Supporting Information for

A naphthalimide-based bifunctional fluorescent probe for the differential detection of Hg^{2+} and Cu^{2+} in aqueous solution

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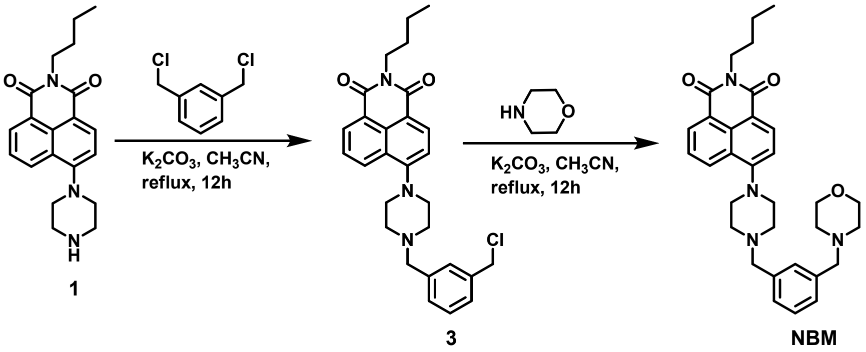
Contents:

1. Synthesis of model compounds NBM and NPP

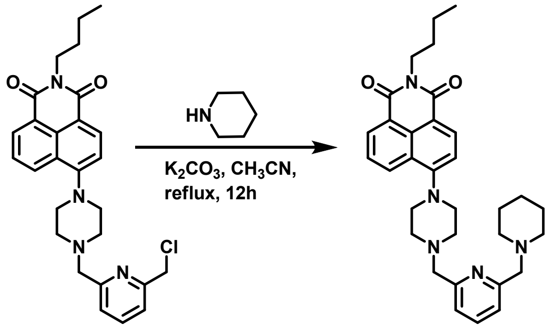


Scheme S1 Synthesis of **NBM**

Compound **1** was prepared according to our previously reported methods (*Dalton Trans.*, 2012, **41**, 7212).

Compound 3. Anhydrous potassium carbonate (276 mg, 2 mmol), compounds **1** (337 mg, 1 mmol) and 1,3-bis(chloromethyl)benzene (1750 mg, 10 mmol) were dissolved in acetonitrile (10 mL), and the reaction mixture was refluxed for 12h under argon atmosphere. The mixture was filtered, and the solvent was removed in vacuum to give a yellow solid. The crude product was then chromatographed on silica gel using dichloromethane/methanol 50: 1 (v/v) as eluant to afford 409 mg (86%) **3** as yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.57 (dd, J = 7.6, 1.2 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.68 (dd, J = 8.3, 7.4 Hz, 1H), 7.44 (s, 1H), 7.41 – 7.31 (m, 3H), 7.21 (d, J = 8.1 Hz, 1H), 4.62 (s, 2H), 4.16 (t, J = 8.0 Hz, 2H), 3.71 (s, 2H), 3.33 (s, 4H), 2.83 (s, 4H), 1.73 – 1.66 (m, 2H), 1.48 – 1.39 (m, 2H), 0.96 (t, J = 8.0 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 164.50, 164.03, 137.76, 132.53, 131.09, 130.01, 129.83, 129.49, 128.94, 127.86, 126.13, 125.69, 123.31, 116.89, 115.03, 62.63, 53.07, 52.76, 46.20, 40.11, 30.27, 20.43, 13.92. EI-MS for $C_{28}H_{30}ClN_3O_2$ [M$^+$]: 475. HR-ESI-MS calcd for $C_{28}H_{31}ClN_3O_2$ [(M + H)$^+$]: 476.2009, found: 476.2114.

Compound NBM. Anhydrous potassium carbonate (138 mg, 1.0 mmol), compounds **3** (238 mg, 0.5 mmol) and morpholine (218 mg, 2.5 mmol) were dissolved in acetonitrile (8 mL), and the reaction mixture was refluxed for 12 h under argon atmosphere. The mixture was filtered, and the solvent was removed in a vacuum to give a yellow solid. The crude product was then chromatographed on silica gel using dichloromethane–methanol 40 : 1 (v/v) as eluant to afford 205 mg (78%) **NBM** as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.50 (d, J = 7.2 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.31 (s, 1H), 7.28 - 7.23 (m, , 3H), 7.14 (d, J = 8.0 Hz, 1H), 4.13 – 4.09 (m, 2H), 3.70 – 3.68 (m, 4H), 3.62 (s, 2H), 3.49 (s, 2H), 3.25 (s, 4H), 2.74 (s, 4H), 2.43 (s, 4H), 1.69 – 1.61 (m, 2H), 1.44 – 1.35 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 164.44, 163.98, 155.93, 137.74, 137.62, 132.50, 131.00, 130.23, 130.07, 129.80, 128.31, 128.17, 126.07, 125.56, 123.23, 116.63, 114.86, 66.93, 63.37, 62.96, 53.59, 53.15, 53.02, 40.06, 30.26, 20.42, 13.92. ESI-MS for $C_{32}H_{39}N_4O_3$ [(M + H)$^+$]: 527.49. HR-ESI-MS calcd for $C_{32}H_{39}N_4O_3$ [(M + H)$^+$]: 527.3017, found: 527.3069.



2 **NPP**

Scheme S2 Synthesis of **NPP**

Compound **2** was prepared according to our previously reported methods (*Dalton Trans.*, 2012, **41**, 7212).

Compound NPP. Anhydrous potassium carbonate (138 mg, 1.0 mmol), compounds **2** (238 mg, 0.5 mmol) and piperidine (213 mg, 2.5 mmol) were dissolved in acetonitrile (8 mL), and the reaction mixture was refluxed for 12 h under argon atmosphere. The mixture was filtered, and the solvent was removed in a vacuum to give a yellow solid. The crude product was then chromatographed on silica gel using dichloromethane–methanol 30 : 1 (v/v) as eluant to afford 181 mg (69%) **NPP** as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.58 – 8.51 (m, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.40 – 8.33 (m, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.65 (dd, *J* = 8.0, 7.6 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.13 (t, *J* = 7.6 Hz, 2H), 3.97 (s, 2H), 3.80 (s, 2H), 3.30 (s, 4H), 2.82 (s, 8H), 1.82 (s, 4H), 1.71 – 1.63 (m, 2H), 1.53 (s, 2H), 1.46 – 1.35 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ:164.48, 164.02, 158.05, 155.84, 137.57, 132.50, 131.05, 130.21, 129.83, 126.12, 125.63, 123.57, 123.28, 122.72, 116.78, 114.92, 64.32, 63.43, 53.96, 53.36, 52.98, 50.69, 40.08, 30.25, 29.69, 24.18, 23.07, 20.40, 13.88. ESI-MS calcd for $C_{32}H_{40}N_5O_2$ [(M + H)$^+$]: 526.31, found: 526.51. HR-ESI-MS calcd for $C_{32}H_{40}N_5O_2$ [(M + H)$^+$]: 526.3177, found: 526.3197.

2. The absorption and emissive properties of NPM on changing the pH

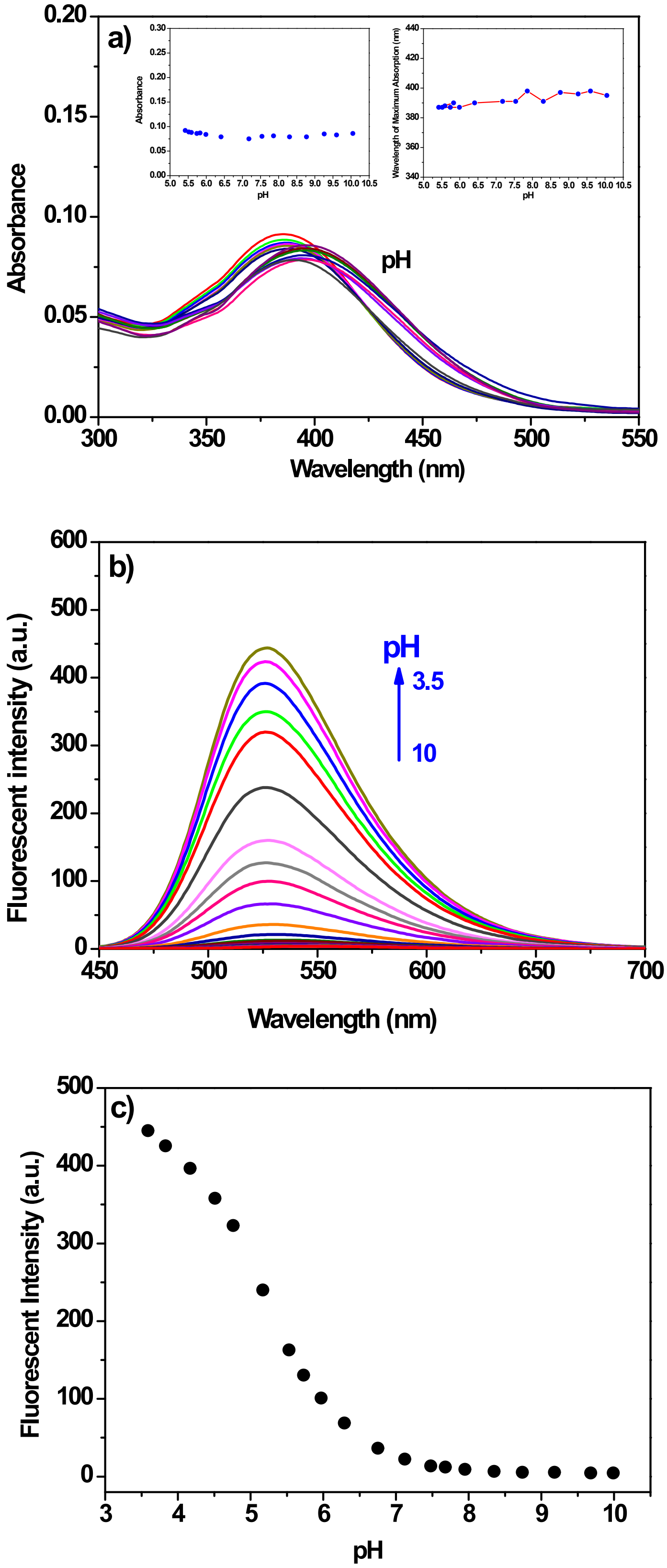


Fig. S1. The influence of pH on the absorption (a) and fluorescence (b, c) of **NPM** (10 µM) in water. Inset: (a, left) absorption intensity as a function of pH value, (a, right) wavelength of maximum absorption as a function of pH value. Excitation was performed at 405 nm. Slits were 2.5, 5 nm.

3. UV-Vis absorption spectra of NPM in the presence of various metal ions

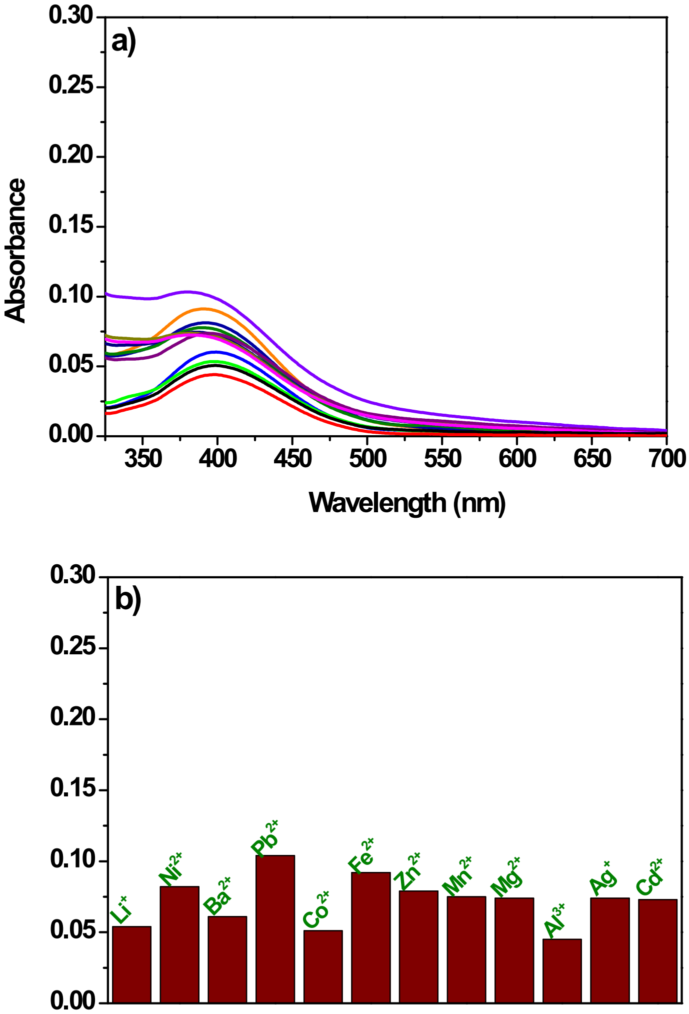


Fig. S2. UV-Vis absorption spectra (a) and absorption intensity (b) of **NPM** (10 μM) in the presence of various metal ions (20 μM) in aqueous solution (10 mM HEPES, pH 7.5).

4. The competitive experiments of Hg^{2+} and Cu^{2+} with the other ions

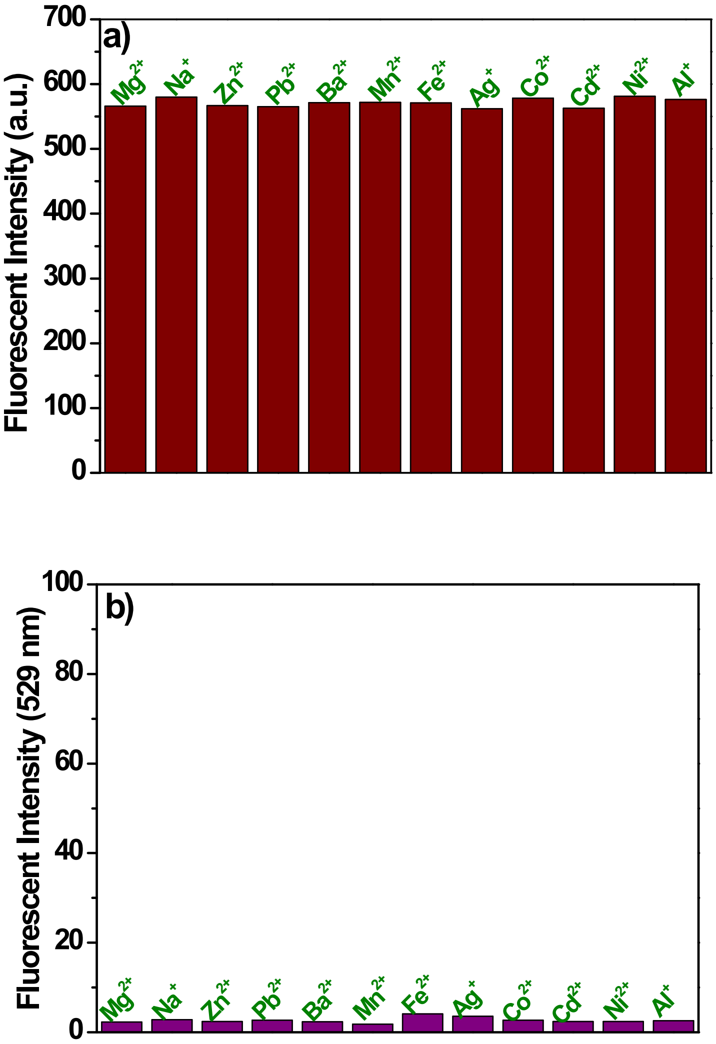
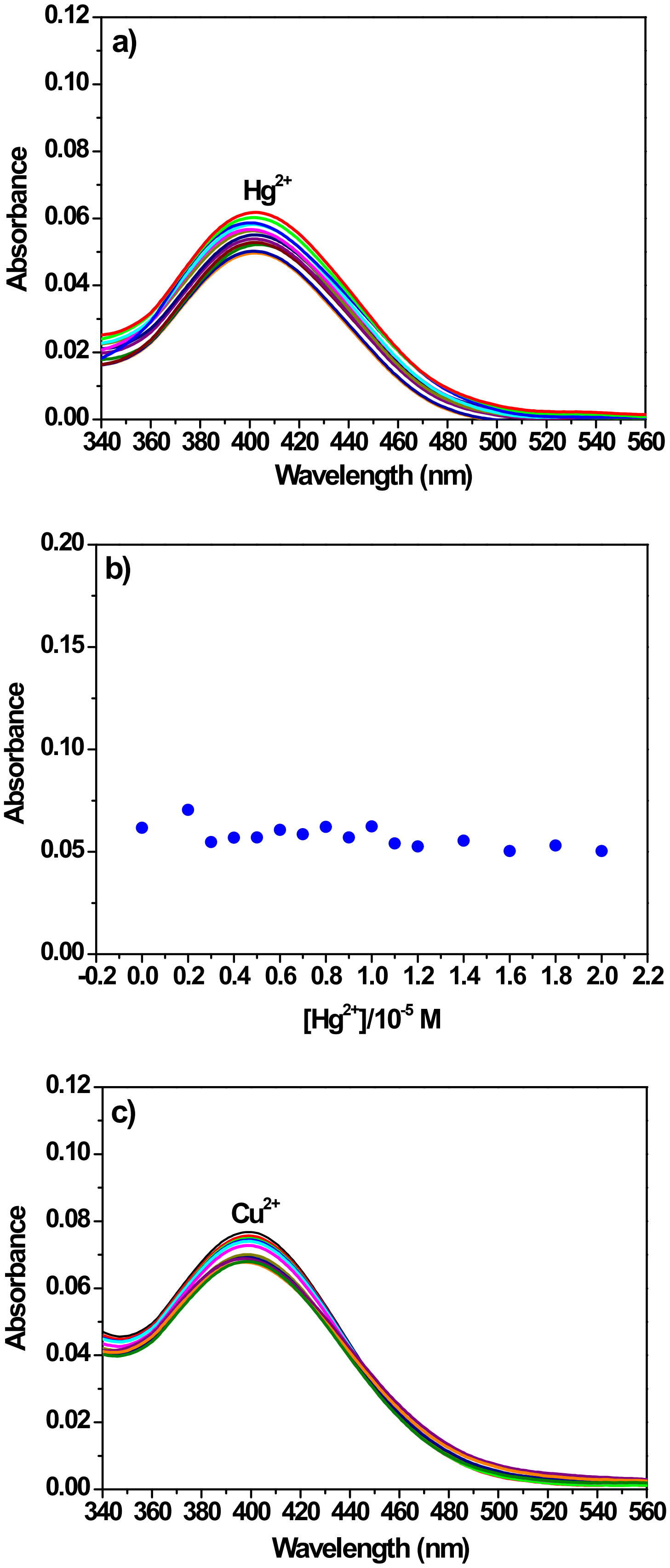


Fig. S3 The fluorescent intensity at 529 nm of **NPM** (10 μM) upon the addition of (a) Hg^{2+} (20 μM) and (b) Cu^{2+} (20 μM) in the presence of background metal ions (20 μM) in aqueous solution (10 mM HEPES, pH 7.5). λ_{ex} = 405 nm.

5. UV-Vis absorption titration spectra of NPM with Hg^{2+} and Cu^{2+}



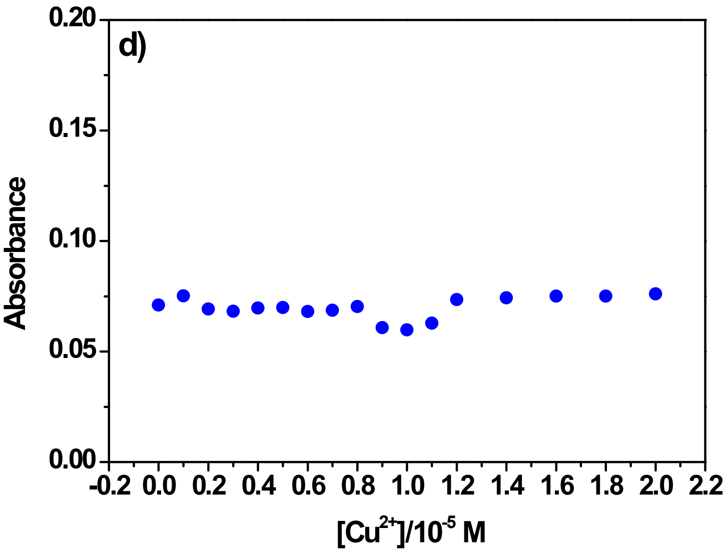
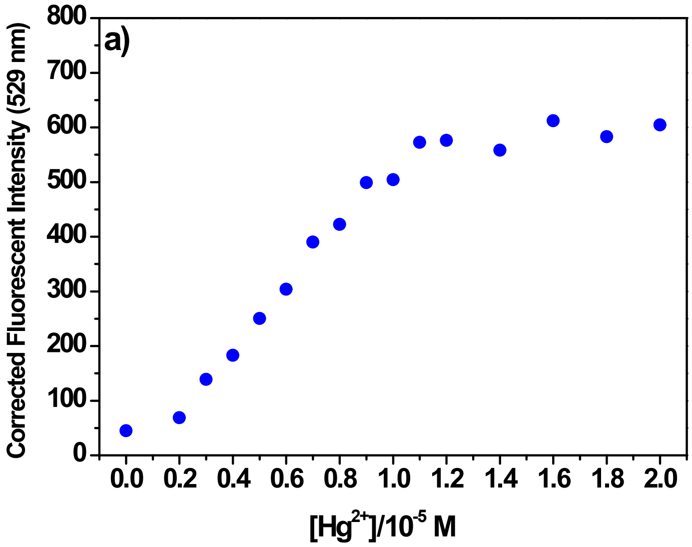
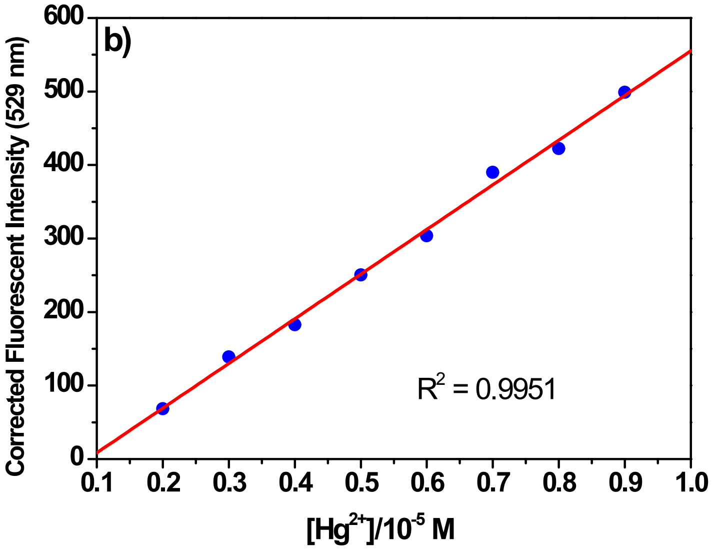
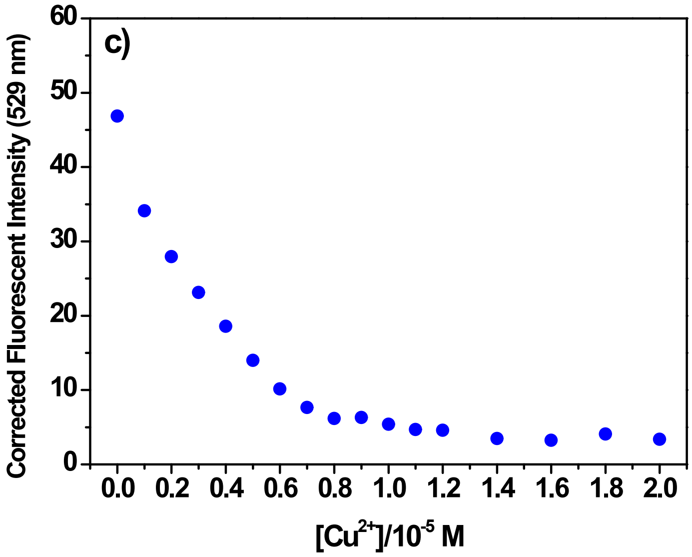


Fig. S4 UV-Vis absorption spectra of **NPM** (10 μM) upon addition of (a) Hg^{2+} (2–20 μM) and (c) Hg^{2+} (1–20 μM) in aqueous solution (10 mM HEPES, pH 7.5). The curves of absorption of **NPM** (10 μM) versus increasing concentrations of Hg^{2+} (b) and Cu^{2+} (d).

6. Hg^{2+} and Cu^{2+}-titration and spectral responses







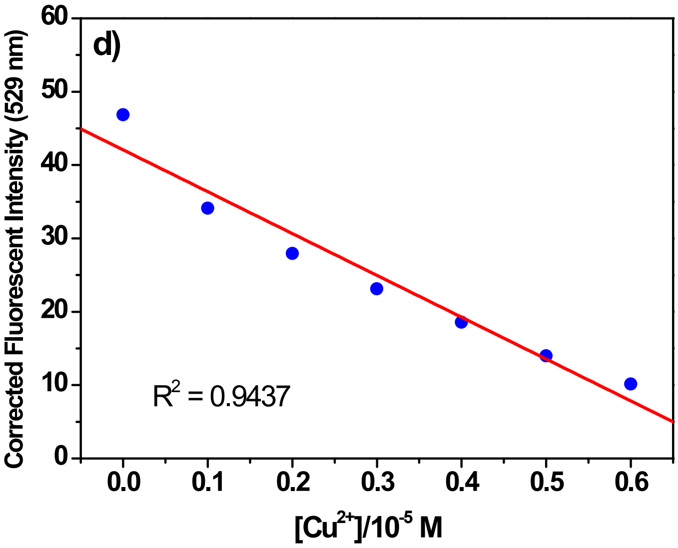


Fig. S5 Curve of corrected fluorescence intensity at 529 nm of **NPM** (10 μM) versus increasing concentrations of Hg^{2+} (a, b) and Cu^{2+} (c, d), respectively. (λex = 405 nm)

8. Fluorescence spectra of NPM, NBM, and NPP in the absence and presence of Hg^{2+} and Cu^{2+}

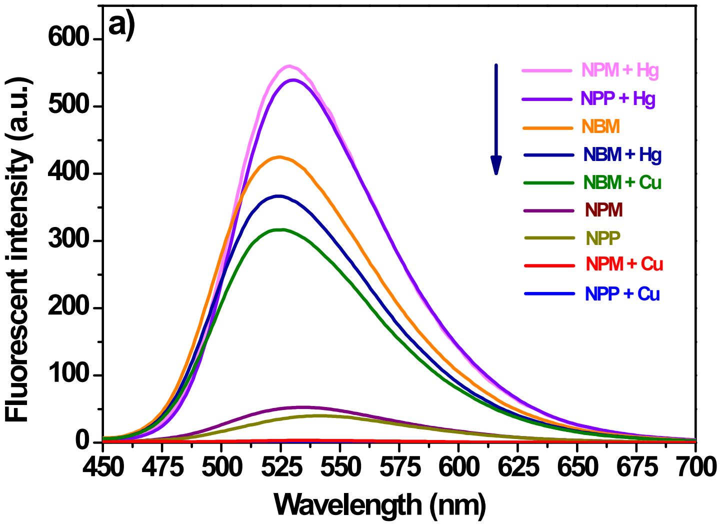


Fig. S6 Fluorescence spectra of **NPM**, **NBM**, and **NPP** (all compounds were 10 μM) in the absence and presence of Hg^{2+} (20 μM) and Cu^{2+} (20 μM) in aqueous solution (10 mM HEPES, pH 7.5). λ_{ex} = 405 nm.