Supporting Information
Highly Sensitive and Selective Turn-on Fluorescent Chemosensor for Pb^{2+} and Hg^{2+} Based on Rhodamine-phenylurea conjugate

Zhi-Qiang Hu, *[†]Cun-sheng Lin, [†] Xiao-Ming Wang, [†] Lei Ding, [†] Cun-Li Cui, [†] Shu-Feng Liu*[†] and Hai-Yan Lu*[‡]

[†]*College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*

[‡] *College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, China.*

huzhiqiang@iccas.ac.cn; haiyanlu@gucas.ac.cn

Contents

1. Apparatus and reagents

A Hitachi F-2500 spectrofluorimeter was used for fluorescence measurements. The absorption spectra were recorded with a Techcomp UV-8500 spectrophotometer (Shanghai, China). NMR spectra were measured on a Bruker DMX-500 spectrometer at 500 MHz in CD_3COCD_3. Elemental analyses were carried out with a Flash EA 1112 instrument. A Delta 320 pH-meter [Mettler-Toledo Instruments (Shanghai) Co., China] was used for pH measurements. All other chemicals used were local products of analytical grade. The solutions of metal ions were prepared from their perchlorate salts. All solvent used in spectrostropic test are spectrostropic grade. Distilled-deionized water

was used throughout the experiment.

2. Synthesis and structural characterization of RPU

Rhodamine B (0.88g, 2mmol) was refluxed in $POCl_3$(15mL) for 4h, and concentrated by evaporation. The obtained crude acid chloride was dissolved in $ClCH_2CH_2Cl$(20mL). NH_3 was pumped into the acid chloride solution until the reaction ended. Water was added to the resultant, and the aqueousphase was extracted with $ClCH_2CH_2Cl$. The organic layer was washed with water twice, dried over Na_2SO_4, and concentrated by evaporation. The residue was dissolved in dry toluene, PhNCO (2mL, 18.4mmoL) was added dropwise. At the end of the addition, the mixture was refluxed for 4 hrs. After the solent was removed by evaporation, the residue was purified by silica gel column chromatography with EtOAc/Cyclohexane (1/40, v/v) as eluent, affording **RPU** as a white solid 0.53g, yield 47%. m.p.: 198-200°C. ^{1}H NMR(CD_3COCD_3, 500MHz, TMS) : δ = 1.14(t, *J* = 7Hz, 12H); 3.38(q, *J* = 7Hz, 8H); 6.30(d, *J* = 7.5Hz, 2H); 6.40 (s, 2H); 6.48(d, *J* = 7.5Hz, 2H); 7.00 (t, *J* = 7.5Hz, 1H); 7.13 (d, *J* = 7.5Hz, 1H); 7.24 (t, *J* = 7.5Hz, 2H); 7.46 (d, *J* = 8Hz, 2H); 7.64 (t, *J* = 8Hz, 1H); 7.72 (t, *J* = 7Hz, 1H); 8.02 (d, *J* = 8Hz, 1H); 10.92 (s, 1H). ^{13}C NMR(CD_3COCD_3, 250MHz, TMS) : δ 169.9, 154.0, 153.4, 148.7, 148.4, 138.3, 135.3, 129.0, 128.9, 128.7, 127.4, 124.5, 123.7, 123.3, 119.1, 107.3, 107.1, 97.7, 65.9, 44.0, 12.0. ESI-MS 561.4 $[M + H]^+$; Anal. Cacld for $C_{35}H_{36}N_4O_3$: C, 74.98; H, 6.47; N, 9.99; Found: C, 74.47; H, 6.65; N, 9.82.

2. Synthesis and structural characterization of RPTU

Through the similar way, RPTU can be synthesized as a yellow solid in 54% yield. m.p.: 194-195°C. ^{1}H NMR(CD_3COCD_3, 500MHz, TMS) : δ = 1.14(t, *J* = 7.0Hz, 12H); 3.37(q, *J* = 7.0Hz, 8H); 6.29(d, *J* = 9.0Hz, 2H); 6.35 (s, 2H); 6.49(d, *J* = 8.0Hz, 2H); 7.03 (d, *J* = 8.0Hz, 1H); 7.16(t, *J* = 7.5Hz, 1H); 7.31 (t, *J* = 7.5Hz, 2H); 7.63-7.59 (m, 3H); 7.69 (t, *J* = 7.5Hz, 1H); 8.02 (d, *J* = 7.5Hz, 1H); 13.05 (s, 1H). ^{13}C NMR(CD_3COCD_3, 250MHz, TMS) : δ 176.7, 170.8, 155.1, 153.1, 148.7, 138.7, 135.4, 128.8，128.5, 127.1, 127.0, 125.7, 124.6, 124.0, 123.9, 107.6, 107.3, 97.4, 69.6, 44.0, 12.1. ESI-MS 577.4 $[M + H]^+$; Anal. Cacld for $C_{35}H_{36}N_4O_2S$: C, 72.89; H, 6.29; N, 9.71; Found: C, 72.67; H, 6.43; N, 9.56.

3. General procedure for Pb^{2+} detection

A 1.0×10^{-3}M stock solution of compound **RPU** was prepared in CH_3CN. To 10-mL glass tubes containing different amounts of metal ions, proper amounts of the solution of **RPU** was added directly with a micropipette. The solutions were diluted with CH_3CN to 10 mL and mixed, then the absorption and fluorescence sensing of metal ions were run immediately.

4. General procedure for Hg^{2+} detection

A 1.0×10^{-3}M stock solution of compound **RPU** was prepared in CH_3CN. To 10-mL glass tubes containing different amounts of metal ions, proper amounts of the solution of **RPU** was added directly with a micropipette. The solutions were diluted with CH_3CN and H_2O to 10 mL and mixed, then the absorption and fluorescence sensing of metal ions were run immediately.

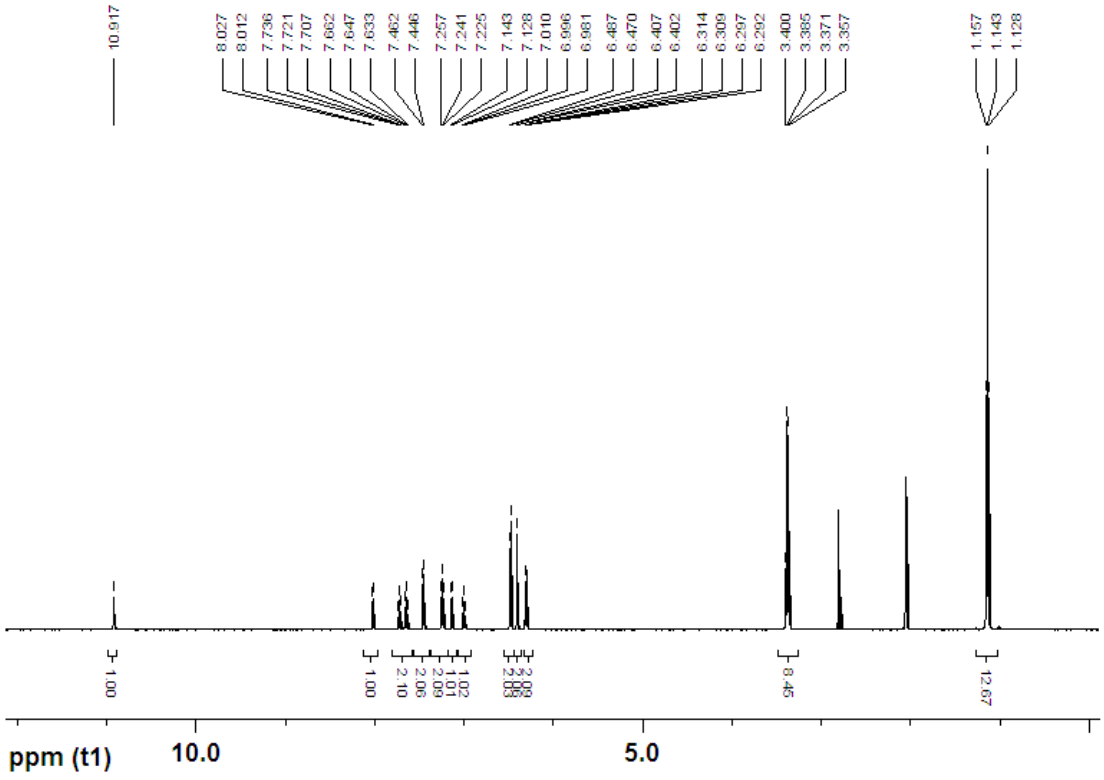

Fig. S1 ^{1}H NMR of RPU

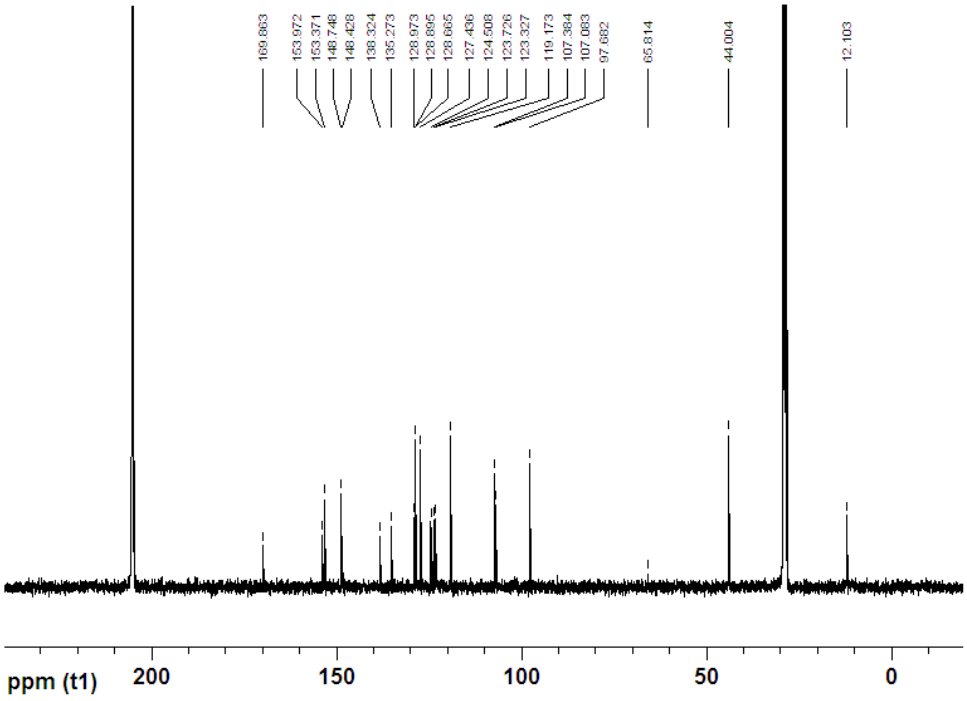

Fig. S2 ^{13}C NMR of RPU

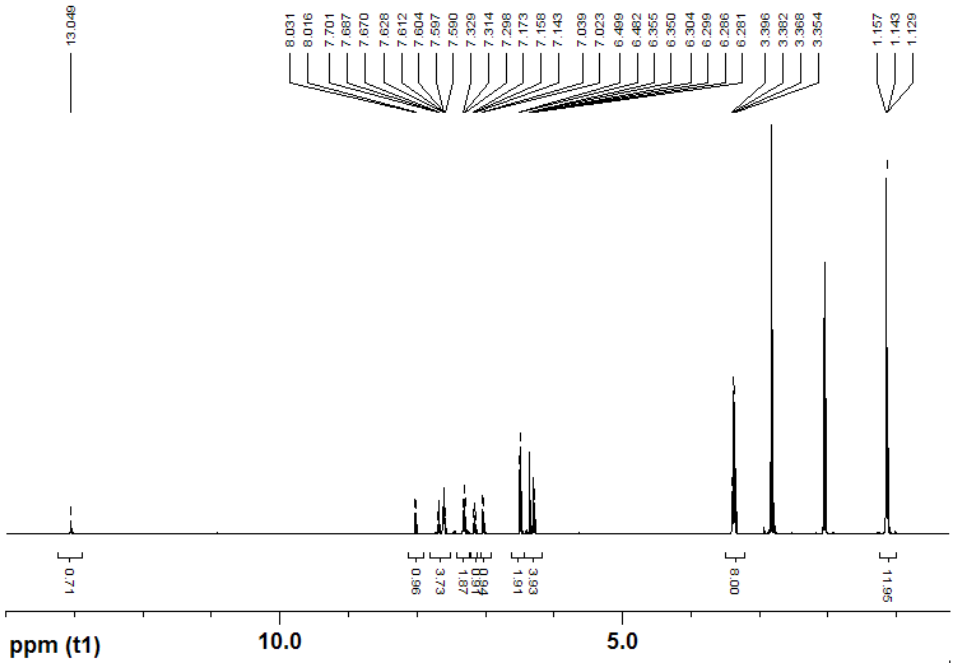

Fig. S3 ^{1}H NMR of RPTU

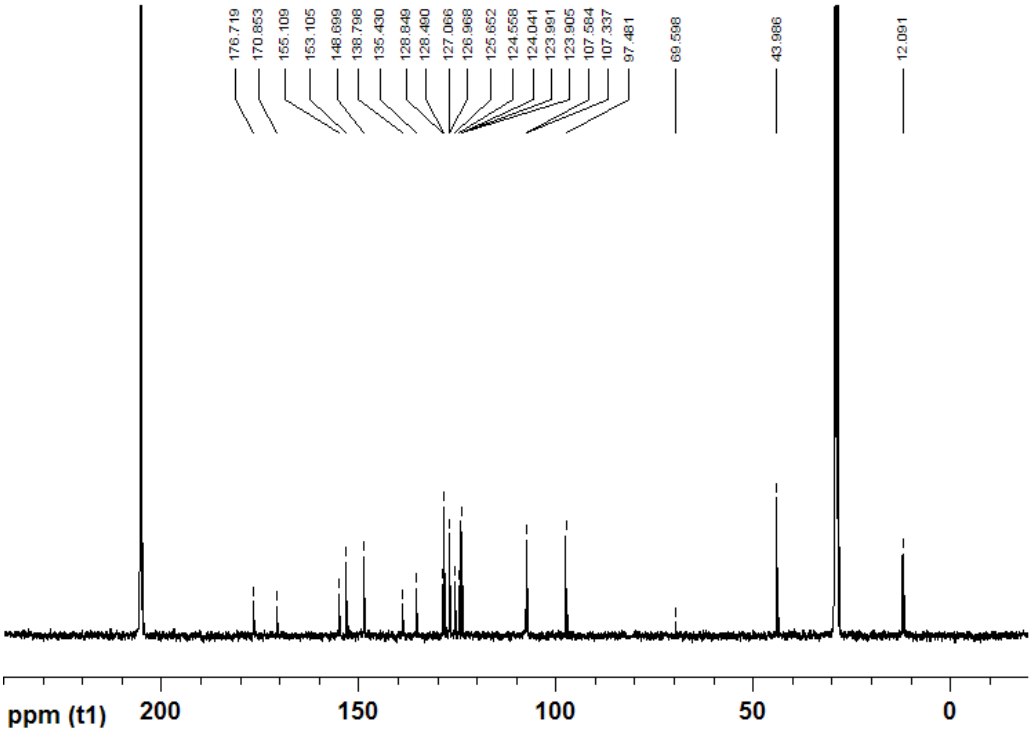

Fig. S4 ^{13}C NMR of RPTU

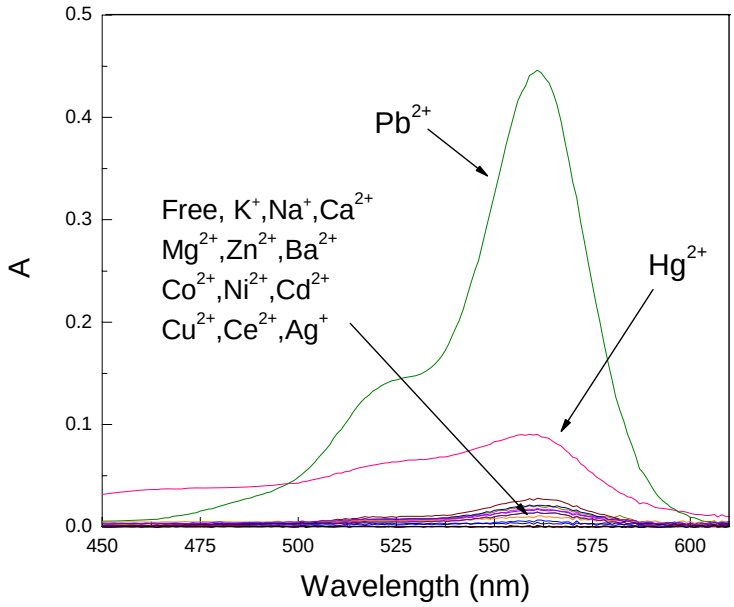

Fig. S5 Absorption spectra of **RPU** (10 μM) upon addition of respective metal ions (as perchlorate salt, 50 equiv.) inCH_3CN.

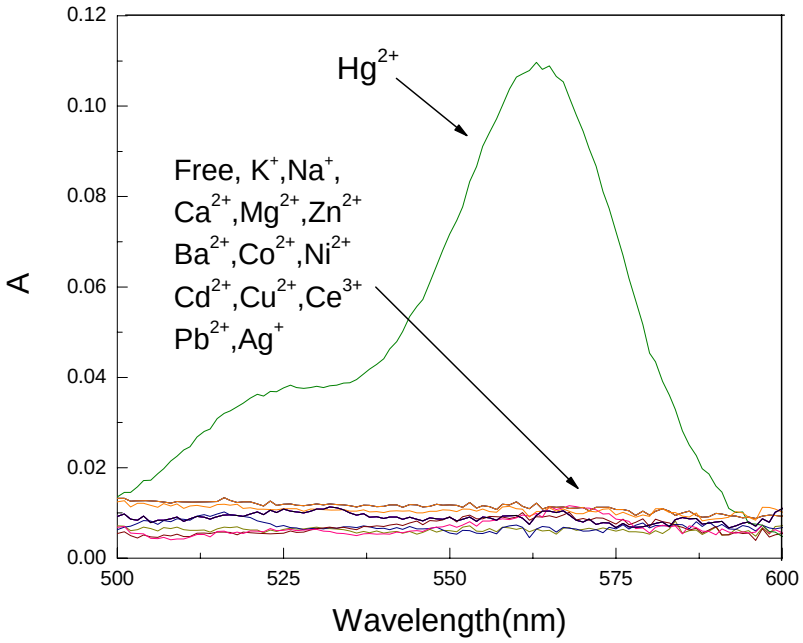

Fig. S6 Absorption spectra of **RPU** (10 μM) upon addition of respective metal ions (as perchlorate salt, 50 equiv.) inCH_3CN/H_2O (3/7, v/v).

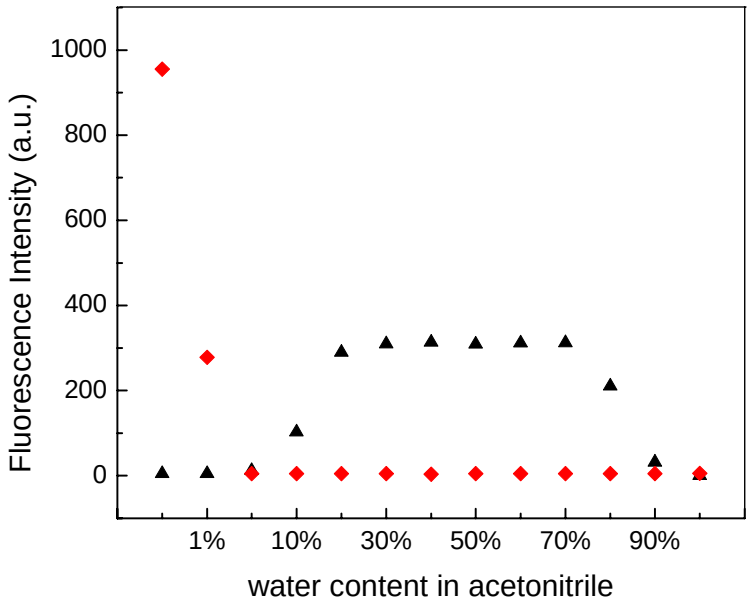

Fig. S7 Fluorescence responses of **RPU**(1μM) toward 100μM Pb^{2+} (♦)and 130μM Hg^{2+}(▲) as the function of water content in acetonitrile.

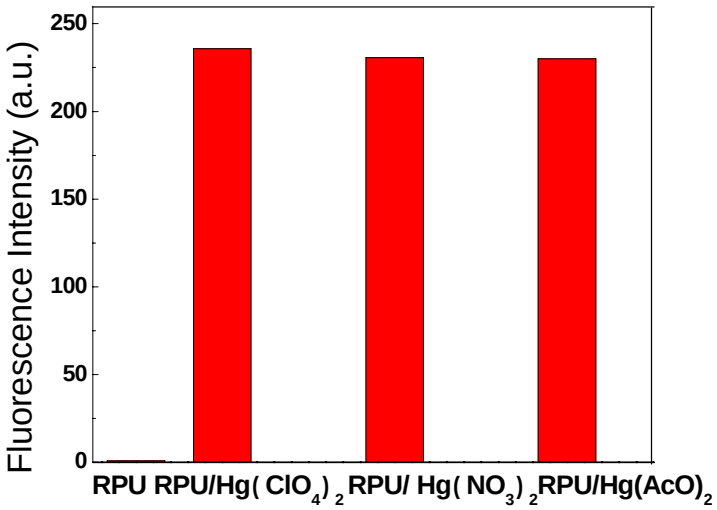

Fig. S8 Fluorescece intensity of **RPU** (1μM) in CH_3CN/H_2O upon the addition of 100 equiv $Hg(ClO_4)_2$, $Hg(NO_3)_2$ and $Hg(AcO)_2$, respectively.

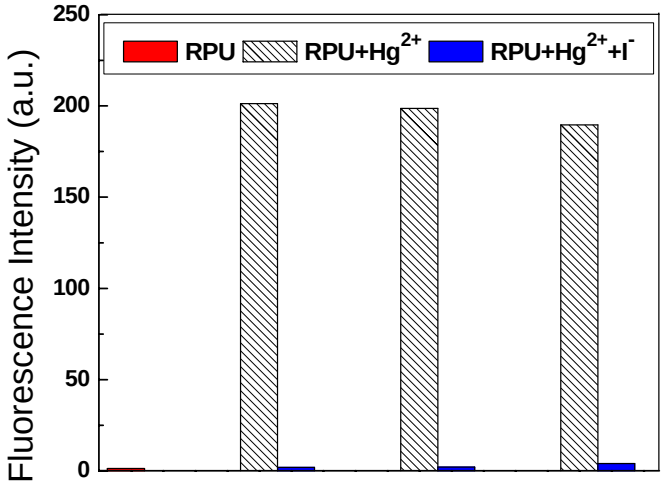

Fig.S9 The reversibility of the interaction between **RPU** in CH_3CN/H_2O (3/7, v/v) and Hg^{2+} by the introduction of I^- to the system. The red column represents the fluorescence intensity of **RPU**(1μM); the miter columns represent the fluorescence intensity of system after addition of 70μM Hg^{2+}; the blue columns representsthe fluorescence intensity of system after introduction of I^- (2 equiv to Hg^{2+}) into the system. The experiments were repeated three times.

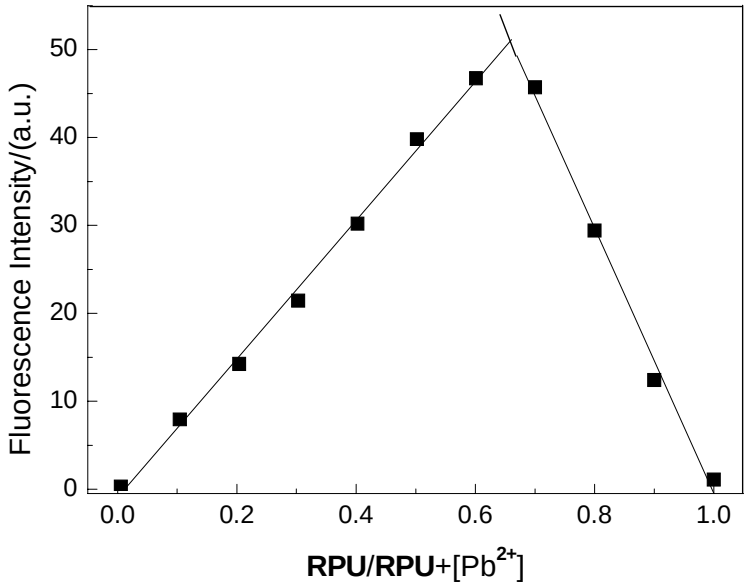

Fig.S10 Job's plot of the complex formed by **RPU/Pb**$^{2+}$

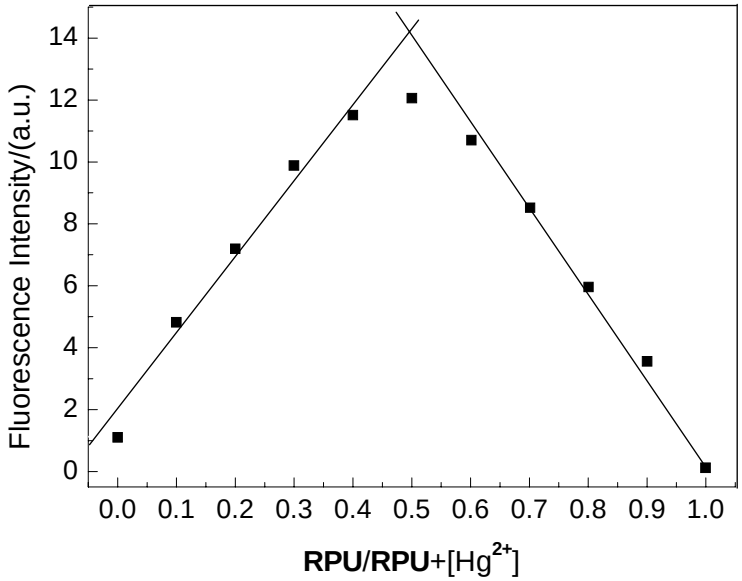

Fig. S11 Job's plot of the complex formed by **RPU/Hg**$^{2+}$

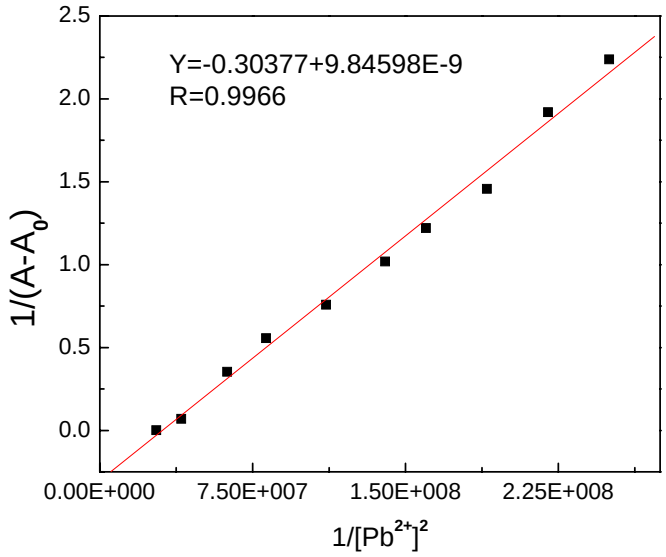

Fig. S12 Benesi-Hildebrand plot of **RPU**(1μM in CH_3CN, 560nm) assuming 2:1 stoichiometry between **RPU** and Pb^{2+}

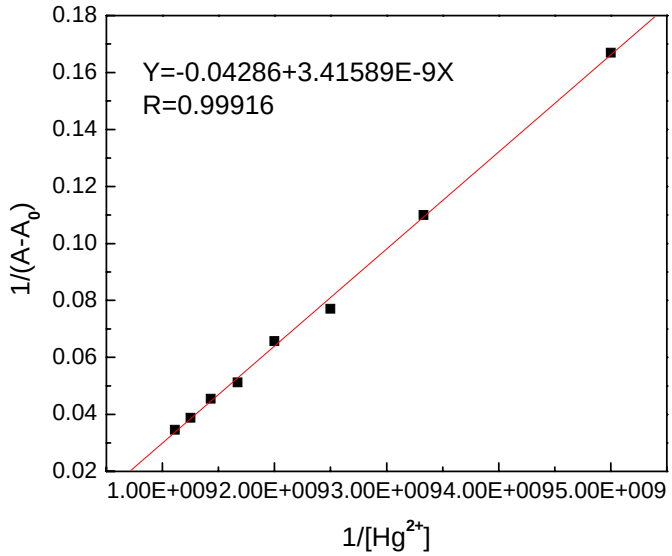

Fig. S13 Benesi-Hildebrand plot of **RPU**(1μM in CH_3CN/H_2O = 3/7 v/v, 558nm) assuming 1:1 stoichiometry between **RPU** and Hg^{2+}

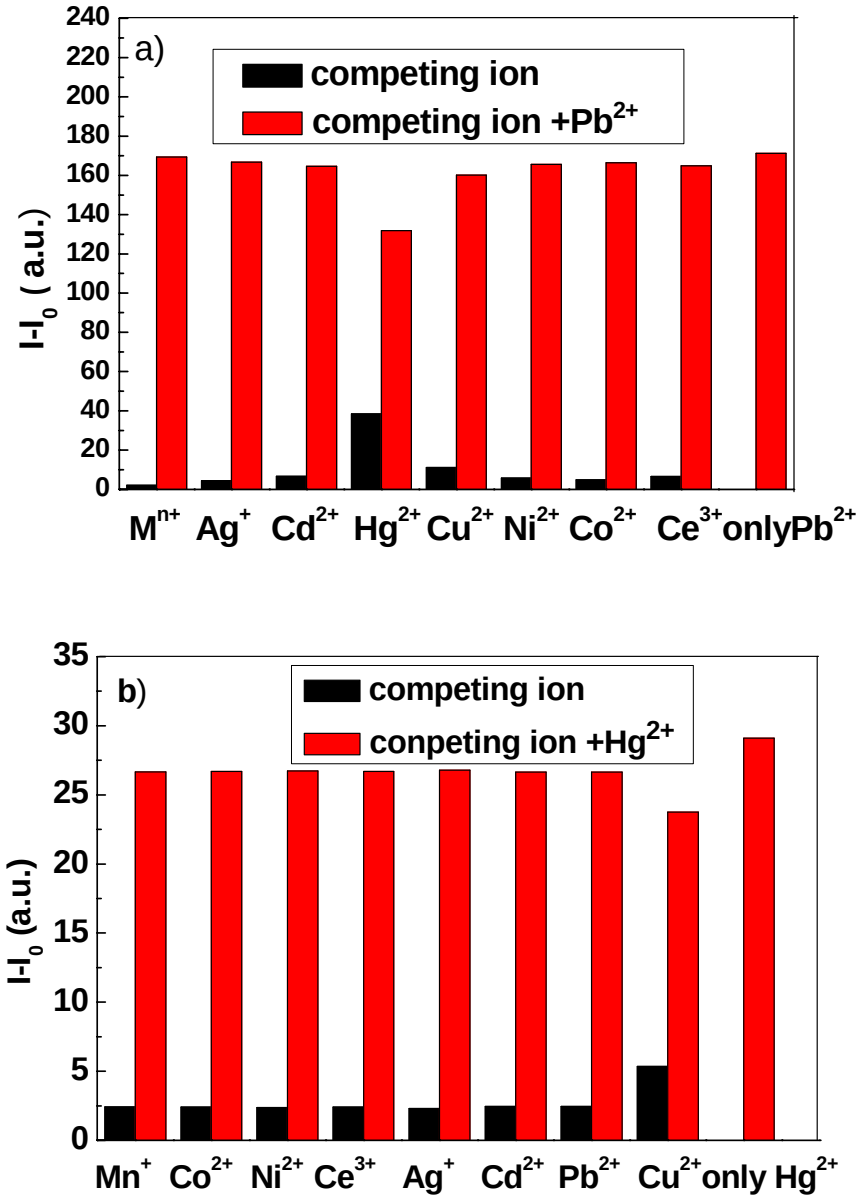

Fig.S14 Fluorescene intensity of **RPU** (1 μM) (a) upon the addition of 10 μM Pb^{2+} in the presence of 200 μM background metal ions in CH_3CN; (b) upon the addition of 30 μM Hg^{2+} in the presence of 200 μM background metal ions (M^{n+} denotes Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ba^{2+}) in CH_3CN/H_2O (3/7, v/v). λex = 530 nm.

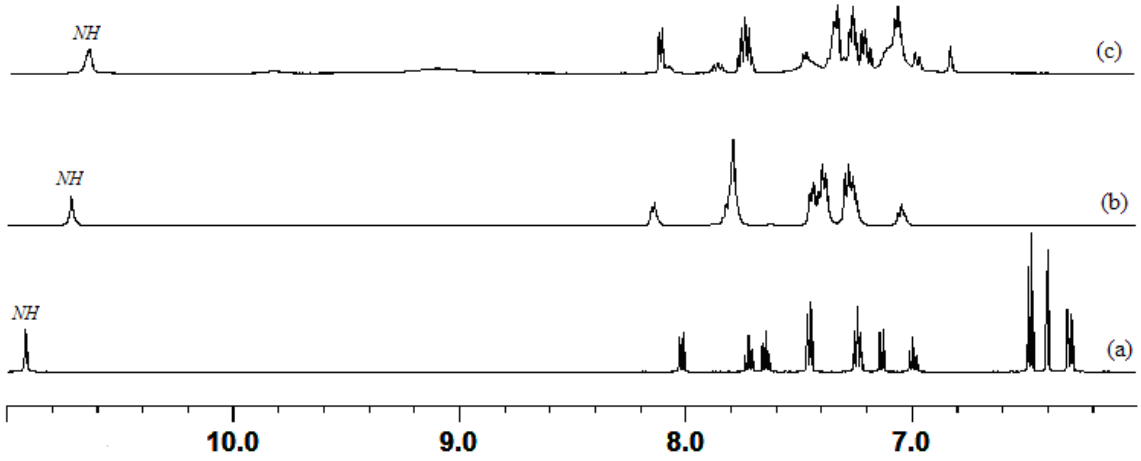

Fig. S15 Partial ^{1}H NMR spectra of (a) **RPU** in CD_3COCD_3; (b) **RPU** in CD_3COCD_3 in the presence of excess Hg^{2+}; (c) **RPU** in CD_3COCD_3 in the presence of excess Pb^{2+} ion.

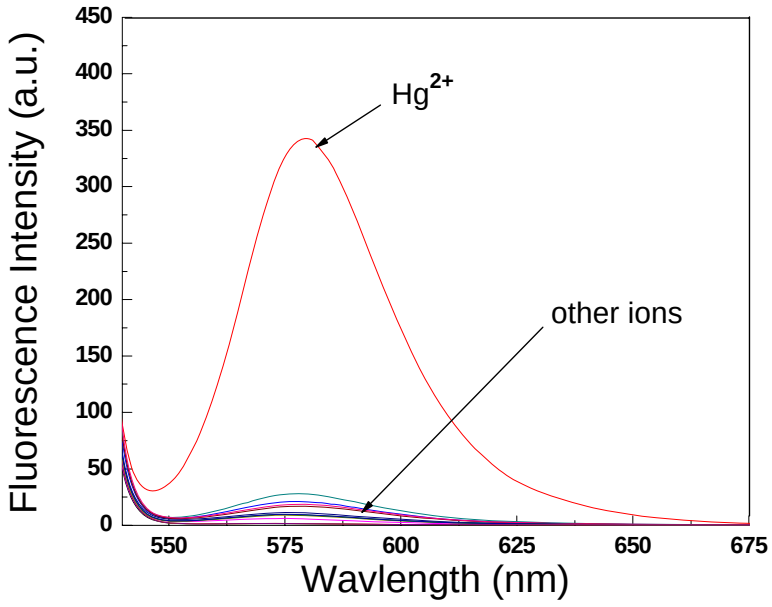

Fig. S16 Fluorescence intensity of **RPTU** (0.1μM) in CH_3CN upon the addition of 20 equiv Hg^{2+} and 100 equiv other metal ions ((Pb^{2+}, Mg^{2+}, Ce^{3+}, Cd^{2+}, Na^{+}, Cu^{2+}, K^{+}, Ag^{+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Ba^{2+} and Ca^{2+})

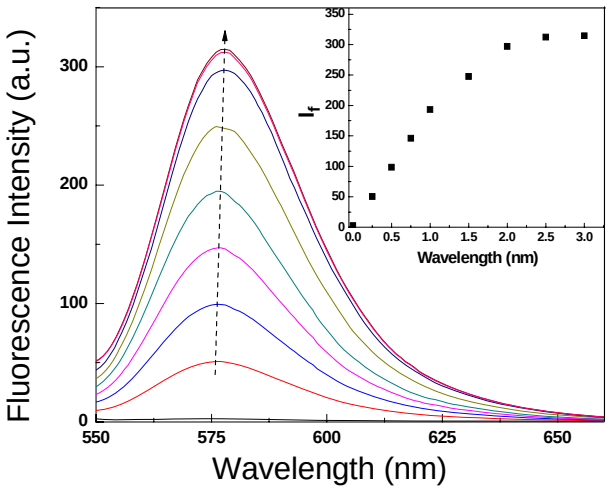

Fig. S17 Fluorescence (λex = 530 nm) titration spectra of **RPTU** (0.1 μM) with Hg^{2+} (0-3 μM) in CH_3CN

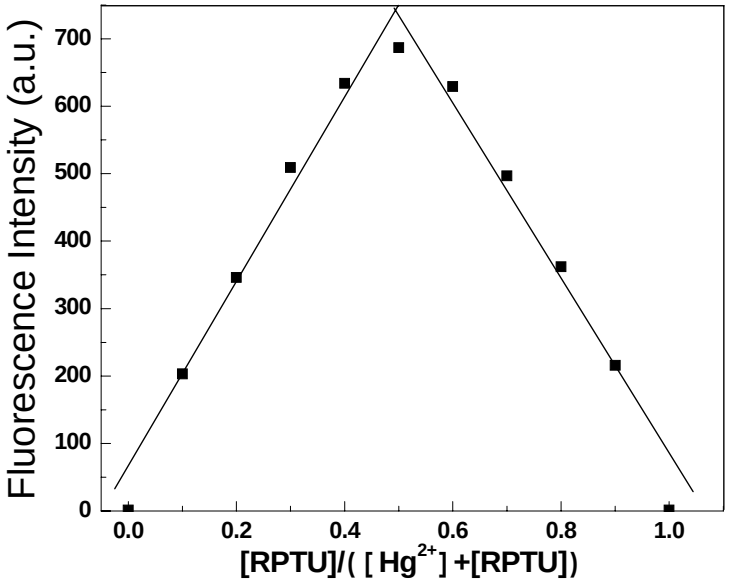

Fig. S18 Job's plot of the complex formed by **RPTU/Hg^{2+}**

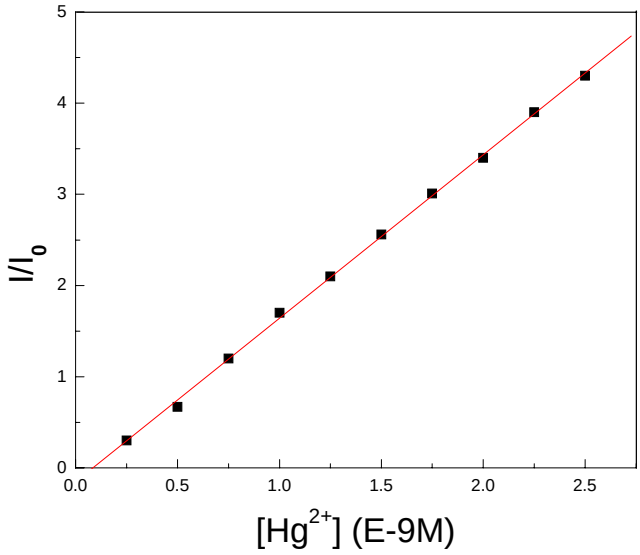

Fig.S19 An assay of **RPTU**(0.01 μM) for Hg^{2+}in CH_3CN ; λex = 530 nm.