

Electronic Supplementary Information (ESI)

Functionalized Ni@SiO₂ core/shell magnetic nanoparticles as a chemosensor and adsorbent for Cu²⁺ ion in drinking water and human blood

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

Preparation of compound 4. A solution of **3** (3g, 0.029mol) and 3-(triethoxylyl) propyl-isocyanate (14.38ml, 0.058mol) was reacted in anhydrous methylenechloride stirred for overnight at 0 °C. The solvent was removed under vacuum.(86.65%) ¹H NMR (300 MHz, CDCl₃-d₆) δ = 6.02 (s, 4H; NH), 3.8 (m, 12H; CH₂), 3.58 (t, ³J (H,H) = 6.78 Hz, 2H; CH₂), 3.28 (m, 6H; CH₂), 2.8(m, 4H; CH₂), 1.6 (m, 4H; CH₂), 1.21 (m, 18H; CH₂), 0.7 (t, ³J (H,H) = 8.14 Hz, 4H; CH₂), ¹³C NMR (CDCl₃-d₆) δ =160, 59, 48, 46, 40, 23, 18, 7.4 . IR (KBr, cm⁻¹): 3350, 2976, 2893, 2361, 1885, 1641, 1564, 1271, 1084, 954, 782, 473. HRMS (FAB⁺) m/z 597.3589 [(M+H)⁺ calcd for C₂₄H₅₅N₅O₈Si₂:598.4301]. Anal. calcd for C₂₄H₅₅N₅O₈Si₂: C, 48.21; H, 9.27; N, 11.71. found: C, 49.23; H, 11.02; N, 11.25.

Preparation of compound 2. A solution of **4** (2.13 g, 0.0035mol) toluene at 120 °C was added to 4-chloro-7-nitrobenzo[c][1,2,5]oxadiazole (0.85ml, 0.0042mol). The reaction mixture was stirred for 2 hour at 120 °C, and then cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (methanol/methylenechloride = 1:20) to afford yellow solid. (22.5 %): ¹H NMR (300 MHz, DMSO-d₆) δ = 8.5 (d, ²J (H,H) = 8.78 Hz, 1H; Ar-H), 6.5 (d, ²J(H,H) = 8.9Hz, 1H; Ar-H), 6.02 (s, 4H; NH), 3.8 (m, 12H; CH₂), 3.65(m, 8H; CH₂), 3.38 (t, ³J (H,H) = 5.98 Hz, 4H; CH₂), 1.6 (m, 4H; CH₂), 1.25 (m, 18H; CH₃), 0.6 (t, ³J (H,H) = 6.72Hz, 4H; CH₂), ¹³C NMR (DMSO-d₆) δ =160, 144, 140.2, 138, 131, 122.2, 98.1, 58, 56.4, 45.6, 39.1, 24.8, 18.4, 7.4 . IR (KBr, cm⁻¹): 3418, 2930, 2846, 2335, 1663, 1072, 786, 645, 451. HRMS (FAB⁺) m/z 760.3607 [(M+H)⁺ calcd for C₃₀H₅₆N₈O₁₁Si₂: 761.3641]. Anal. calcd for C₃₀H₅₆N₈O₁₁Si₂: C, 47.35; H, 7.42; N, 14.72. found: C, 48.98; H, 9.58; N, 14.23.

Preparation of nickel nanoparticles. A solution of poly(vinyl pyrrolidone) (5.35 g, 9.73×10^{-5} mol, Mw = 55,000) and Ni(acetylacetonate)₂ (1.0 g, 3.89×10^{-3} mol) in 1,5-pentandiol (50 mL) was refluxed at 200 °C for 4 h, and the reflux was continued at 240

°C for another 1 h, and then the reaction mixture was cooled in an ice–water bath. The product was separated by centrifugation at 12000 rpm for 20 min and was washed with ethanol by a repetitive dispersion/precipitation cycle in ethanol (100 mL) to remove excess poly(vinyl pyrrolidone). Monodisperse nickel nanoparticles were obtained via a careful size selection in 40% yield.

Preparation of Ni@SiO₂ core/shell particles: 1.0 mL of ammonium hydroxide (28% in water, Junsei) in 1.0 mL of water was added to the nickel colloidal solution (6.20×10^{-2} M with respect to the original nickel precursor concentration). After 30 s, 0.1 mL of tetraethyl orthosilicate (TEOS) and 0.1 mL of octadecyltrimethoxy-silane (C₁₈TMS, 9%) were added, and the mixture was vigorously stirred for 1 h to ensure complete polymerization of silica. The product was separated by centrifugation at 6000 rpm for 10 min. Ni@SiO₂ core/shell particles with a shell thickness of 40 nm were chosen for 1 synthesis.

Preparation of nitrobenzofurane-functionalized core/shell magnetic nanoparticles
1. Compound **2** (100 mg, 0.054 mmol) was dissolved in anhydrous toluene (5 mL) to which Ni@SiO₂ core/shell particles (100 mg) was added, and it was stirred under reflux in N₂ 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.

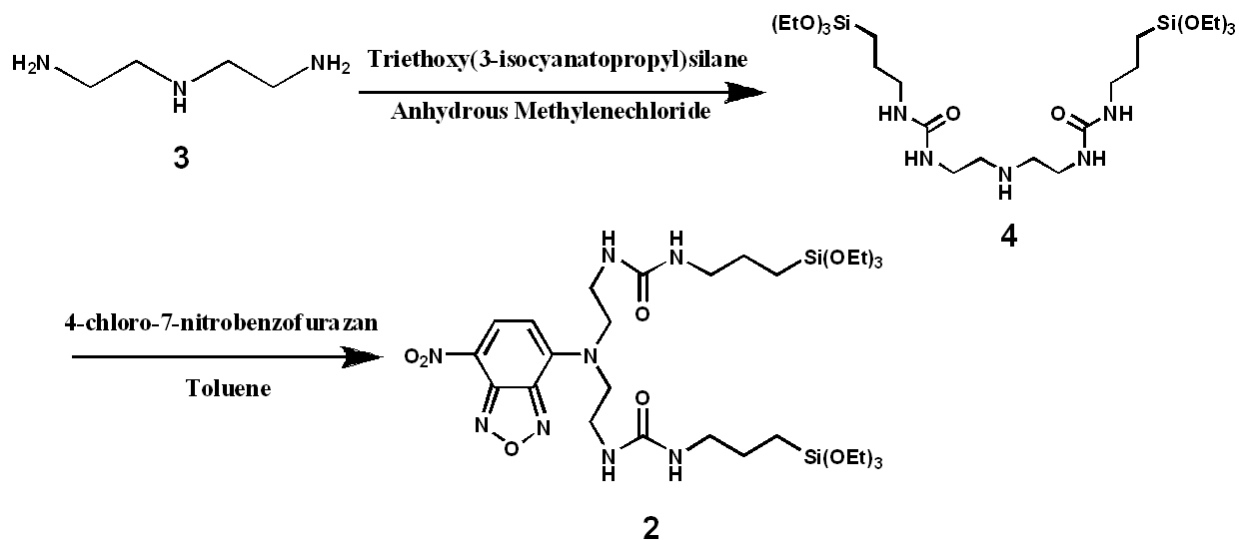
Characterization. ¹H and ¹³C NMR spectra were measured with a Bruker ARX 300 MHz spectrometer. MS spectra were obtained with a JEOL JMS-700 mass spectrometer. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 F instrument operated at 150 keV. IR spectra were obtained for KBr pellets, in the range 400–4000 cm⁻¹, with a Shimadzu FTIR 8400S instrument, and the MS spectrum was obtained with a JEOL JMS-700 mass spectrometer. Time-of-flight Second Ion Mass Spectrometer (TOF-SIMS) was analyzed on Model PHI 7200 equipped with Cs and Ga ion guns for positive and negative ion mass detection.

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 H₂O at pH 7. Stock solutions of **1** were prepared in H₂O. 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 ($\Phi = 0.04$).¹

Separation of Cu²⁺ 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, Cu²⁺ contained drinking water 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) and Ion chromatography.

References

1. J. Olmsted III, *J. Phy. Chem.*, 1979, **83**, 2581.



Scheme S1. Synthetic route of 2.

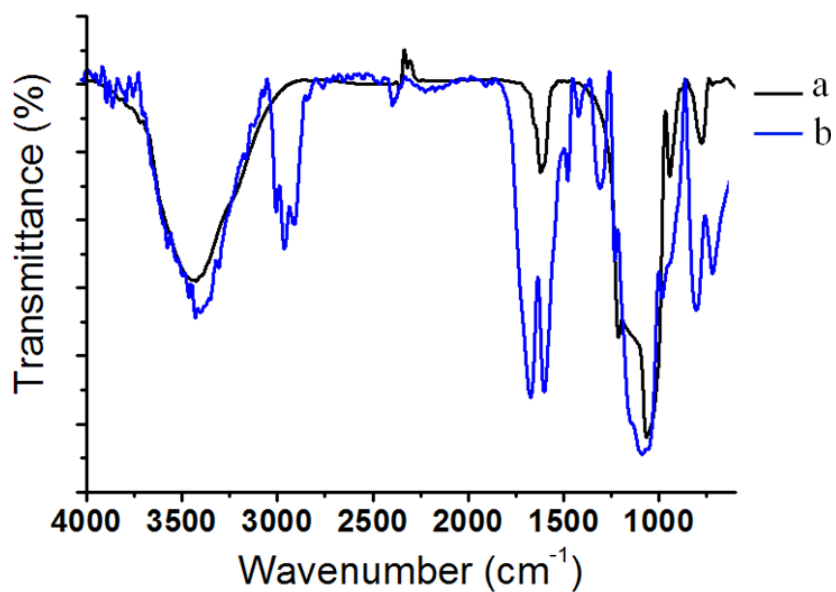


Fig. S1 FT-Infrared spectra of (a) Ni@SiO₂ and (b) 1.

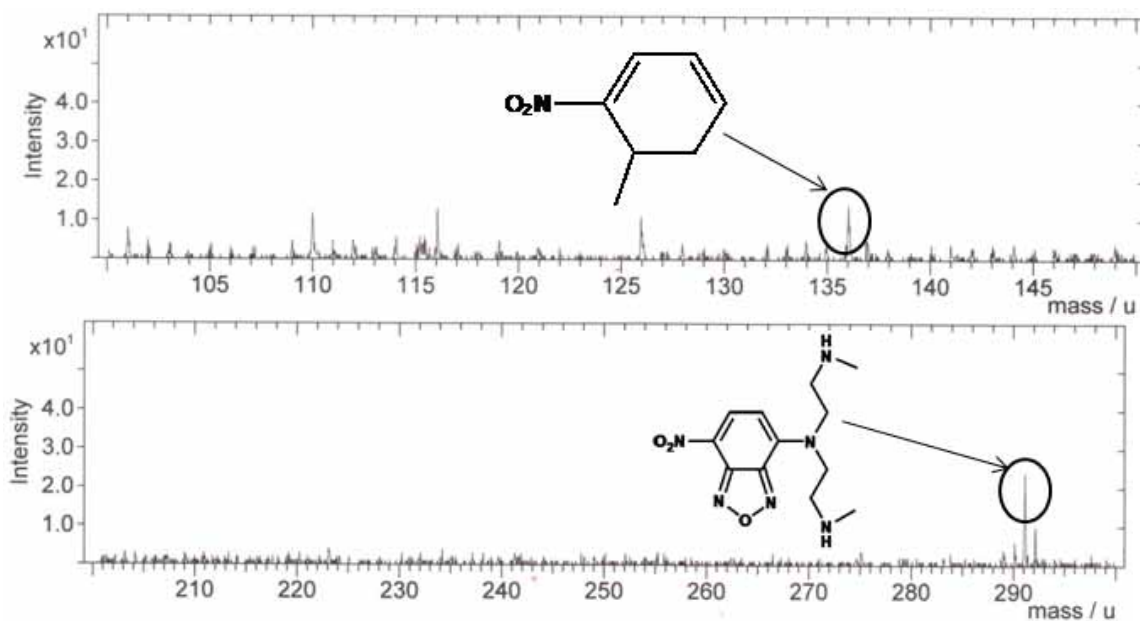


Fig. S2 TOF-SIMS spectrum of **1**.

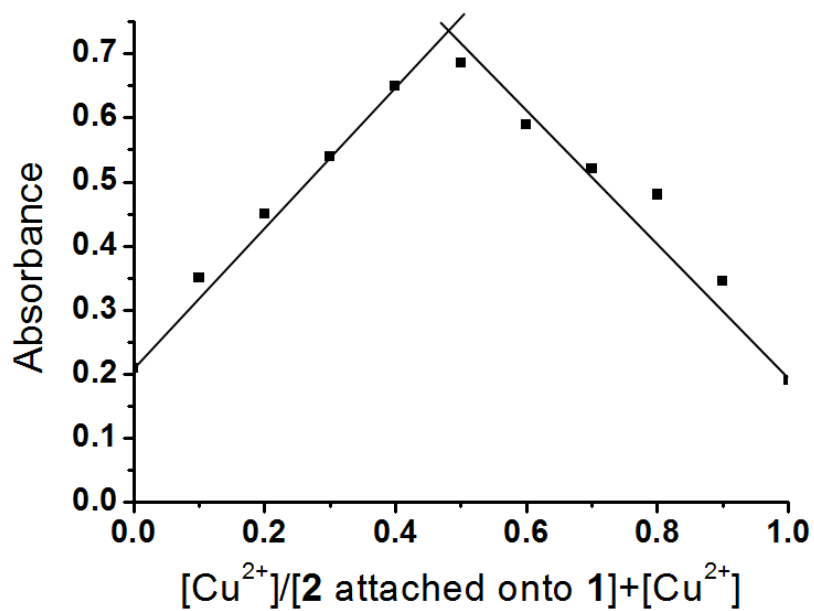


Fig. S3 Job's plot of 1:1 complex of receptor **2** attached onto **1** and Cu^{2+} .

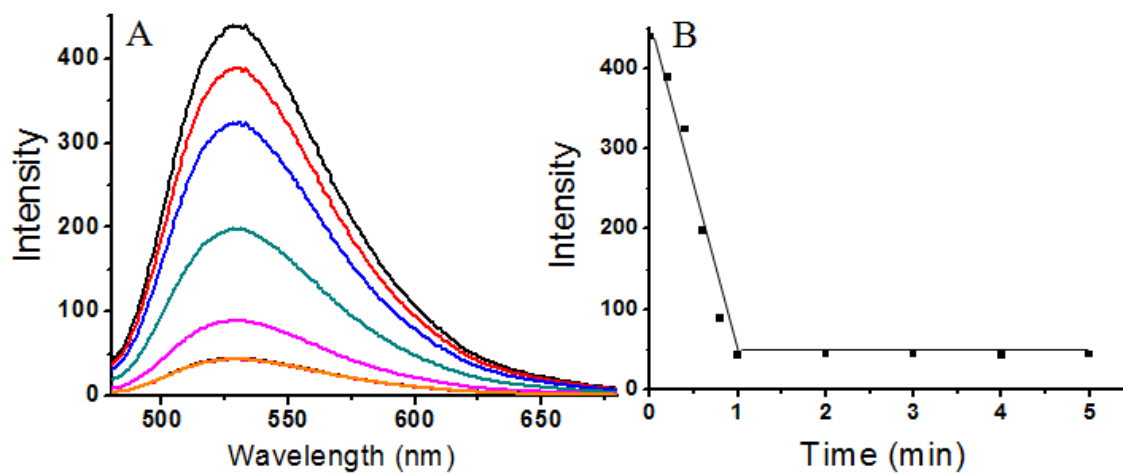


Fig. S4 Time course of the fluorescence intensity of **1** (1.0 μM) in water at pH 7 at the addition of Cu^{2+} (10.0 equiv).

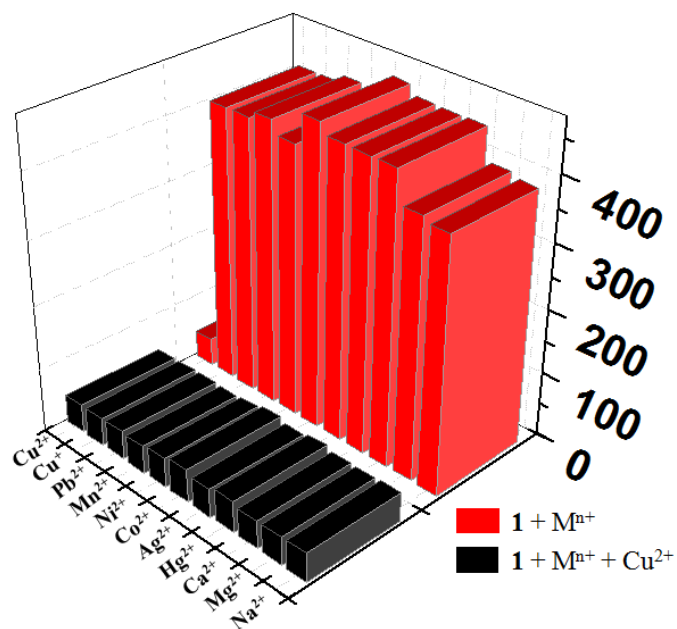


Fig. S5 Fluorescence intensity of **1** (1.0 μM) with Cu^{2+} (10.0 equiv) in the presence of other metal ions such as Na^{+} , Ca^{2+} , Cu^{2+} , Ag^{+} , Zn^{2+} , Mn^{2+} , Hg^{2+} , Cu^{+} and Pb^{2+} ions (10.0 equiv) in water at pH 7.

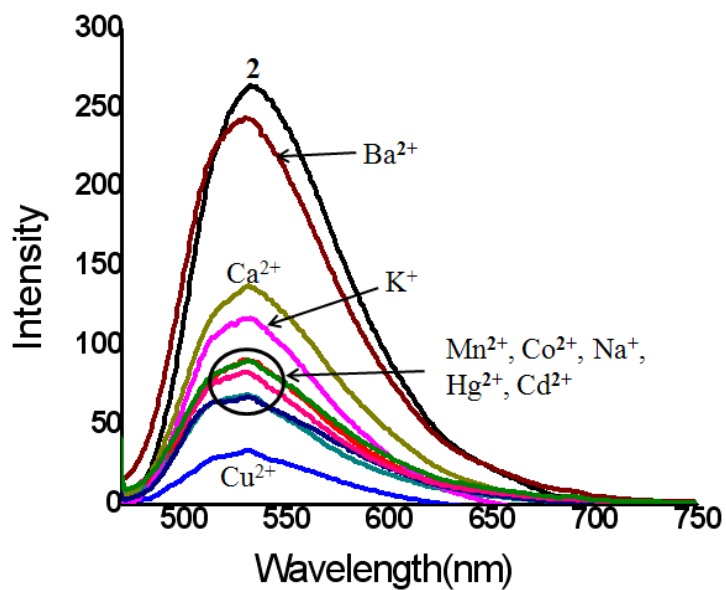


Fig. S6 Fluorescence changes of **2** (1.0 μM) upon the addition of metal ions (10.0 equiv) in acetonitrile.

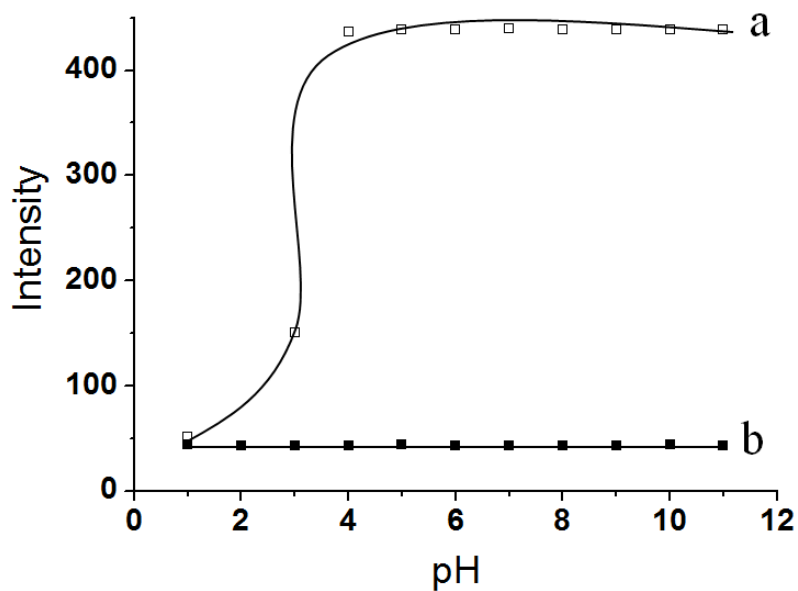


Fig. S7 Plot of pH values against fluorescence intensity of **1** (1.0 μM) in the (a) absence and the presence of (b) Hg²⁺ (10.0 equiv) in water.