Electronic Supplementary Information (ESI)

Ultraefficient separation and sensing of mercury and methylmercury ions in drinking water by using aminonaphthalimide-functionalized Fe_3O_4@SiO_2 core/shell magnetic nanoparticles

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Chemicals. Unless otherwise stated, all reagents were purchased Aldrich and used without further purification.

Preparation of compound 3. The compound **3** was prepared by a method reported previously.[1]

Preparation of compound 2. A solution of **3** (0.1 g, 0.118mmol) triethylamine at 80 °C was treated with 3-(triethoxylyl) propyl-isocyanate (58 μL, 0.237mmol). The reaction mixture was stirred for overnight at 80°C, and then cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1:4 to 1:2) to afford yellow solid. (60 %): ^{1}H NMR (300 MHz, Aceton-d$_6$) δ = 8.63 (q, ^{4}J (H,H) = 8.4 Hz, 4H; Ar-H), 8.46 (d, ^{2}J(H,H) = 3.4 Hz, 2H; Ar-H), 7.83 (t, ^{3}J (H,H) = 7.35 Hz, 3H; Ar-H) 7.4 (d, ^{2}J(H,H) = 8.1Hz, 4H; Ar-H), 6.07(t, 2J(H,H) = 6.0 Hz, 2H; NH), 4.2 (m, 4H; CH_2), 3.9 (m, 4H; CH_2), 3.83 (m, 16H; CH_2), 3.65 (m, 4H; CH_2), 3.44 (m, 8H; CH_2), 2.6 (m, 8H; CH_2), 1.62 (m, 4H; CH_2), 1.21 (t, ^{3}J (H,H) = 6.9 Hz, 18H; CH_3), 0.63 (t, ^{3}J (H,H) = 8.7 Hz, 4H; CH_2) ^{13}C NMR (Aceton-d$_6$) δ =161, 159, 158, 157, 138.2, 137, 135, 125, 124, 123, 122, 121, 118, 70, 63, 61, 60.8, 58, 46.5, 45, 43, 38, 23, 17.8, 0.83. IR (KBr, cm^{-1}):3428, 2913, 2841, 2354, 1700, 1640, 1457, 1358, 770, 666. HRMS (FAB$^+$) m/z 1335.6238 [(M+H)$^+$ calcd for $C_{67}H_{93}N_9O_{16}Si_2$:1335.6279]. Anal. calcd for $C_{67}H_{93}N_9O_{16}Si_2$: C, 60.20; H, 7.01; N, 9.43. found: C, 60.22; H, 7.03; N,9.45.

Preparation of Fe_3O_4@SiO_2 core/shell particles: Fe_3O_4 nanocrystals having 4 nm of average core size were prepared through the previously reported procedure in Ref. S1. The encapsulation of Fe_3O_4 nanocrystals with the silica shell was conducted by the modification of a reverse microemulsion technique. Polyoxyethylene (5) nonylphenyl ether (7.68 g, 18.0 mmol, Igepal CO-520, containing 50 mol% hydrophilic group, Aldrich) was dispersed in a round bottom flask containing cyclohexane (170 ml) by stirring. Next, 8.0 mg of Fe_3O_4 nanocrystals dispersed in cyclohexane were added to the reaction solution. The resulting mixture was vortexed until the mixture became transparent. Lastly, tetraethylorthosilicate (1.5 ml, TEOS) was added, and stirred for 12 hr. The resulting silica nanospheres, Fe_3O_4@SiO_2 nanocrystals were collected by magnetic decantation. The collected nanospheres of Fe_3O_4@SiO_2 were redispersed in EtOH and recovered by using a magnet. The dispersion of Fe_3O_4@SiO_2 into EtOH suspension and magnetic separation was repeated three times for the purification.

Preparation of aminonaphthalimide-functionalized core/shell magnetic nanoparticles 1. Compound **2** (50 mg, 0.054 mmol) was dissolved in anhydrous toluene (5 mL) to which Fe_3O_4@SiO_2 Core/shell Particles (100 mg) was added, and it was stirred under reflux in N_2 for 24 h. The collected solid was washed several times with dichloromethane and acetone to rinse away any excess **2** and then dried under vacuum.

Characterization. ^1H and ^{13}C NMR spectra were measured with a Bruker ARX 300 MHz sepctrometer. MS spectra were obtained with a JEOL JMS-700 mass spectrometer. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 F instrument operated at 50 keV. Images were recorded on an imaging plate (Fuji Photo Film Co. Ltd. FDL5000 system) with 20 eV energy windows at 3000–250000X magnification and were digitally enlarged. All fluorescence spectra were recorded in RF-5301PC spectrophotometer.

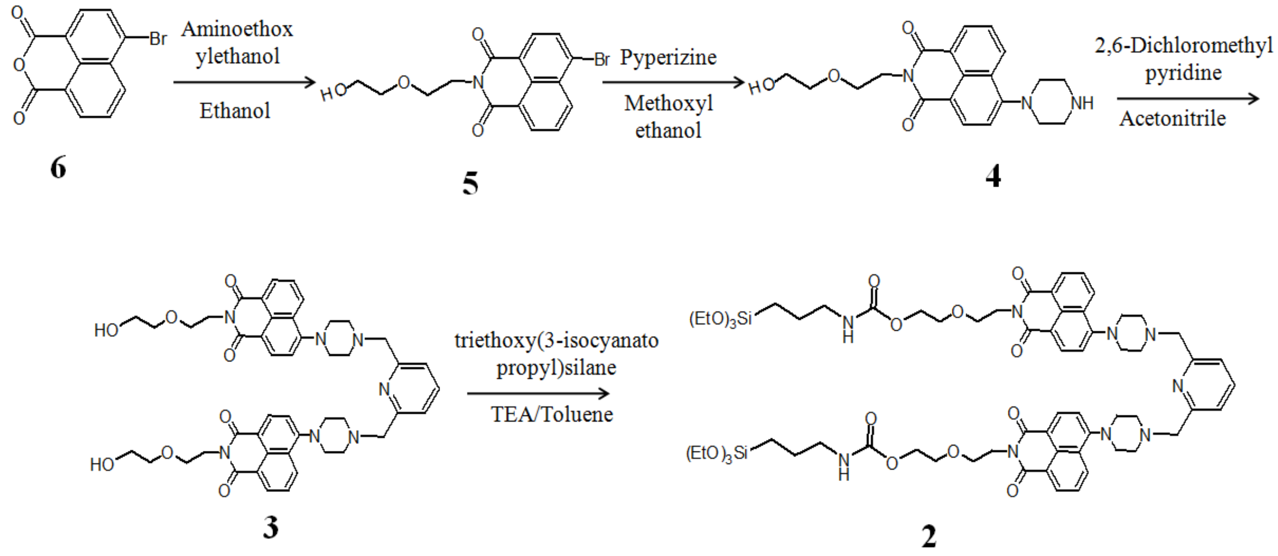
Photospectroscopy. Fluorescence emission spectra were recorded with a Shimadzu RF-5301-PC instrument. Stock solutions (0.01 M) of the hydrated metal perchlorate salts were prepared in H_2O at pH 7. Stock solutions of **1** were prepared in H_2O. For all measurements, excitation was at 350 nm, with excitation and emission slit widths of 1.5 nm. The pH value was adjusted by using 0.2 M MOPS. Fluorescence quantum yields were determined by reference to methylene blue ($\Phi = 0.04$).[2]

Separation of Hg^{2+} and CH_3Hg^+ from drinking water. The column (1 cm x 5 cm) was prepared by using core/shell nanoparticle **1**. The column as adsorbent was connected before analytical column in ion chromatography. Then, Hg^{2+} or CH_3Hg^+

contained waste solution was injected. The eluent was flowed with 1.0 ml/min into columns. The solution was analyzed by ICP-MS (ELAN DRC II, Perkin Elmer).

References

1. X. Guo, X. Qian and L. Jia, *J. Am. Chem. Soc.*, 2004, **126**, 2272.
2. J. Olmsted III, *J. Phy. Chem.*, 1979, **83**, 2581.



Scheme S1. Synthetic route of **2.**

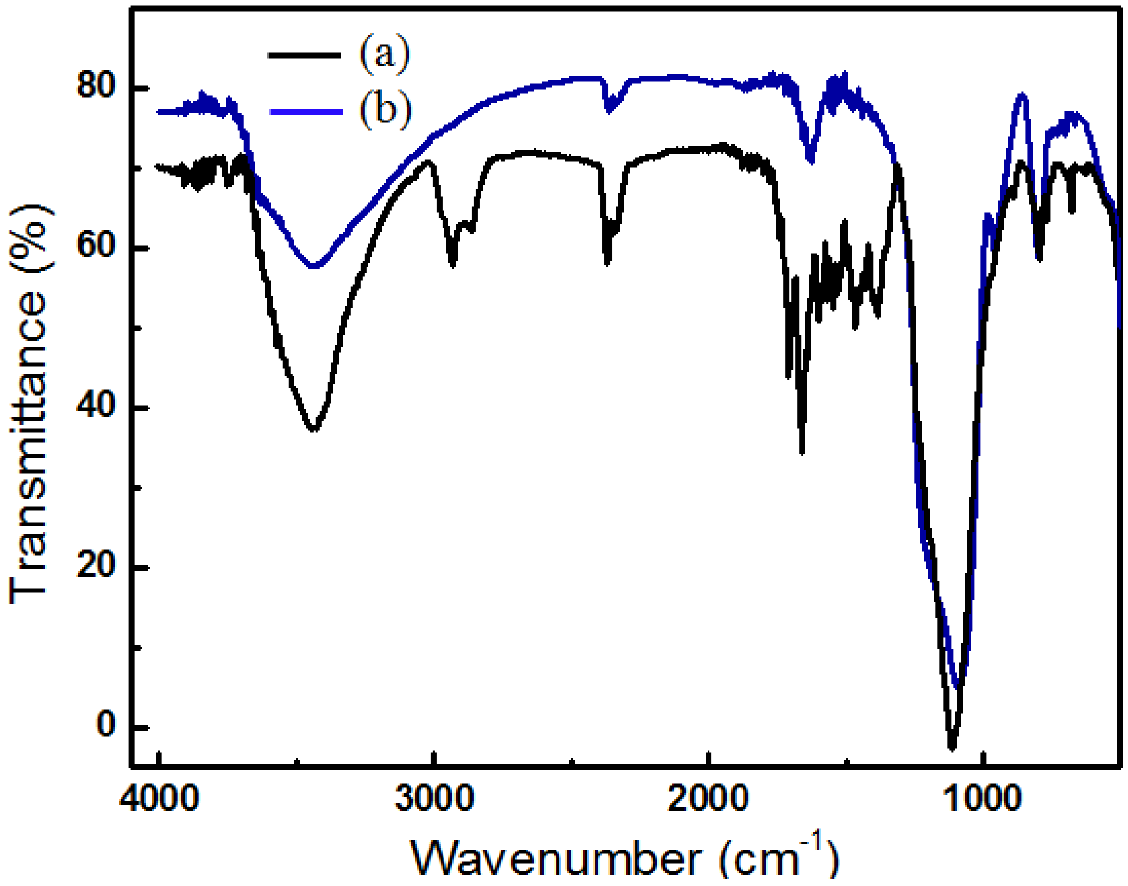


Fig. S1 FT-Infrared spectra of (a) **1** and (b) **Fe_3O_4@SiO_2**.

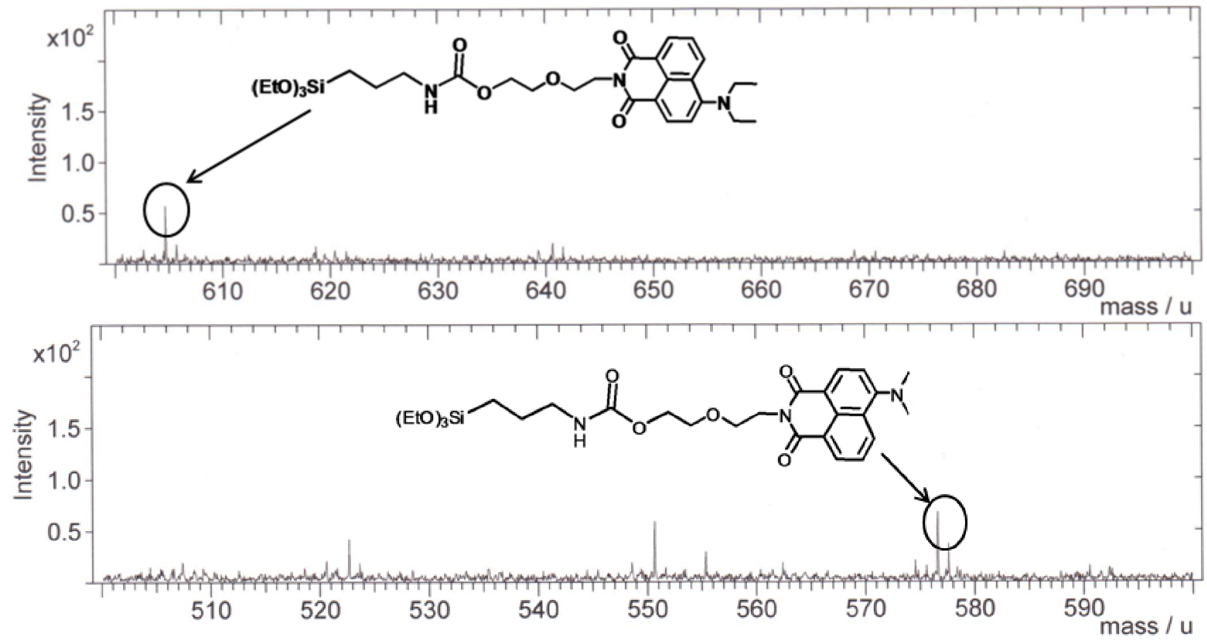


Fig. S2 TOF-SIMS spectrum of **1.**

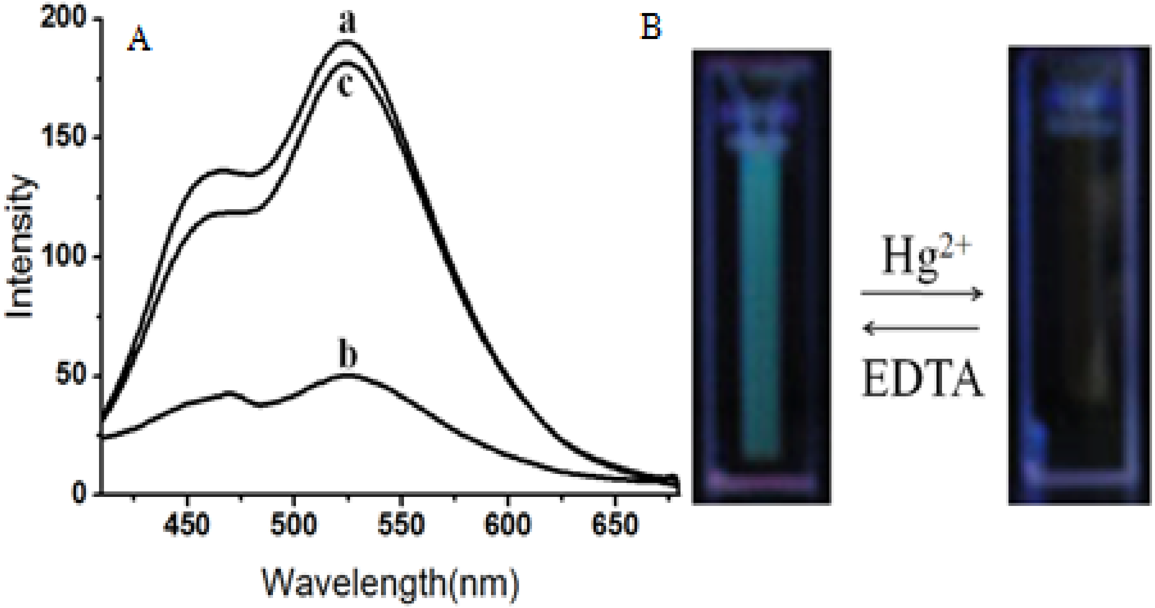


Fig. S3 (A) Fluorescence spectra of **1** (1.0 μM) in (a) without and (b) with Hg^{2+} ions, and (c) after treatment with EDTA (0.01 N, 1ml). (B) Photograph of **1** with Hg^{2+} by treatment of EDTA (0.01N, 1ml).

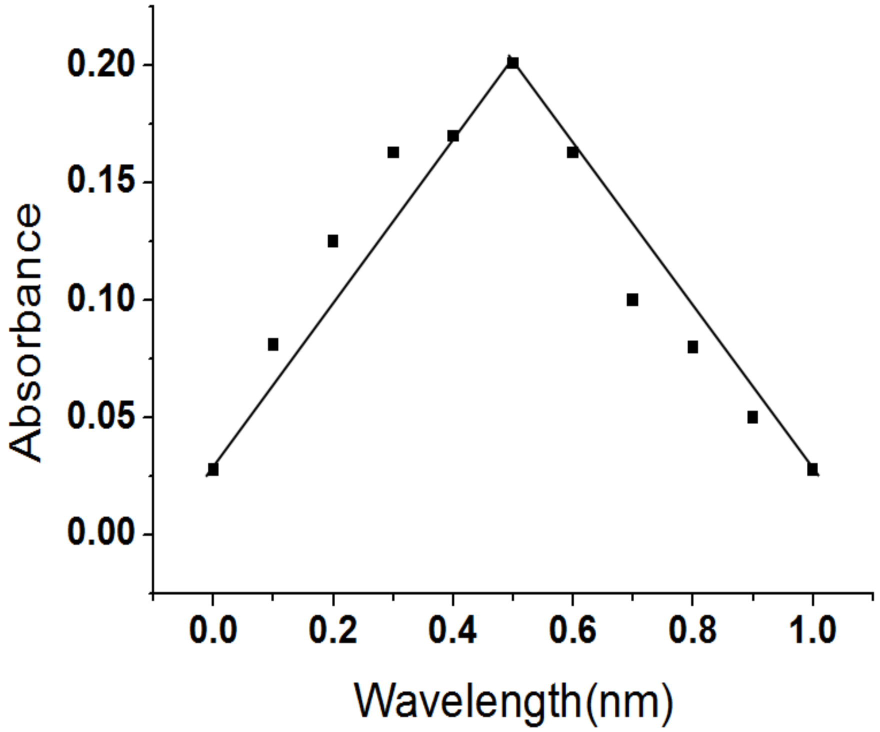


Fig. S4 Job′s plot of 1:1 complex of **1** and Hg^{2+}. The pH value was adjusted by using MOPS buffer solution (pH 7).

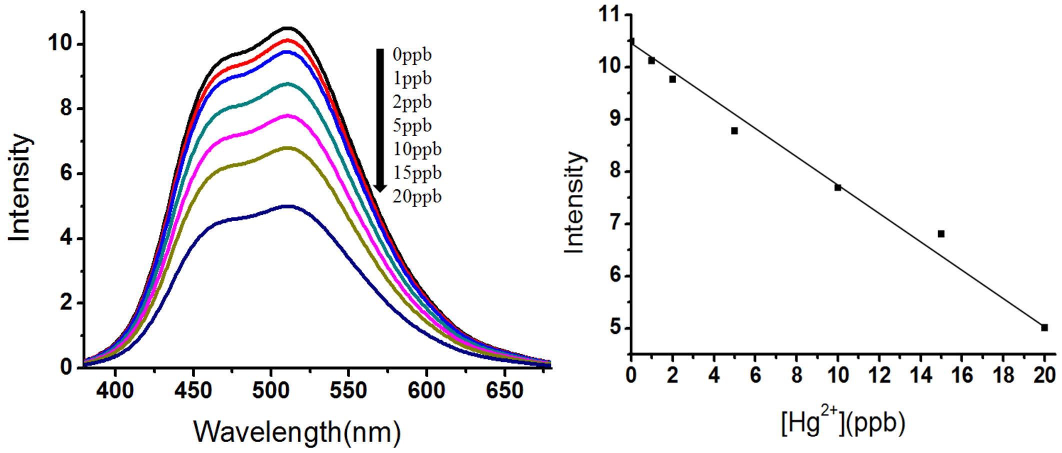


Fig. S5 Fluorescence spectra of **1** (0.05 μM) upon addition of increasing Hg^{2+} concentrations in water at pH 7. (B) Calibration curve of concentration of Hg^{2+} ion against fluorescence intensity of **1**.

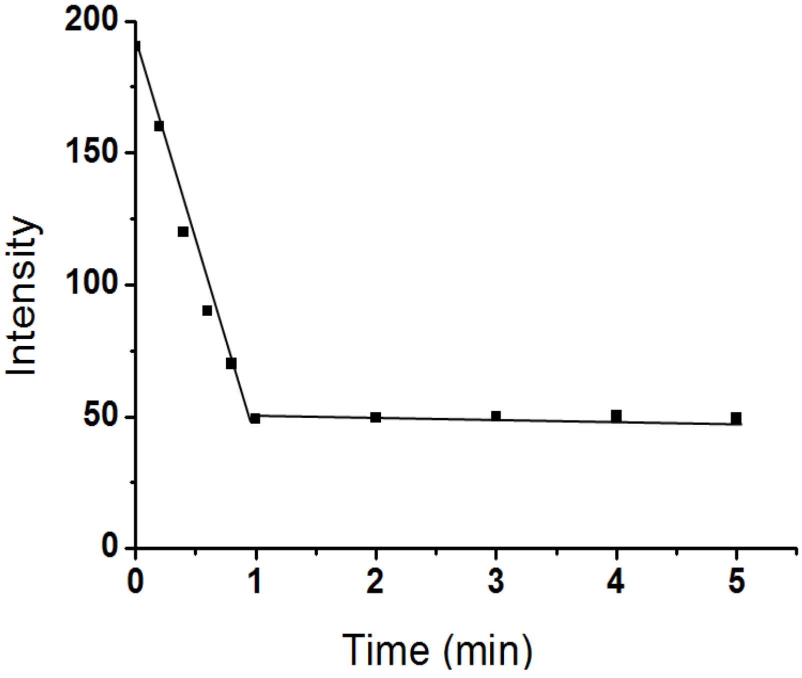


Fig. S6 Time course of the fluorescence intensity of **1** (1.0 μM**)** in water at pH 7 at the addition of Hg^{2+} (2.0 equiv).

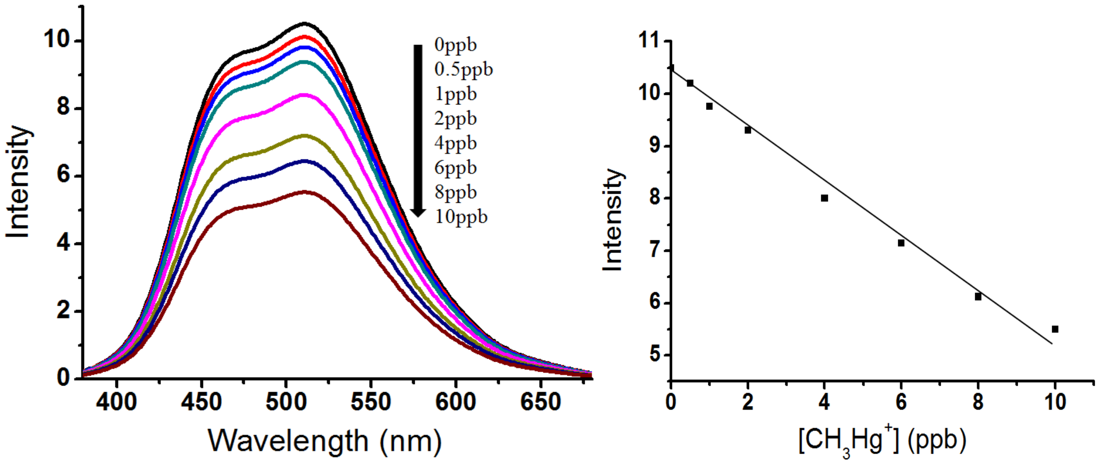


Fig. S7 Fluorescence spectra of **1** (0.05 μM) upon addition of increasing CH_3Hg^+ concentrations in water/ethanol (9:1 v/v) at pH 7. (B) Calibration curve of concentration of CH_3Hg^+ ion against fluorescence intensity of **1**.

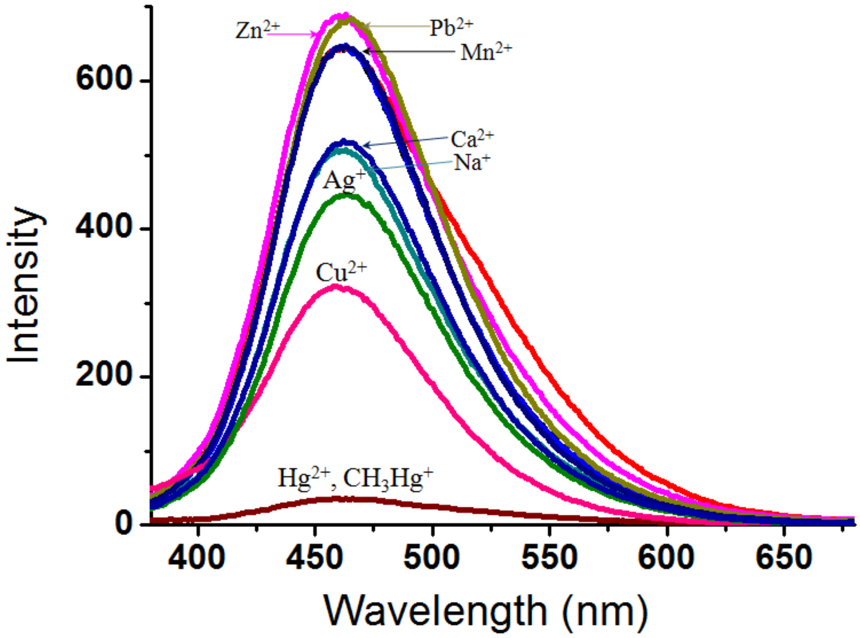


Fig. S8 Fluorescence changes of **2** (1.0 μM) upon the addition of metal ions (2 equiv) in acetonitrile.