{2+} (10) $\mathbf{Z_1}$+ Zn^{2+} (11) $\mathbf{Z_1}$+ Cr^{3+} (12) $\mathbf{Z_1}$+ Mg^{2+} (13) $\mathbf{Z_1}$+ Co^{2+} (14) $\mathbf{Z_1}$+ Al^{3+} (15) $\mathbf{Z_1}$+ Ni^{2+}.

15. IR spectra of compound Z_1 and Z_1+Hg^{2+}

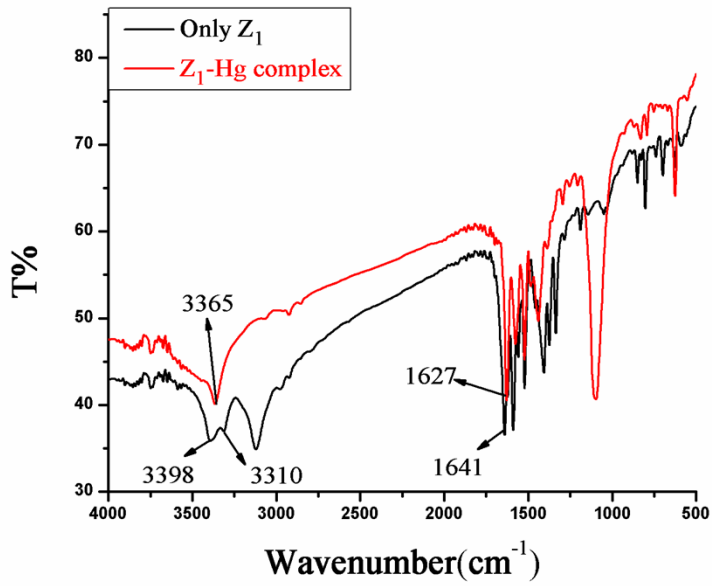


Figure S12 IR spectra of compound $\mathbf{Z_1}$ and $\mathbf{Z_1}$+Hg^{2+} complex in KBr disks.

16. ESI-MS spectrum of Z_1

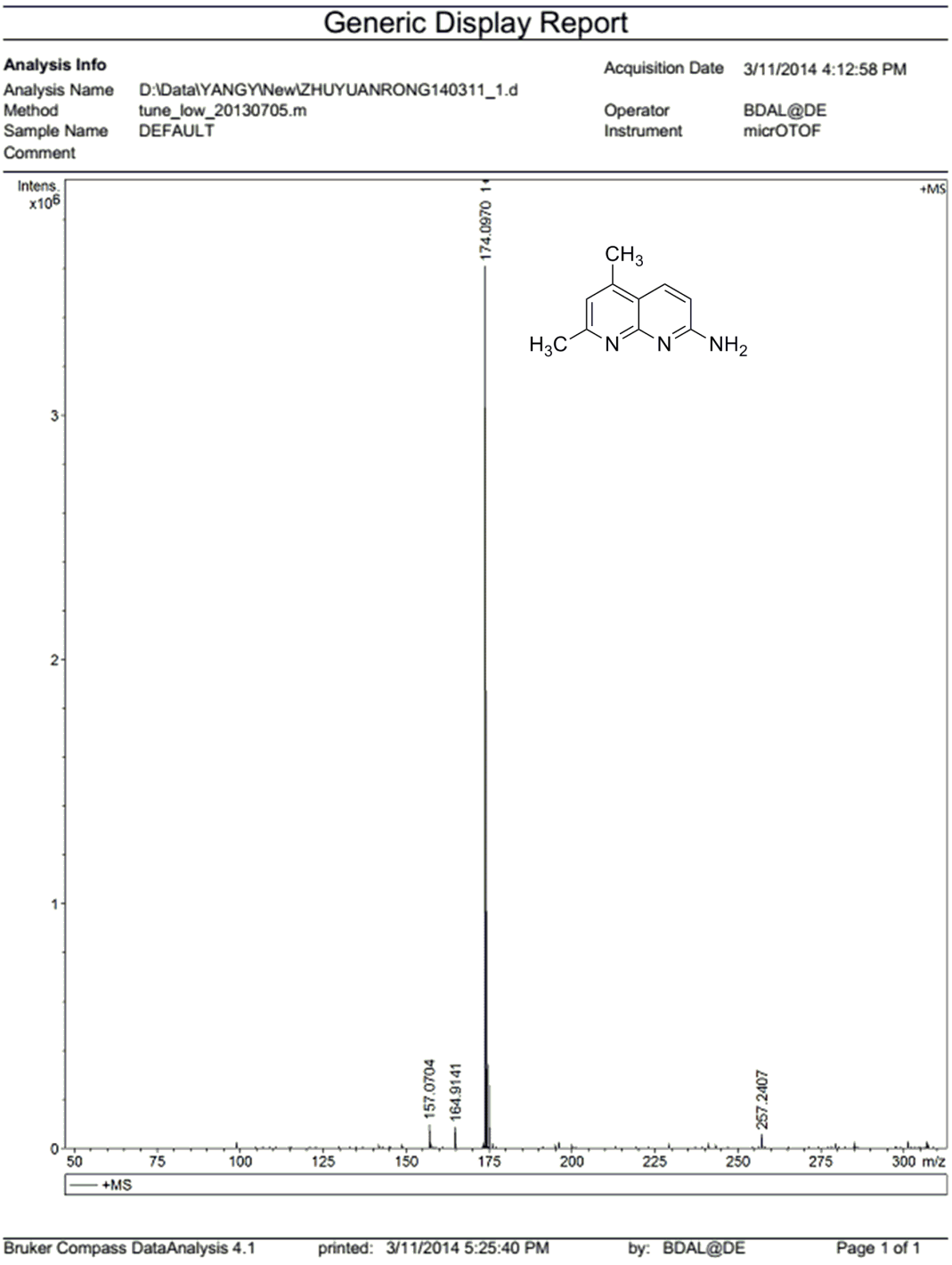


Figure S13 ESI-MS spectrum of $\mathbf{Z_1}$.

17. ESI-MS spectrum of Z_1+Hg^{2+} complex

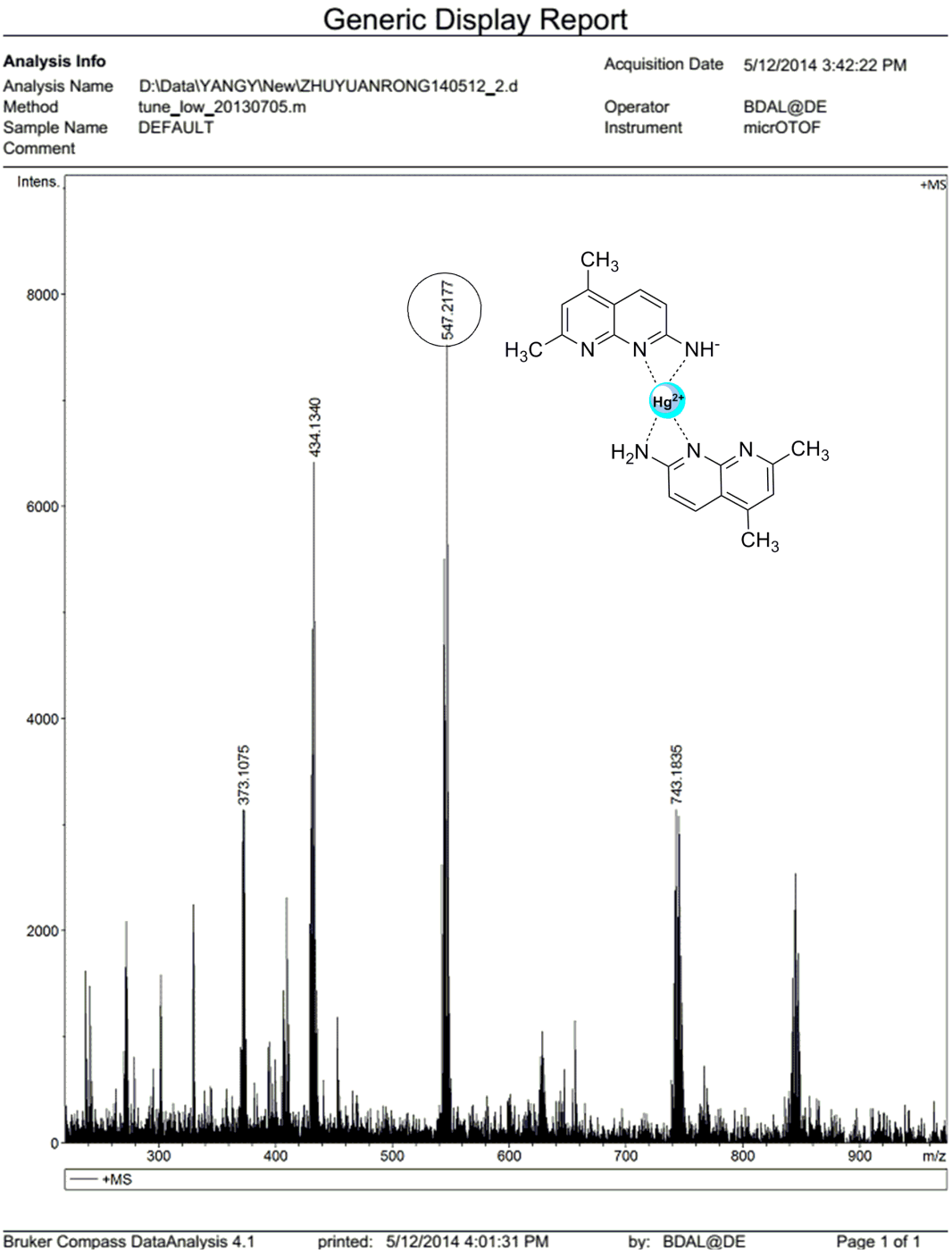


Figure S14 ESI-MS spectrum of Z_1+Hg^{2+} complex.

18. The Fluorescence Intensity Changes of Z_1 in the Presence of $Hg^{2+}$and Br^-

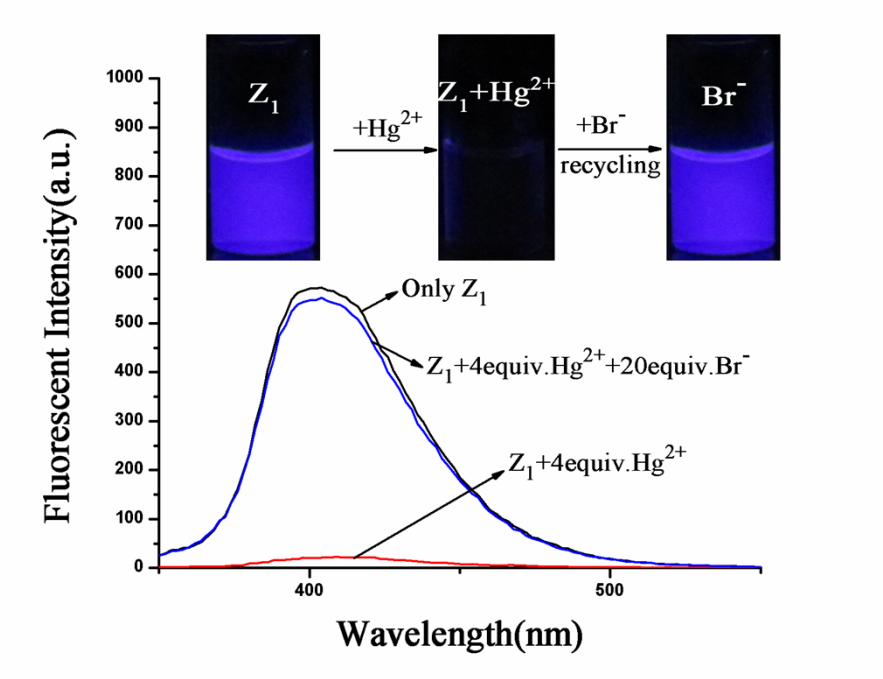


Figure S15 Fluorescence emission spectra of $\mathbf{Z_1}$ (20 μM) in the presence of Hg^{2+} (4 equiv.) or Br^- (20 equiv.) in water (PH=7.0). The excitation wavelength was 343nm. Inset: photograph from left to right shows the change in the fluorescence of only $\mathbf{Z_1}$, $\mathbf{Z_1}$+Hg^{2+} (4 equiv.) and $\mathbf{Z_1}$+Hg^{2+} (4 equiv.) plus Br^- (20 equiv.) in water (PH=7.0) on excitation at 365 nm.

References

1 M. H. Yang, P. Thirupathi and K. H. Lee, *Org. Lett.*, 2011, **13**, 5028.