

A new magnetic nanocomposite for selective detection and removal of trace copper ions from water

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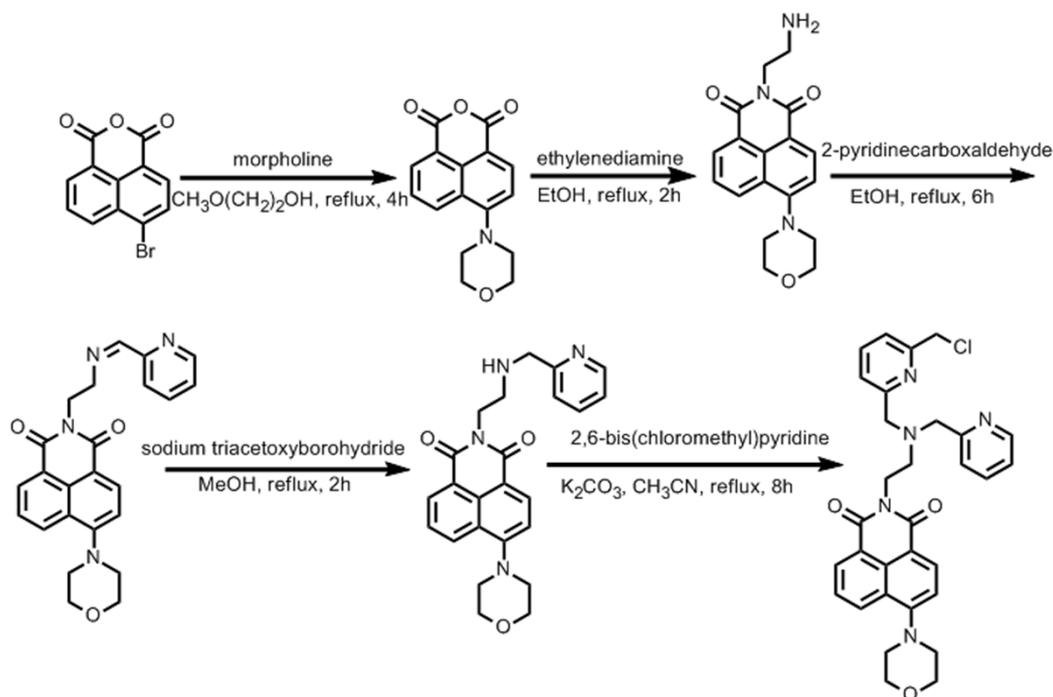
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Supplementary Information

1. Synthesis of NDPA

The compound NDPA was synthesized as the literature¹ reported. The specific synthetic route for NDPA is shown in **Scheme S1**.



Scheme S1 The synthetic routine of NDPA

1.1 Synthesis of compound 1

To a solution of 4-bromoanhydride naphthalene (5 g, 18.2 mmol) in ethylene glycol monomethyl ether was added morpholine (4.74 g, 54.3 mmol). After 4 h under reflux conditions, the reaction was cooled to room temperature and yellow needle crystals were filtered. Crude product (4-morpholinoanhydride naphthalene) was used directly without further purification. To a solution of ethylenediamine (4.2 g, 70 mmol) in ethanol was added 4-morpholinoanhydride naphthalene (2 g, 7 mmol), and the resulting mixture was refluxed for 2 h. The reaction was cooled to room temperature and concentrated via rotary evaporation. The crude product was purified on a silica gel column, eluting with 10% methanol in dichloromethane. Compound 1 was collected in 60% yield as an orange solid. [SiO₂; 9:1 (v/v) CH₂Cl₂/MeOH]. ¹H-NMR (400 MHz, DMSO): δ 8.35–8.58 (m, 3H, ArH), 7.80 (t, 1H, ArH), 7.34 (d, 1H, ArH), 4.04 (t, 2H, –CH₂CH₂–), 3.91 (t, 4H, –CH₂CH₂–), 2.50–3.21 (m, 8H, 4H for –CH₂CH₂–, –2H for –CH₂CH₂–, 2H for –NH₂).

1.2 Synthesis of compound 2

Compound 1 (1 g, 3 mmol) was dissolved in ethanol with 2-pyridinecarboxaldehyde (0.39 g, 3.6 mmol). The reaction was stirred and refluxed for 6 h. The yellow solid was precipitated, and the reaction was cooled to room temperature and filtered. Compound 2 was obtained as a yellow powder. Yield: 1.26 g, 83%. [SiO₂; 40:1 (v/v) CH₂Cl₂/MeOH]. ¹H-NMR (400 MHz, CDCl₃): δ 8.60 (m, 2H, 1H for –N=CH–, 1H for ArH), 8.54 (d, 1H, ArH), 8.42 (m, 2H, ArH), 7.99 (d, 1H, ArH), 7.21 (m, 2H, ArH), 7.26–7.30 (m, 2H, ArH), 4.58 (t, 2H, –CH₂CH₂–), 4.01–4.05 (m, 6H), 3.27 (t, 4H, –CH₂CH₂–).

1.3 Synthesis of compound 3

Sodium triacetoxyborohydride (1.5 g, 7.2 mmol) was added to a solution of compound 2 (1 g, 2.4

mmol) in methanol and refluxed for 2 h. Then the reaction mixture was cooled to room temperature. After concentration under reduced pressure, the mixture was poured into a KOH solution and extracted with dichloromethane, dried over MgSO_4 , and evaporated under reduced pressure. The crude product **3** was purified on flash silica gel using dichloromethane/methanol (40:1) as the eluent. Yield: 0.8 g, 80%. [SiO_2 ; 40:1 (v/v) $\text{CH}_2\text{Cl}_2/\text{MeOH}$]. ^1H -NMR (400 MHz, CDCl_3): δ 8.59 (d, 1H, ArH), 8.53 (d, 1H, ArH), 8.49 (d, 1H, ArH), 8.42 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.58 (d, 1H, ArH), 7.30 (d, 1H, ArH), 7.23 (d, 1H, ArH), 7.11 (t, 1H, ArH), 4.39 (t, 2H, $-\text{CH}_2\text{CH}_2-$), 4.00–4.03 (m, 6H, 4H for $-\text{CH}_2\text{CH}_2-$, 2H for $-\text{CH}_2-$), 3.27 (t, 4H, $-\text{CH}_2\text{CH}_2-$), 3.06 (t, 2H, $-\text{CH}_2\text{CH}_2-$).

1.4 Synthesis of compound NDPA

2,6-bis(chloromethyl)pyridine was synthesized as described,² 2,6-bis(hydroxymethyl)pyridine (2.40 g, 17.3 mmol) was added slowly to 20 mL of SOCl_2 at 0 °C. The reaction mixture was stirred for 1 h and then refluxed for 2 h. The crude mixture was concentrated under vacuum and 20 mL of H_2O was added. The solution was filtrated and saturated aqueous solution of sodium bicarbonate was added in drops into the filtrate. The precipitate was isolated by filtration to afford 2,6-bis(chloromethyl)pyridine as a white solid. Yield: 2.57g, 85%. ^1H NMR (400 MHz, CDCl_3): δ 7.77 (t, 1H, ArH), 7.44 (d, 2H, ArH), 4.67 (s, 4H, $-\text{CH}_2-$). The solution of compound **3** (600 mg, 1.44 mmol) in acetonitrile was slowly added to a solution of 2,6-bis(chloromethyl)pyridine (757 mg, 4.32 mmol) and potassium carbonate (796 mg, 5.76 mmol) in acetonitrile. The reaction mixture was stirred and refluxed for 8 h. After the solvent was evaporated under reduced pressure, the crude product was purified by silica gel column chromatography using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (50:1, v/v) as the eluent to afford a yellow solid. Yield: 480 mg, 60%. [SiO_2 ; 50/1 (v/v) $\text{CH}_2\text{Cl}_2/\text{MeOH}$]. ^1H NMR (400 MHz, CDCl_3): δ 8.52 (d, 1H, ArH), 8.41–8.51 (m, 3H, ArH), 7.72 (d, 1H, ArH), 7.38 (d, 1H, ArH), 7.29–7.31 (m, 3H, ArH), 7.24 (d, 1H, ArH), 7.18 (d, 1H, ArH), 7.01 (d, 1H, ArH), 4.55 (s, 2H, $-\text{CH}_2-$), 4.40 (t, 2H, $-\text{CH}_2\text{CH}_2-$), 4.04 (t, 4H, $-\text{CH}_2\text{CH}_2-$), 3.93 (s, 2H, $-\text{CH}_2-$), 3.90 (s, 2H, $-\text{CH}_2-$), 3.30 (t, 4H, $-\text{CH}_2\text{CH}_2-$), 2.94 (t, 2H, $-\text{CH}_2\text{CH}_2-$).

2. Analytical method of Cu^{2+} by UV-Vis spectrophotometry

First, series of different concentrations of copper ion solutions were prepared, and then 1 mL of 0.2% fresh sodium diethyldithiocarbamate trihydrate solution was added in each 10 mL copper ions solution. At last these copper ions solutions were analyzed by UV-Vis spectrometry to get the standard curve (**Fig. S1**). The absorbance of Cu^{2+} solutions in adsorption and detection experiments were measured by UV-Vis spectrometry and the concentrations were calculated by this standard curve.

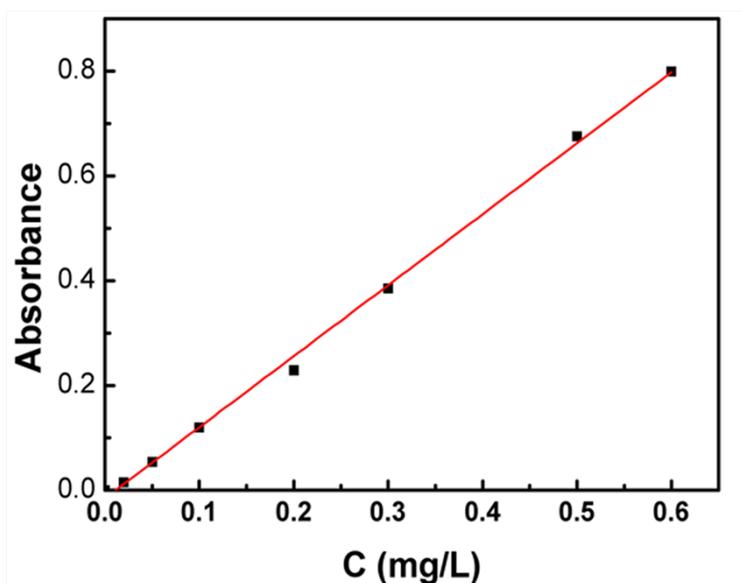


Fig. S1 Standard curve of absorbance vs Cu²⁺ concentration

3. Competitive adsorption

Selectivity of SDMA was investigated by competitive adsorption of Ni²⁺, Fe³⁺, Zn²⁺, Mn²⁺, Cu²⁺, Cr⁶⁺ and Pb²⁺ from their mixture under the same molarity. 6 mg of SDMA was added into 10 mL of the aqueous solution containing 100 μmol/L above-mentioned metal ions. Subsequently, the solutions were shaken at 20 °C for 3 h to reach adsorption equilibrium. The equilibrium concentrations were analyzed by atomic absorption spectrometry, and removal efficiencies were calculated out (Fig. S2). Although the exact removal efficiency value of Cu²⁺ from the mixed solution was lower than that in the single metal ion (only Cu²⁺) solution in Fig.6, there is an obvious selectivity to Cu²⁺ and the removal efficiency of Cu²⁺ is still distinct higher than other metals. Hence the selectivity of SDMA to Cu²⁺ is satisfying.

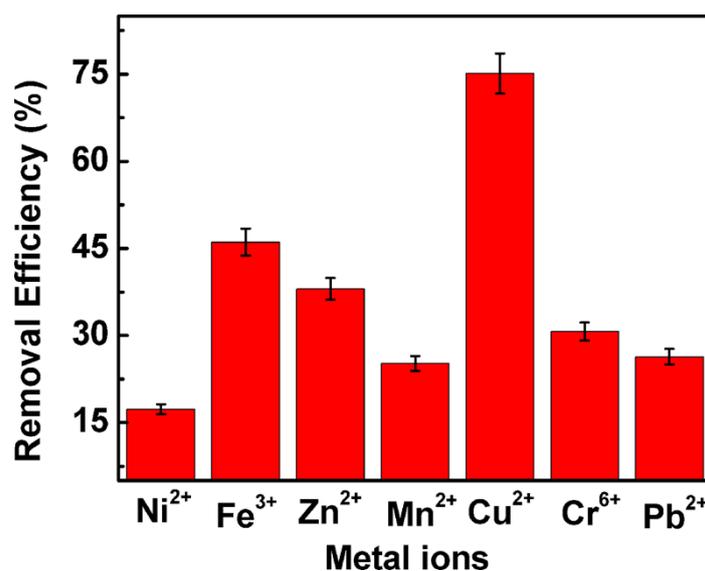


Fig. S2 Bar graph of the removal efficiencies of different metal ions from mixture

References

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