Organic-inorganic hybrid nanomaterial as a new fluorescent chemosensor and adsorbent for copper ion

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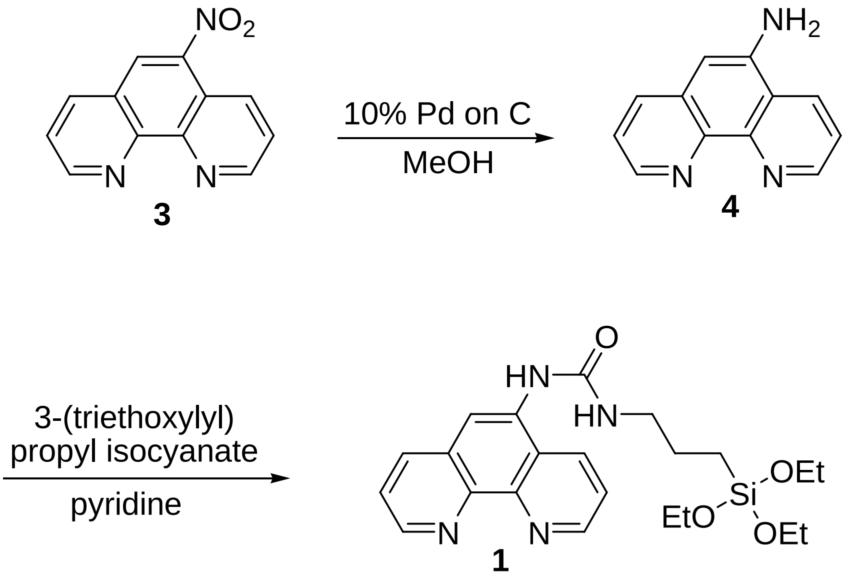


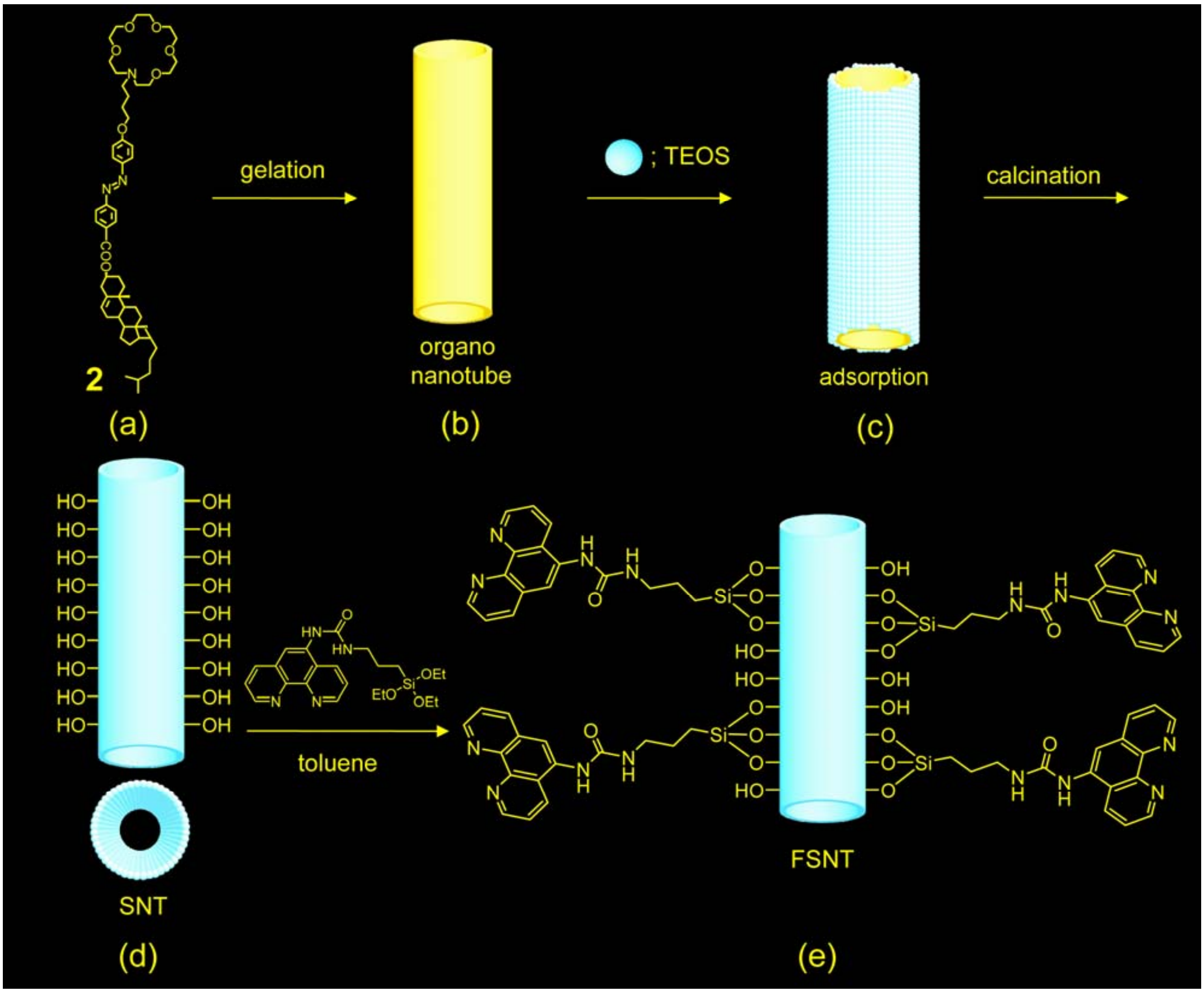
Scheme S1. Synthetic method of compound **1**.

Compound 3.

Compound **3** (200 mg, 0.89 mmol) was diluted in methanol (5 ml). After 5 min of N_2 purging, Pd on activated carbon (10% wt, 40 mg) was added to compound **3** solution. Under 3 atm of H_2, the reaction was allowed to proceed for 1 h. After filtration by celite 545 and evaporation, compound **4** was obtained as a yellow solid (173 mg, quantitative). ^{1}H NMR(300MHz, $CDCl_3$, 25 ^{o}C) δ 8.75 (d, 1H), 8.55 (d, 1H), 7.73 (d, 1H), 7.46 (d, 1H), 7.26 (d, 1H), 6.80 (d, 1H), 5.20 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$, 25 ^{o}C) δ 146, 145, 141, 136, 132, 130, 128, 122, 120, 118, 115; MS(FAB) 196 $(M+H)^+$; Anal. Calcd for $C_{12}H_9N_3$: C: 73.83, H: 4.65, N: 21.52, found C: 13.51, H: 4.51, N: 21.22.

Compound 1.

A solution of **4** (175 mg, 0.9 mmol) in pyridine (5 mL) at 80 ^{o}C was treated with 3-(triethoxylyl)propyl isocyanate (115 mg, 1.17 mmol). The reaction mixture was stirred overnight at 80 ^{o}C, and then cooled to room temperature. After removed solvent. the crude product was purified by flash column chromatography on aluminium oxide eluting with ethyl acetate to provide the title compound (215 mg, 81%). ^{1}H NMR(300MHz, $CDCl_3$, 25 ^{o}C) δ 8.72 (d, 1H), 8.57 (d, 1H), 7.74 (d, 1H), 7.39 (d, 1H), 7.22 (d, 1H), 6.75 (d, 1H), 3.77 (m, 6H), 3.13 (d, 1H), 1.45 (m, 2H) , 1.18 (m, 9H), 0.84 (m, 2H); ^{13}C NMR(75MHz, $CDCl_3$, 25 ^{o}C) δ 146, 145, 141, 136, 132, 130, 128, 122, 120, 118, 115; MS(FAB) 443 $(M+H)^+$; Anal. Calcd for $C_{22}H_{30}N_4O_4Si$: C: 59.70, H: 6.83, N: 12.66, found C: 60.21, H: 6.51, N: 12.11.



Scheme S2. Schematic representation for the creation of FSNT by sol-gel transcription. (a) gelator **2**, (b) formation of organogel nanotube, (c) sol-gel polycodensation of TEOS onto the surface of the organogel nanotube, (d) SNT obtained from calcination and (e) immobilization of receptor **1** onto the surface of SNT.

45

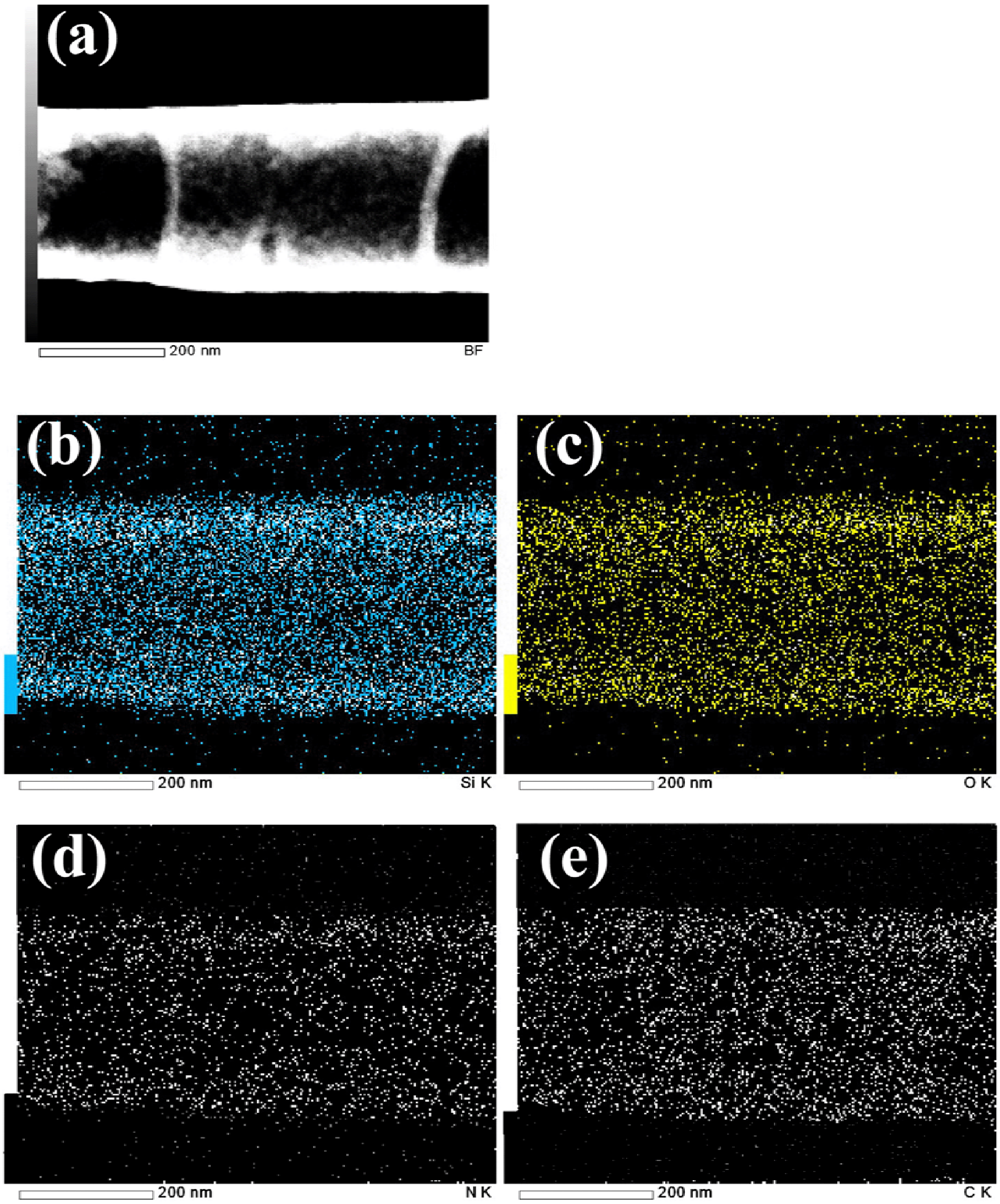


Fig. S1 TEM images with electron energy-loss spectoscopy (EELS) of the FSNT. (a) Zero-loss image, (b) silicon component, (c) oxygen component, (d) nitrogen component and (e) carbon component.

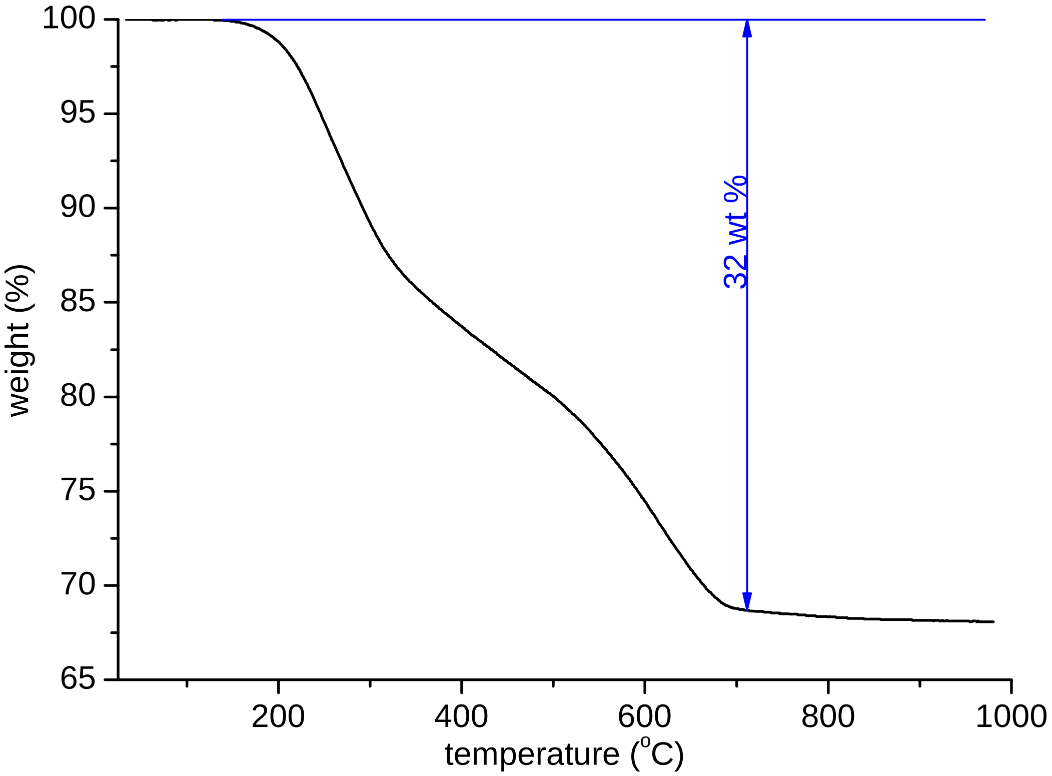


Fig. S2 Thermogravimetric analysis data of FSNT.

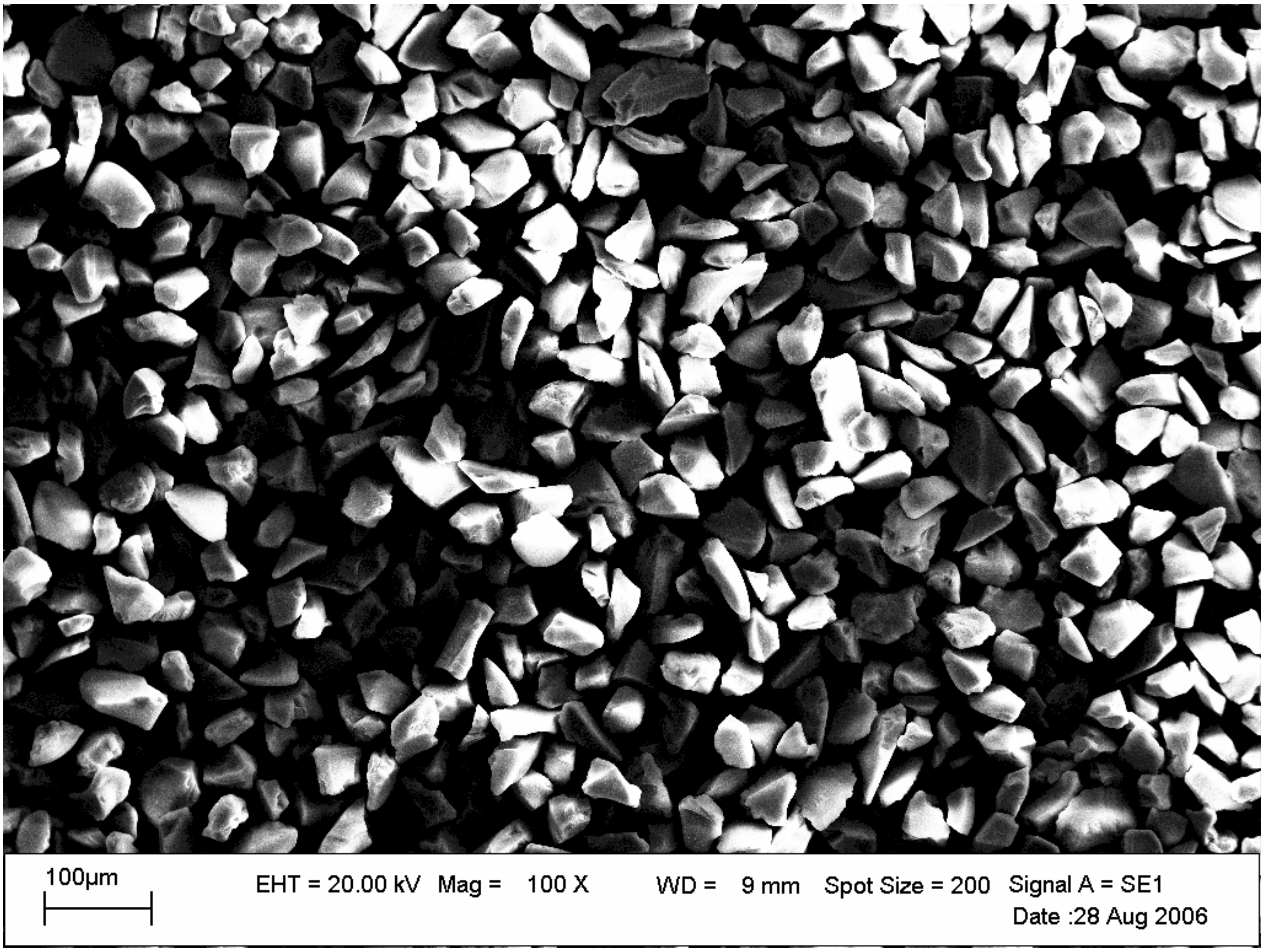


Fig. S3 SEM image of the the commercial silica gel after immobilization of the receptor **1**.

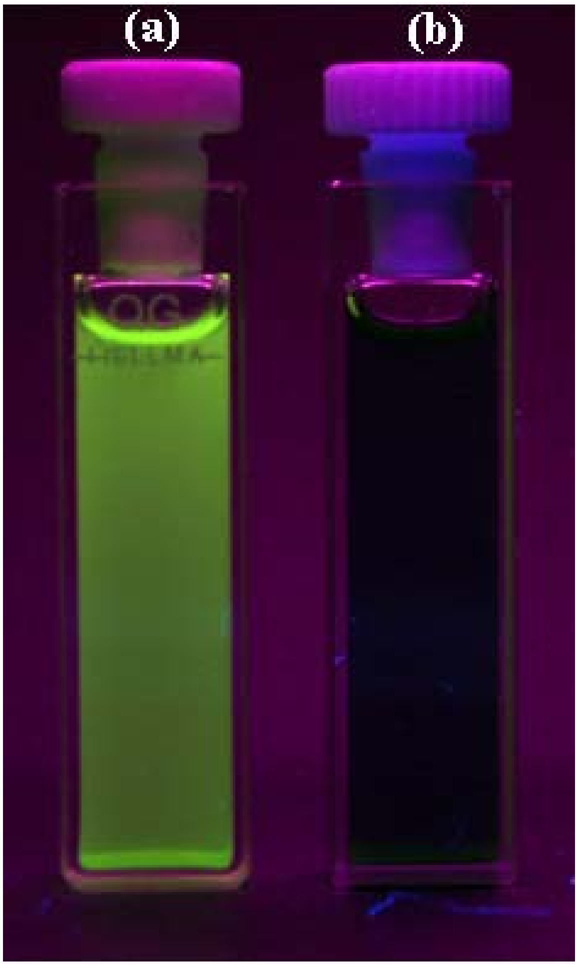


Fig. S4 Picture of FSNT (a) before and (b) after addition of Cu^{2+} by irradiation of 325 nm.

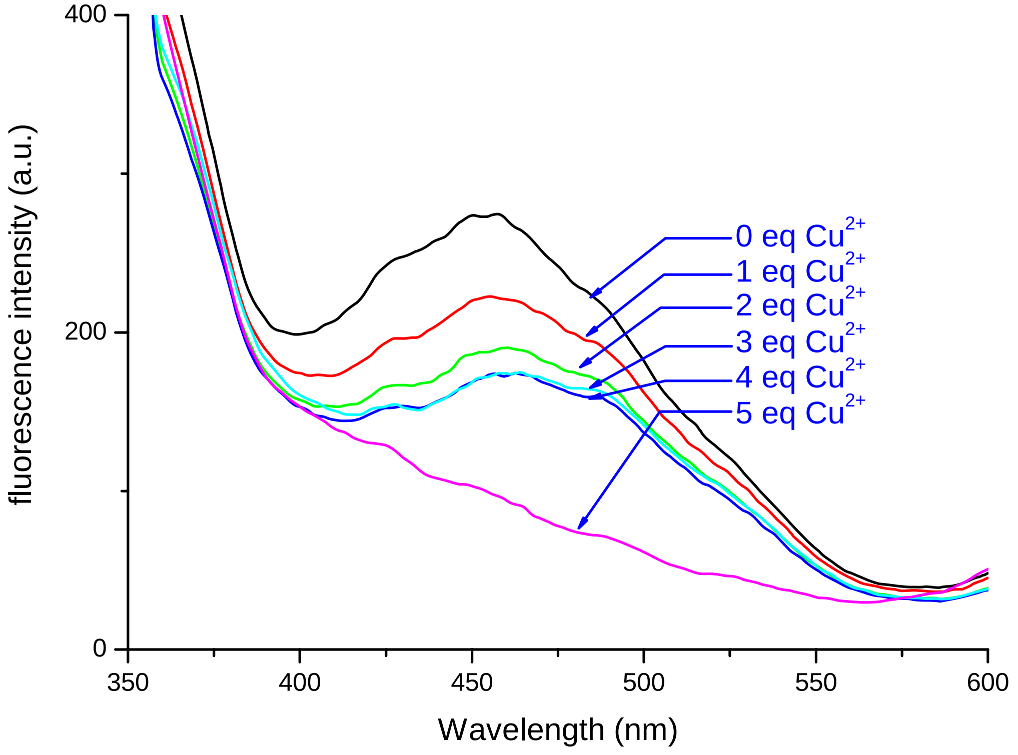


Fig. S5 Fluorescent spectra of FSNT by addition of $Cu(NO_3)_2$ in acetonitrile.

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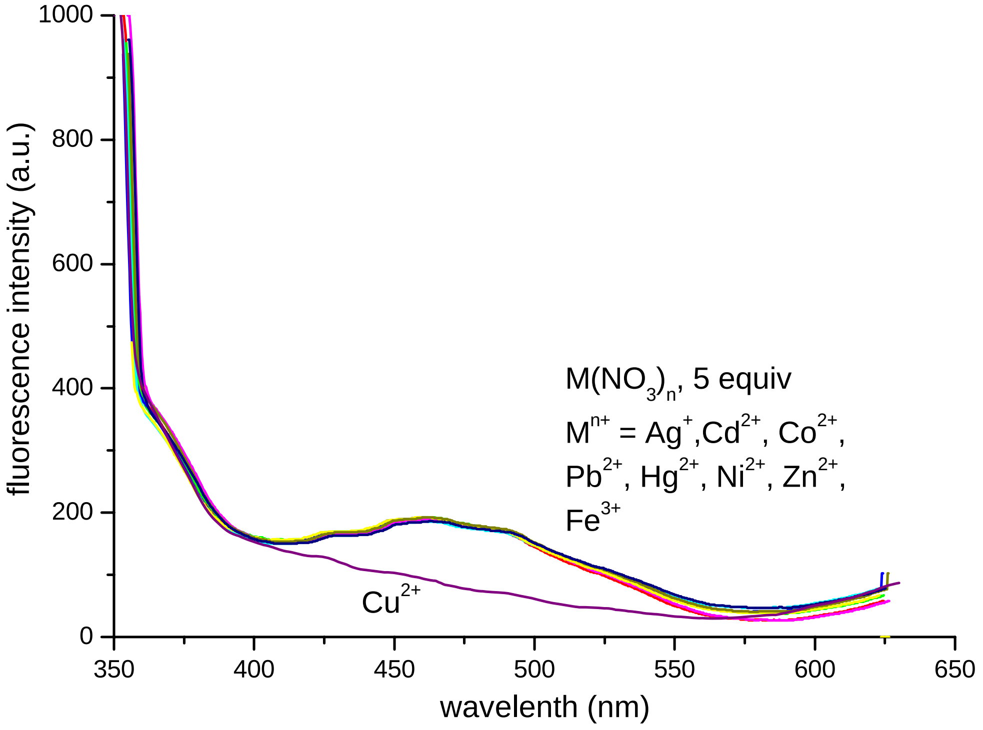

Fig. S6 Fluorescent spectra of the commercial silica gel with immobilized receptor **1** (0.30 mM) upon the addition of metal nitrates (5.0 equiv) in acetonitrile.

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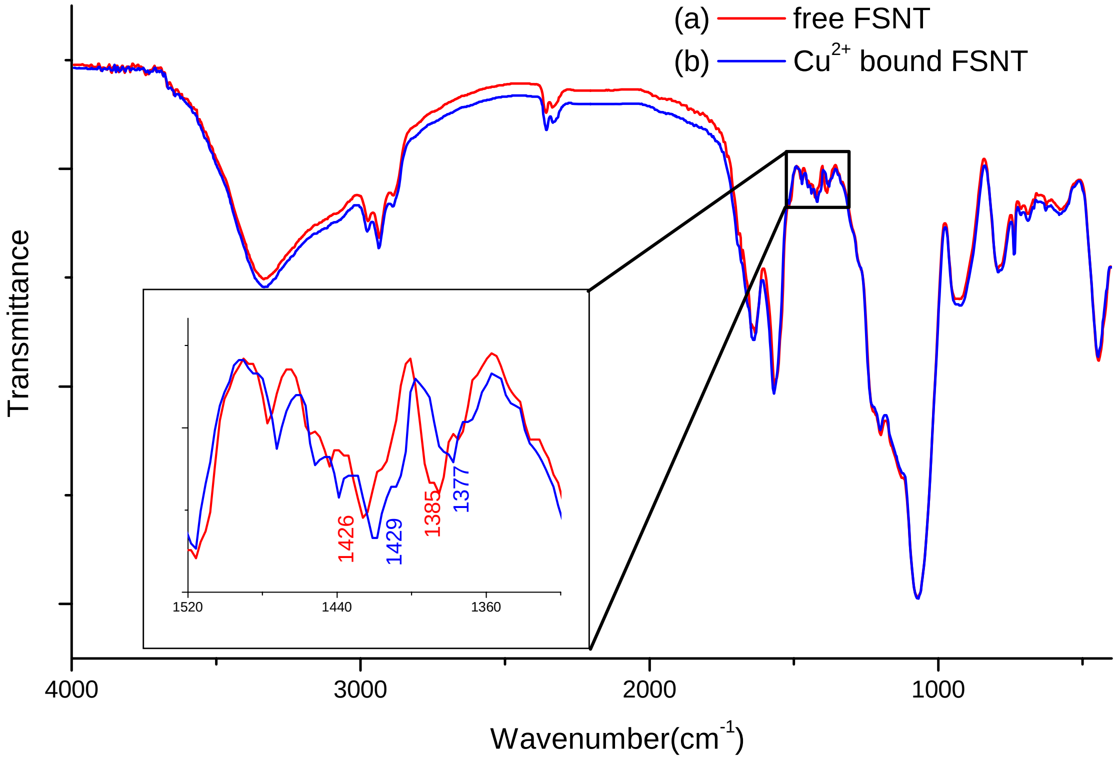

Fig. S7 FT-IR spectra of (a) free-FSNT and (b) Cu^{2+}-bound FSNT.

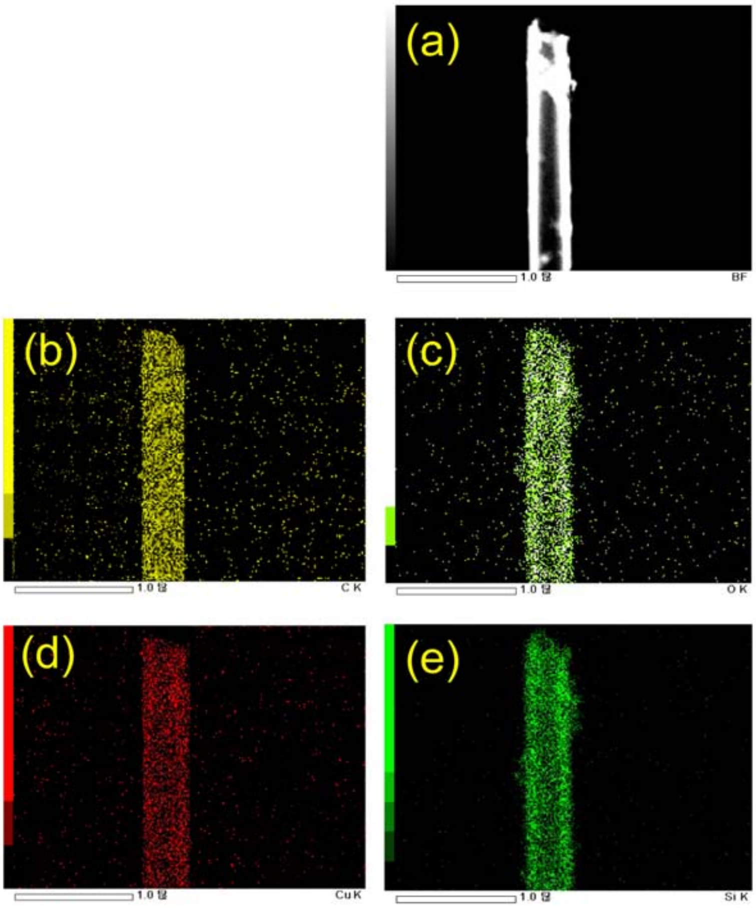

Fig. S8 TEM images with electron energy-loss spectroscopy (EELS) of the FSNT+Cu^{2+}. (a) Zero-loss image, (b) silicon component, (c) oxygen component, (d) nitrogen component and (e) carbon component.

Table S1. Absorption ability of FSNT upon the addition of metal ions in water.

Metal ions	Adsorption ability (%)
Cu^{2+}	75
Zn^{2+}	3
Cd^{2+}	2
Pb^{2+}	1
Co^{2+}	3