
Neocuproine-functionalized silica-coated magnetic nanoparticles for extraction of copper(II) from aqueous solution

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1.0 Experimental Procedures

General procedure

NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform (CDCl_3) and Deuterated DMSO (dimethyl sulfoxide- d_6) were used as solvents. Chemical shifts (δ values) were reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, ddd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublets, doublet of doublets of doublets and broad resonances respectively. Coupling constants (J) are quoted in Hertz.

IR spectra were recorded as Nujol[®] mulls (N) on a Perkin Elmer RX1 FT-IR instrument.

All the melting points were determined on a Gallenkamp melting point apparatus.

Mass spectra (m/z) were recorded under conditions of electrospray ionisation (ESI). The ions observed were quasimolecular ions created by the addition of a hydrogen ion denoted as $[\text{MH}]^+$. The instrument used was Xcalibur Tune 2.1 (SP1).

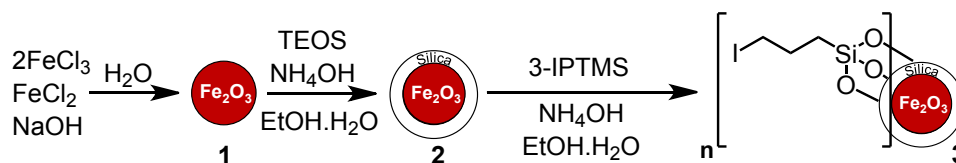
The structure of the precipitated powders was investigated by X-ray powder diffraction (XRD) with a Siemens D5000 diffractometer, using a monochromatized X-ray beam with nickel-filtered $\text{Cu K}\alpha$ radiation.

The size and morphology of the MNPs at various stages of functionalization were observed by Philips/FEI CM20 transmission electron microscopy and samples were obtained by placing a drop of colloid solution onto a copper grid and allowing evaporating in air at room temperature.

Volume statistics of particle sizes were determined by dynamic light scattering (DLS) (ZETA-SIZER, MALVERN Nano-ZS).

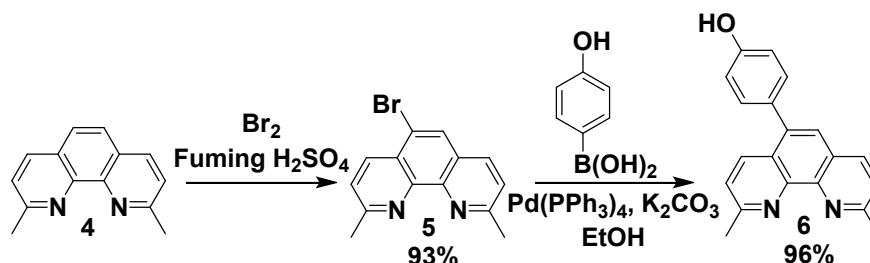
Thermo-gravimetric (TGA) analyses were performed using a TGA-Q50 thermo-gravimetric analyzer.

Iodoalkyl-functionalized silica coated magnetic nanoparticles (3)



Complete precipitation of Fe_2O_3 was achieved under alkaline conditions, while maintaining a molar ratio of $\text{Fe}^{2+}:\text{Fe}^{3+} = 1:2$ under nitrogen. To obtain 0.7 g of $\gamma\text{-Fe}_2\text{O}_3$ MNPs **1**, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (0.8 g, 4 mmol) and FeCl_3 (1.3 g, 8 mmol) dissolved in degassed deionized water 40 mL were added dropwise into 2M NaOH solution (200 mL) with vigorous stirring. After 1 hour, the resulting $\gamma\text{-Fe}_2\text{O}_3$ MNPs **1** were separated by putting the vessel on a neodymium magnet and decaying the supernatant. The MNPs **1** were washed with degassed deionized water (2×100 mL) and 0.01M HCl (17 %, 100 mL) to remove unreacted iron salts. $\gamma\text{-Fe}_2\text{O}_3$ MNPs **1** were coated with SiO_2 using a sol-gel method. Typically, 0.7 g of $\gamma\text{-Fe}_2\text{O}_3$ MNPs **1** were dispersed in a mixed solution of degassed ethanol (400 mL) and degassed deionized water (100 mL) by sonication for 10 min. NH_4OH (35 %, 36 mL) and tetraethyl orthosilicate (3.6 mL, 16 mmol) were consecutively added to reaction mixture and the reaction was allowed to proceed at room temperature for 2 h under continuous sonication. 3-iodopropyltrimethoxysilane (6.3 mL, 32 mmol) was then added and the reaction was allowed to proceed for further 3 h. The resultant functionalized particles **3** were obtained by magnetic separation and thoroughly washed with degassed ethanol ($2\times 100\text{mL}$). Finally the resultant yellow powder (2.3 g) was dried at 120°C .

Preparation of 5-(4-hydroxyphenyl)-2,9-dimethyl-1,10-phenanthroline (6)

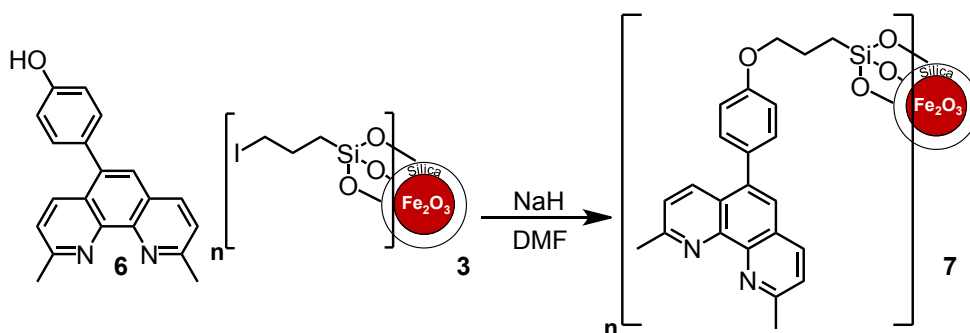


Fuming sulfuric acid (75 mL) was added to 2,9-dimethyl-1,10-phenanthroline **4** (5.11 g, 24.5 mmol). Bromine (0.76 mL, 14.7 mmol, 0.6 eq) was then added and the mixture was heated under reflux overnight. The flask was allowed to cool to room temperature and the solution was quenched with water (200 mL). NaOH pellets were added until the pH of the solution was between 7-8. The resulting mixture was extracted with chloroform (2×200 mL) and the combined organic phases were dried over MgSO_4 , filtered and the solvent removed under

vacuum to afford *5-bromo-2,9-dimethyl-1,10-phenanthroline* **5** as a yellow solid (6.51 g, 93 %); Mp 175-178 °C; ¹H-NMR (400.1 MHz, CDCl₃): δ_H (ppm) = 2.94 (s, 3H), 2.98 (s, 3H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ_C (ppm) = 25.7, 26.0, 119.7, 124.1, 124.3, 126.0, 127.1, 128.6, 135.4, 136.1, 144.8, 145.8, 160.0, 160.3; C₁₄H₁₁N₂Br [MH]⁺ requires *m/z* 287.0178; (FTMS + p ESI) MS found *m/z* 287.0180; IR *v*_{max} / cm⁻¹ = 3385, 3048, 2916, 2163, 1603, 1589, 1546, 1491, 1435, 1400.

A suspension of *5-bromo-2,9-dimethyl-1,10-phenanthroline* **5** (0.53 g, 1.8 mmol), tetrakis(triphenylphosphane)palladium(0) (0.07 g, 0.06 mmol, 0.03 eq), (4-hydroxyphenyl)boronic acid (0.28 g, 2.0 mmol, 1.1 eq) and K₂CO₃ (0.29 g, 2.1 mmol, 1.3 eq) in degassed EtOH (75 mL) was heated to reflux for 18 h under nitrogen. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with EtOH (10 mL). The filtrate was evaporated and the solid was triturated with Et₂O (25 mL). The insoluble solid was filtered and washed with chloroform (25 mL) and Et₂O (25 mL) and allowed to dry in air to afford **6** as a yellow solid (0.53 g, 96 %); Mp (above 350 °C); ¹H NMR (400.1 MHz, DMSO-*d*₆) δ_H (ppm) = 2.77 (s, 6H), 6.71 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ_C (ppm) = 24.8, 25.0, 117.0, 122.9, 123.5, 124.2, 125.8, 126.4, 130.7, 134.7, 136.1, 138.3, 143.6, 145.1, 157.3, 157.5, 164.1; C₂₀H₁₇N₂O [MH]⁺ requires *m/z* 301.1335; (FTMS + p ESI) MS found *m/z* 301.1335; IR *v*_{max} / cm⁻¹ = 3214 (O-H, phenol), 1608, 1591, 1490, 1373, 1277, 1238, 1165, 1144, 1102, 1010.

Immobilisation of (6) on silica coated magnetic nanoparticles (7)



Sodium hydride (60 % dispersion in mineral oil, 0.15 g, 3.8 mmol, 1.4 eq) was added to a solution of 5-(4-hydroxyphenyl)-2,9-dimethyl-1,10-phenanthroline **6** (0.83 g, 2.8 mmol) in DMF (100 mL) at 120 °C and stirred for 30 min. Iodoalkyl-functionalized SiO₂-coated MNPs **3** (0.80 g) were slowly added and the reaction mixture was stirred at 120 °C overnight. Neocuproine functionalized MNPs **7** were separated by an external magnet and were thoroughly washed with degassed ethanol (3×100mL). Finally, the product (0.6 g) was allowed to dry at 120 °C.

^1H and ^{13}C NMR spectra

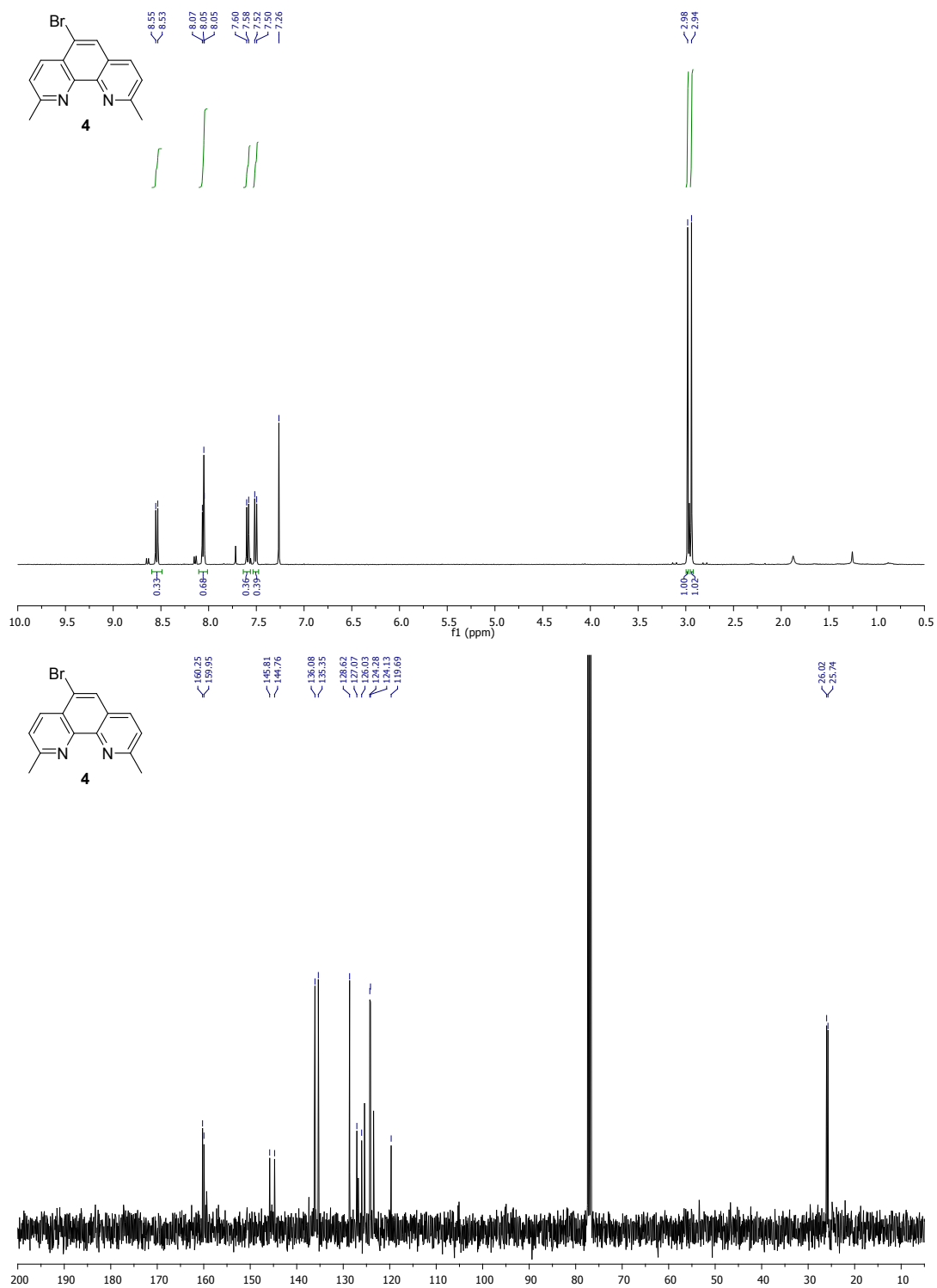


Figure S1. ^1H and ^{13}C NMR spectra of 5-bromo-2,9-dimethyl-1,10-phenanthroline **5**.

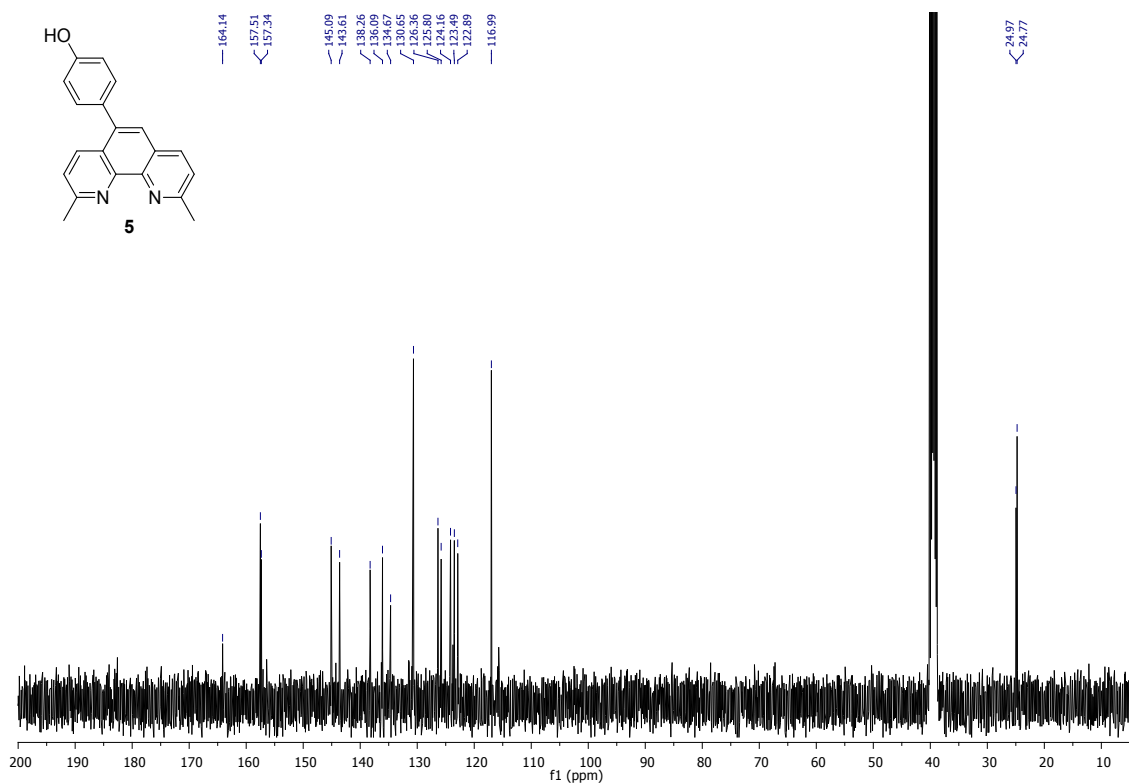
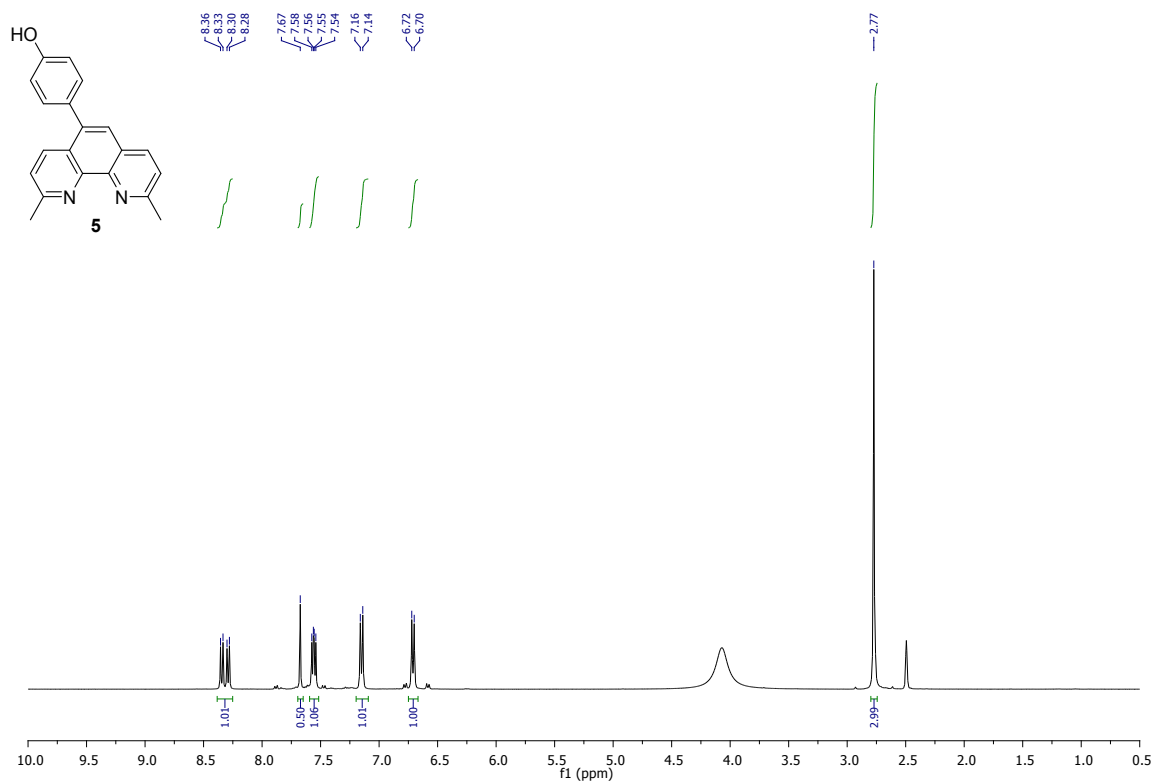


Figure S2. ¹H and ¹³C NMR spectra of 5-(4-hydroxyphenyl)-2,9-dimethyl-1,10-phenanthroline **6**.

X-ray powder diffraction data

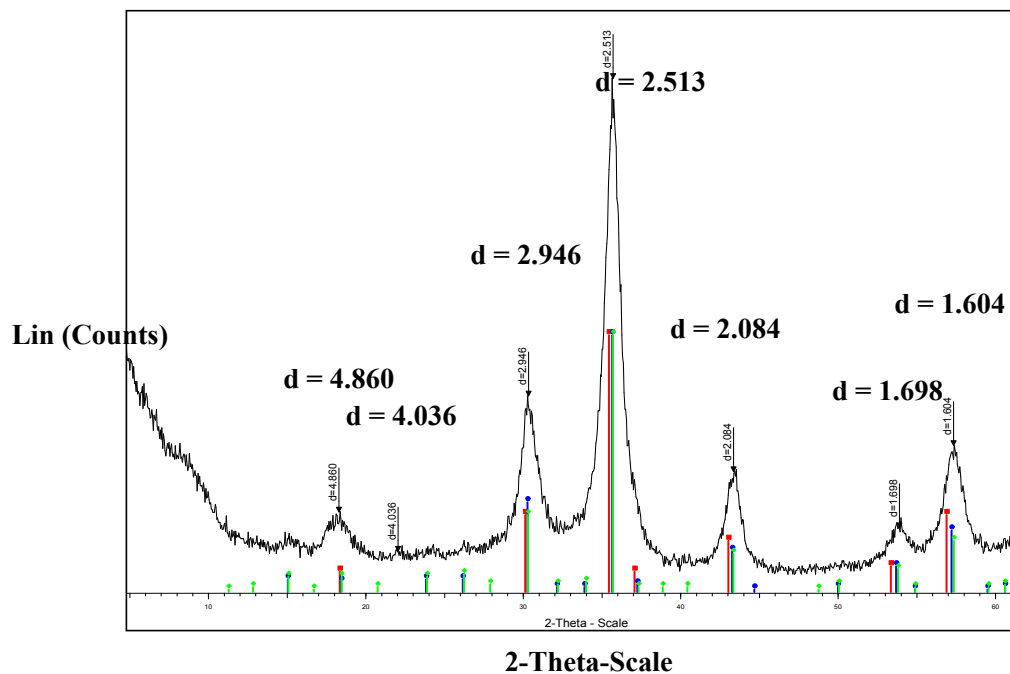


Figure S3. X-ray powder diffraction pattern of $\gamma\text{-Fe}_2\text{O}_3$ MNPs 1 overlapping the theoretical pattern for maghemite.

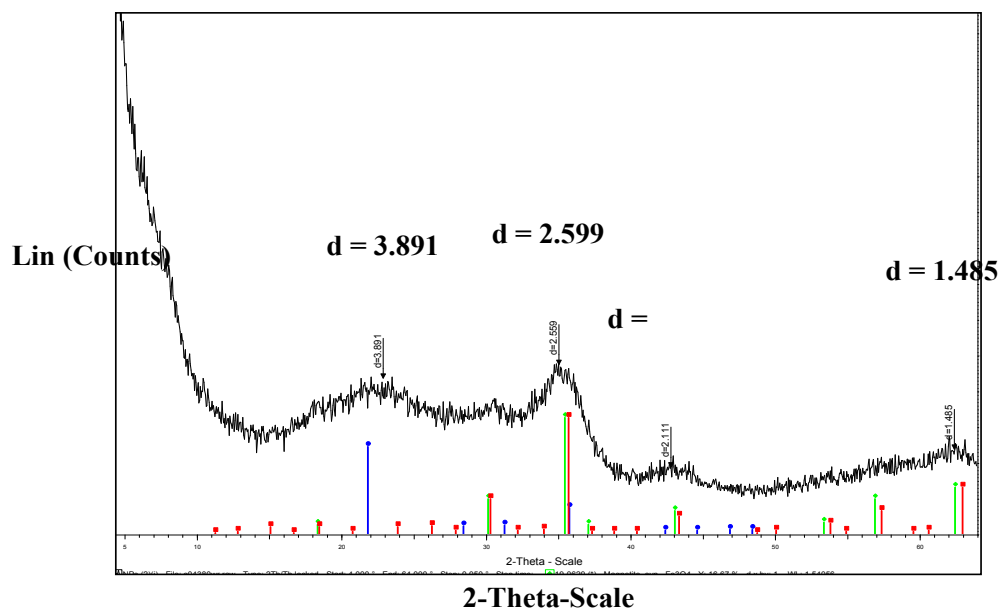


Figure S4. X-ray powder diffraction pattern of SiO_2 -coated Fe_2O_3 MNPs 2.

Dynamic light scattering data

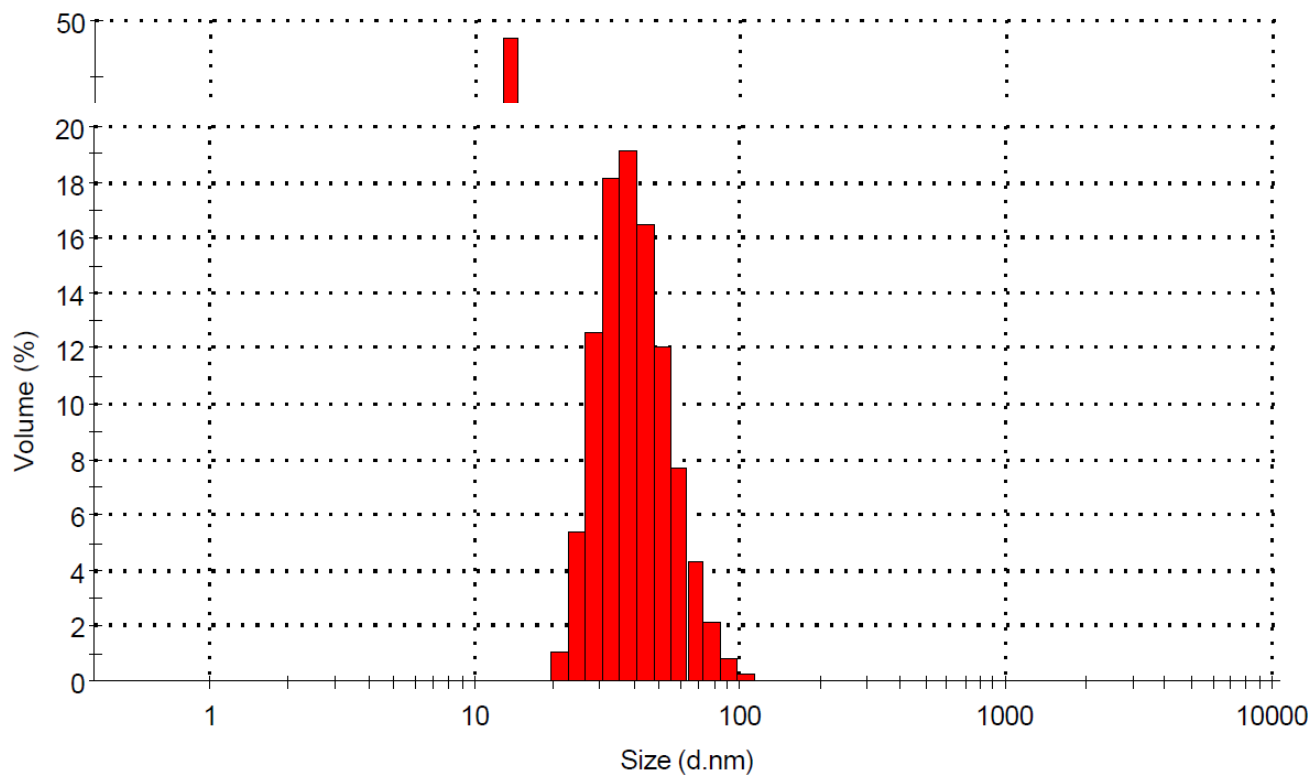


Figure S5. Size distribution of γ -Fe₂O₃ MNPs 1.

Figure S6. Size distribution of iodoalkyl-functionalized SiO₂-coated Fe₂O₃ MNPs 3.

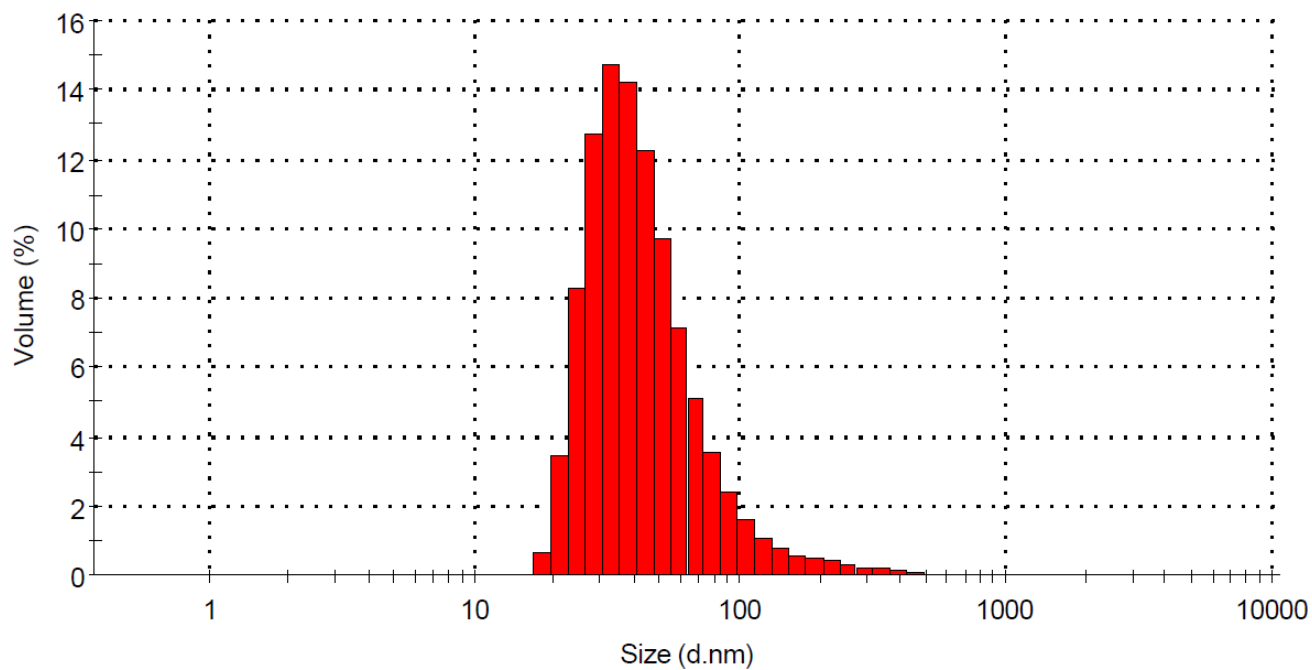


Figure S7. Size distribution of neocuproine-functionalized SiO₂-coated MNPs 7.

Thermal-gravimetric analysis

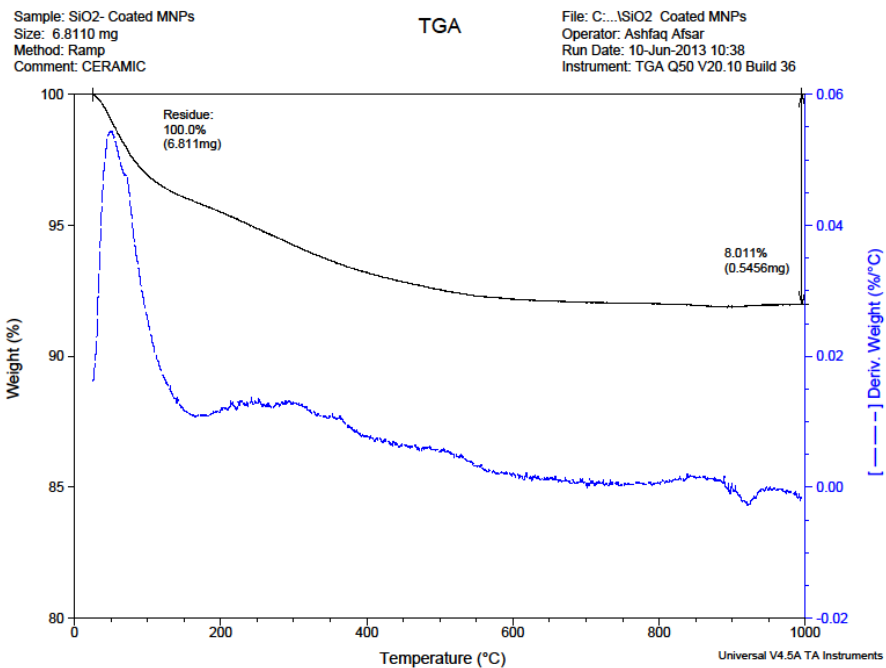


Figure S8. TGA curve of SiO₂-coated Fe₂O₃ MNPs 2.

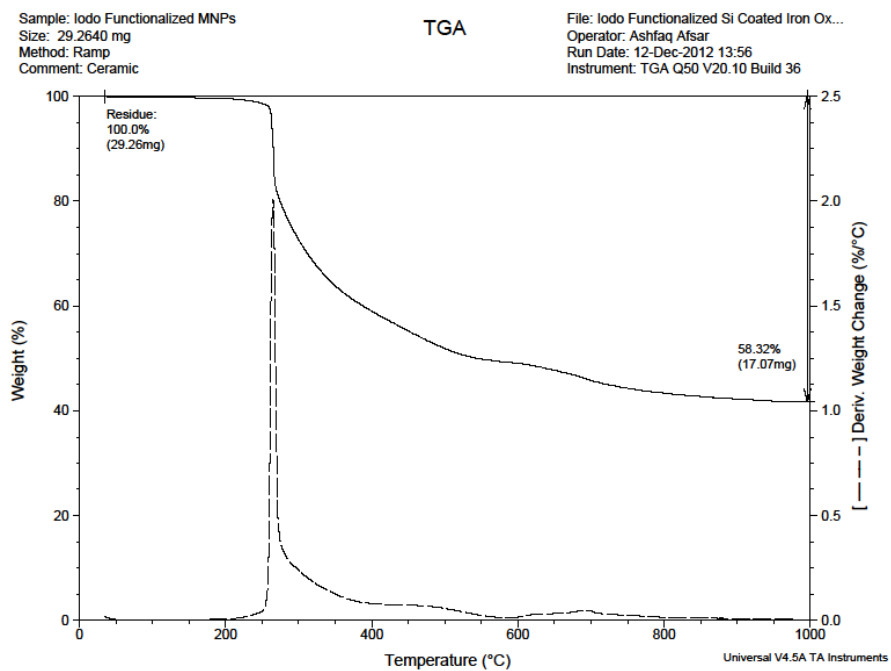


Figure S9. TGA curve of iodoalkyl-functionalized SiO₂-coated Fe₂O₃ MNPs 3.

Sample: 2-Functionalised MNPs
Size: 12.1080 mg
Method: Ramp
Comment: Ceramic

TGA

File: C:\...Ligand 2 Funtionalised MNPs
Operator: Ashfaq Afsar
Run Date: 16-Jan-2013 15:26
Instrument: TGA Q50 V20.10 Build 36

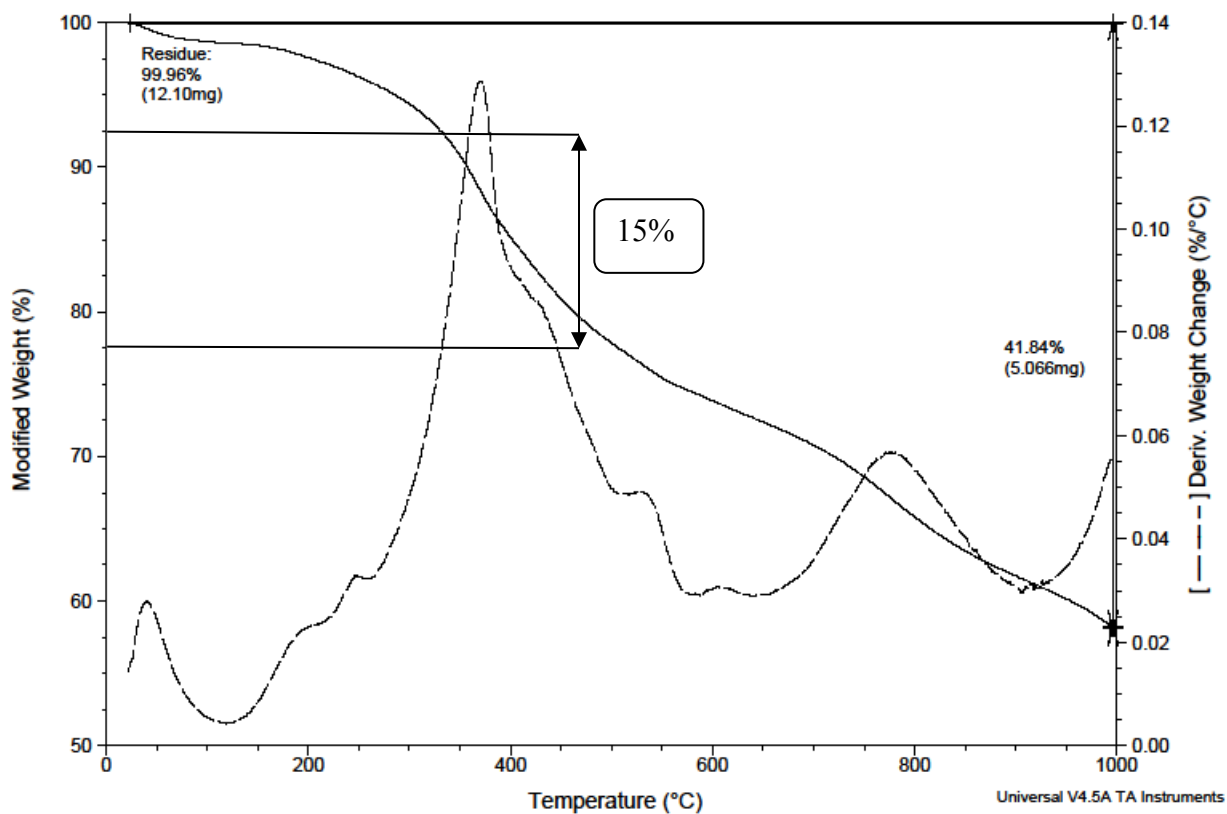


Figure S10. TGA curve of neocuproine-functionalized SiO₂-coated MNPs 7.

2.0 Solvent Extraction Properties

General Procedure

Extraction of Cu(II) by neocuproine functionalized MNPs **7** was investigated by means of the batch experiments at 25 °C. A known amount of neocuproine functionalized MNPs **7** was mixed with 10 mL of the corresponding Cu(II) solution over a period of time on a shaker at 200 rpm. After, the aqueous phase was extracted by magnetic decantation, the concentration of Cu(II) in the solution was determined by using an atomic absorption spectrometer (Perkin Elmer, 1100B). The extraction of Cu(II) by neocuproine functionalized MNPs **7** was investigated at pH range of 2-8. The solution pH was adjusted by 0.1 M NaOH or 0.1 M HNO₃. The effects of the contact time (5-60 min) and the amount of MNPs **7** dosage (3-15 mg) were also examined throughout the experiments at 25 °C and 200 rpm shaking speed maintained. The amount of Cu(II) removal was calculated from the difference between Cu(II) taken and that remained in the solution. All extraction experiments were carried out in triplicate and error bars in figures represent standard deviations.

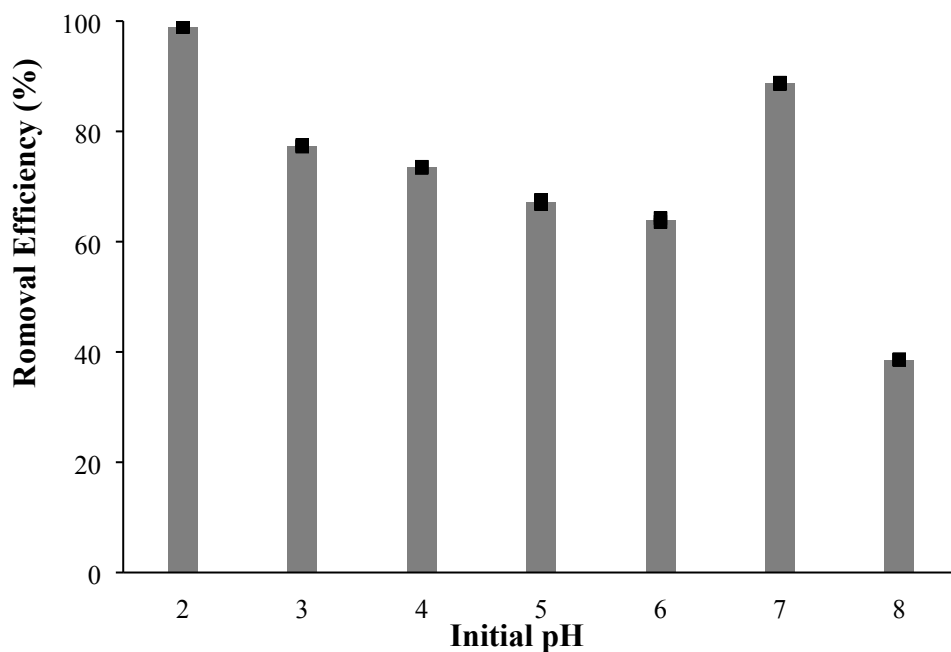


Figure S11. Effect of initial pH on the extraction efficiency of Cu(II) by MNPs **7**.

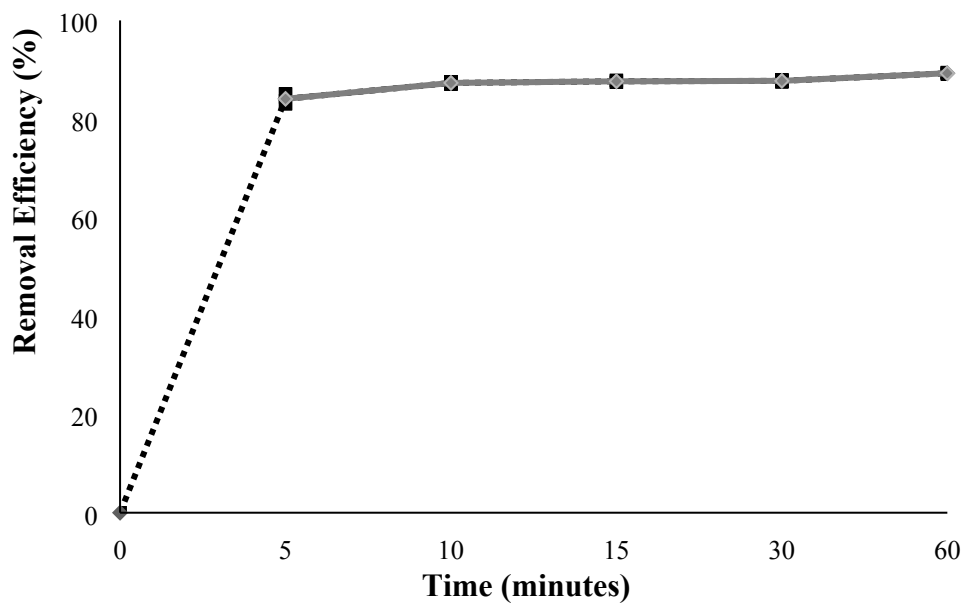


Figure S12. Effect of contact time on extraction of Cu(II) by MNPs 7.

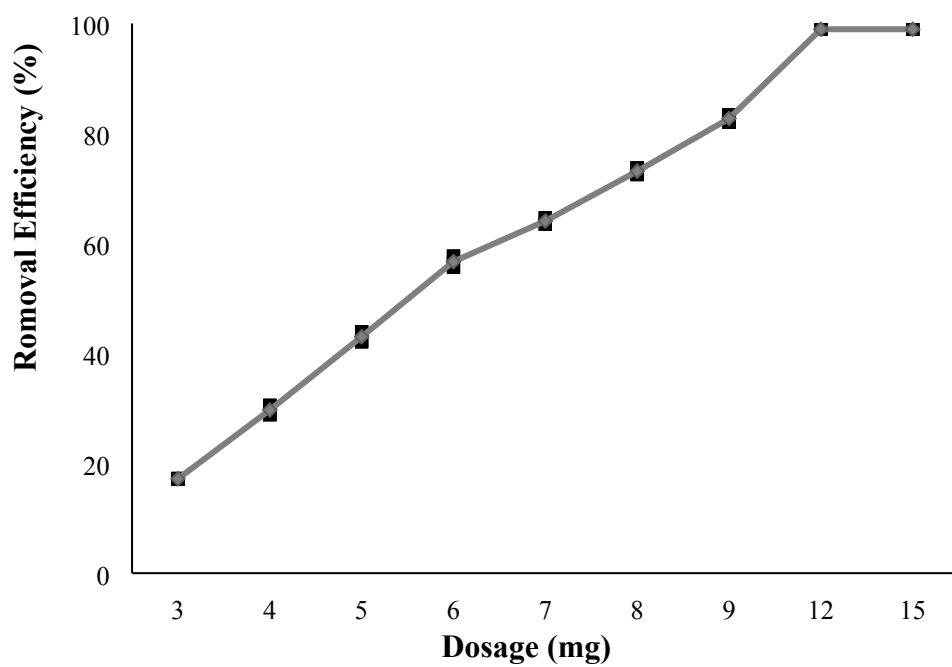


Figure S13. Effect of MNPs 7 dosage on extraction of Cu(II).