Highly selective fluorescent chemosensor for Zn\textsuperscript{2+} derived from inorganic-organic hybrid magnetic core/shell Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} nanoparticles

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Abstract
Magnetic nanoparticles with attractive optical properties have been proposed for applications in such areas as separation and magnetic resonance imaging. In this paper, a simple and novel fluorescent sensor of Zn\textsuperscript{2+} was designed with 3,5-di-tert-butyl-2-hydroxybenzaldehyde [DTH] covalently grafted onto the surface of magnetic core/shell Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} nanoparticles [NPs] (DTH-Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} NPs) using the silanol hydrolysis approach. The DTH-Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} inorganic-organic hybrid material was characterized by transmission electron microscopy, dynamic light scattering, X-ray power diffraction, diffuse reflectance infrared Fourier transform, UV-visible absorption and emission spectrometry. The compound DTH exhibited fluorescence response towards Zn\textsuperscript{2+} and Mg\textsuperscript{2+} ions, but the DTH-Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} NPs only effectively recognized Zn\textsuperscript{2+} ion by significant fluorescent enhancement in the presence of various ions, which is due to the restriction of the N-C rotation of DTH-Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} and the formation of the rigid plane with conjugation when the DTH-Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} is coordinated with Zn\textsuperscript{2+}. Moreover, this DTH-Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} fluorescent chemosensor also displayed superparamagnetic properties, and thus, it can be recycled by magnetic attraction.

Background
Zinc is the second abundant transition metal ion in the human body, which plays a vital role in various biological processes, such as gene expression [1], apoptosis [2], enzyme regulation [3], and neurotransmission [4,5]. It is also believed that the Zn\textsuperscript{2+} homeostasis may have some bearing on the pathology of Alzheimer’s disease and other neurological problems [6-8]. Therefore, there is an urgency to develop approaches to detect Zn\textsuperscript{2+} in vivo. Besides, techniques for the separation and removal of metal ions and additives in the detection process are very important to prevent poisoning in environmental and biological fields. Conventional analytical methods including atomic absorption spectrophotometry [9], inductively coupled plasma atomic emission spectrometry [10], and electrochemical method [11] can hardly be applied for Zn\textsuperscript{2+} ion detection in biological systems due to their complicated pretreatment steps and expensive equipment. Hence, for convenience in future in vivo applications, various fluorescent probes based on small molecules have been designed. They were fairly efficient as reported [12-22]; however, the small molecules would be toxic [23], and it is impossible to recover or remove them from organisms [24]. The limitation of recoverability blocked the practical applications of small molecular fluorescent probes. To resolve this challenge, the inorganic supports incorporated with small molecular fluorescent probes were applied for the improvement on recoverability.

Various mesoscopic or nanoscopic materials can be acted as the inorganic supports in the design of fluorescent probes, including magnetic nanoparticles, nanotubes, mesoporous silica, metal nanoparticles, and TiO\textsubscript{2} [25-34]. Among all these inorganic materials, magnetic silica core/shell nanoparticles have advantages over other competitors for biological and environmental applications [35-41]. Firstly, they could be simply separated or recovered via external magnetic field. Besides, with magnetic silica core/shell nanoparticles as delivery, their low toxicity and biocompatibility also had advantages for the design of biological fluorescent probes.
Furthermore, the silica shell around magnetic core has large surface area, and it can be grafted by fluorescent probes. Therefore, to develop nontoxic, biocompatible, and recoverable fluorimetric Zn$^{2+}$ sensors, introducing the magnetic silica nanoparticles with small molecular fluorescent probes incorporated is very necessary and highly desirable.

In this work, we designed and synthesized a magnetic recoverable fluorescence Zn$^{2+}$ sensor based on 3,5-di-tert-butyl-2-hydroxybenzaldehyde [DTH] covalently grafted onto Fe$_3$O$_4$@SiO$_2$ nanoparticles [NPs] (DTH-Fe$_3$O$_4$@SiO$_2$) to provide highly selective fluorescence changes and efficient magnetic recoverability (Figure 1). This Zn$^{2+}$-selective fluorescent switch of the immobilized chemosensors displayed excellent reversibility, combined with its superparamagnetic property, enabling the recovery of material and repeated uses for Zn$^{2+}$ sensing.

**Experimental details**

**Materials and methods**

All reagents are purchased commercially. Besides, ethanol was used after purification by standard methods. Other chemicals were used as received without further purification.

[Figure 1 Syntheses of DTH-APTES and DTH-Fe$_3$O$_4$@SiO$_2$.]
quartz cells of 1.0-cm path length. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer (Tokyo, Japan) and a Shimadzu RF-540 spectrofluorophotometer (Chorley, UK) equipped with quartz cuvettes of 1.0-cm path length with a xenon lamp as the excitation source. An excitation and emission slit of 10.0 nm was used for the measurements in the solution state. All spectrophotometric titrations were performed with a suspension of the sample dispersed in ethanol.

**Synthesis of Fe₃O₄@SiO₂ NPs**

Fe₃O₄@SiO₂ NPs were synthesized according to the study of Nigam et al. [42]. The process can be briefly described in the following two steps: (1) FeCl₂ and FeCl₃ (molar ratio, 1:2) were added to a concentrated solution of base (25% ammonium hydroxide) under N₂. The solution was mechanically stirred for 1 h at 20°C and then heated at 70°C for 1 h. The mixture was then stirred for 30 min at 90°C upon addition of citric acid (0.5 g/ml). After cooling the reaction mixture to room temperature, the magnetite NPs were obtained by permanent magnet, and then it was rinsed with deionized water to remove excess citric acid and other nonmagnetic particles thoroughly. (2) Then, the magnetite NPs were further coated with a thin silica layer via a modified Stöber method [43] to obtain stable Fe₃O₄@SiO₂. Tetraethyl orthosilicate was hydrolyzed with magnetic NPs as seeds in an ethanol/water mixture. The resulting silica-coated magnetite NPs with an average diameter of 60 to 70 nm were used.

**Synthesis of DTH-Fe₃O₄@SiO₂ NPs**

As shown in Figure 1, the synthetic procedure for 2,4-di-tert-butyl-6-((3-(triethoxysilyl)propylimino)methyl)phenol [DTH-APTES] followed the method previously described in the literatures [44,45]. DTH (234 mg, 1 mmol) and (3-aminopropyl)triethoxysilane [APTES] (221 mg, 1 mmol) were mixed in dry ethanol (15 mL) at room temperature. Then, the solution was refluxed for 3 h under N₂. After that, the solvent was evaporated, and the crude product was further purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether 1:2) to produce 371 mg (84.9%) of DTH-APTES. The product was characterized by 1H NMR, 13C NMR, FT-IR, and ESI-MS. ESI-MS: m/z 438.5 (M + H⁺). ¹H NMR: (400 MHz, CDCl₃): δ (ppm) 0.69 (t, 2H, CH₂Si); 1.22 (t, 9H, CH₃); 1.30 (s, 9H, C(CH₃)₃); 1.82 (m, 2H, CH₂); 3.58 (t, 2H, NCH₂); 3.82 (q, 6H, SiOCH₂); 7.07, 7.36 (d, 2H, Ar); 8.34 (s, 1H, HC = N). ¹³C NMR (100 MHz, CDCl₃): 7.92 (CH₂Si); 18.30 (CH₃); 24.38, 29.40, 29.70, 31.50 (CH₃); 34.11 (C), 35.01 (C); 58.41 (CH₂); 62.08 (CH₂); 117.83, 125.69, 126.66, 136.65, 139.75, 158.27 (Ar); 165.80 (C = N). FT-IR (KBr pellet) (cm⁻¹): 1,637 (ν Ş, ν₃), 1,275-1,252 (νC-O), 1,596-1,342 (νC = C), 1,106-1,085 (νSi-O).

One hundred milligrams of dried Fe₃O₄@SiO₂ NPs and 356 mg (0.81 mmol) of DTH-APTES were suspended in 10 mL of anhydrous ethanol. The mixture was refluxed for 8 h at 80°C under N₂ to obtain DTH-Fe₃O₄@SiO₂. The nanoparticles were collected by centrifugation and repeatedly washed with anhydrous ethanol thoroughly. Unreacted organic molecules were removed completely and monitored by the fluorescence of the upper liquid. Then, the DTH-Fe₃O₄@SiO₂ NPs were finally dried under vacuum over night. About 2.81% DTH-APTES in the precursors was finally grafted on the NPs, and the rest could be recycled if no hydrolysis occurred.

**Results and discussion**

**Characterization of DTH-Fe₃O₄@SiO₂**

The TEM image (Figure 2A) of DTH-Fe₃O₄@SiO₂ reveals that iron oxide NPs have entrapped in the silica shell successfully, in which the core/shell structures are in a narrow size distribution of 60 to 70 nm [46,47], and the diameter of the magnetic core is about 10 nm. The weight ratio of iron vs. silicon was measured to be 2.63:38.94 by EDX. Hence, according to TGA, each magnetic NP has about 6,000 DTH-APTES molecules grafted (see Additional file 1). More importantly, the right size of magnetic core/shell NPs smaller than 100 nm is an advantage for their good dispersibility. In addition, an inert silica coating on the surface of magnetite nanoparticles prevents their aggregation in liquid [48]. Hence, such a good performance on the dispersibility can improve their chemical stability and provide better protection against toxicity.

In addition, dynamic light scattering [DLS] was performed to further reveal the colloidal stability of NPs. According to DLS results (Figure 2B), DTH-Fe₃O₄@SiO₂ presents good stabilization and a narrow size distribution with peak centered at 147 nm, confirming its good stabilization in ethanol. In a common sense, the diameter achieved by DLS is mostly higher than the one observed in TEM since the size of NPs identified by DLS includes the grafted molecules’ steric hindering and the hydrodynamic radius of first few solvent layers [49-51]. Besides, according to the calculated size of DTH-APTES which covalently grafted on the surface of Fe₃O₄@SiO₂, the grafted molecules’ steric hindering could increase the diameter by about 2.72 nm.

Figure 3 shows the XRD powder diffraction patterns of two NPs for the identification of Fe₃O₄ in core/shell NPs. XRD patterns of the synthesized Fe₃O₄@SiO₂ (a) and DTH-Fe₃O₄@SiO₂ (b) display relative diffraction peaks in the 2θ region of 10° to 80°. We could find that XRD patterns show very low intensities for the peaks attributed to the Fe₃O₄ cores, due to the coating of
amorphous silica shell, which deduced the efficient content of Fe₃O₄ cores and then affected the peak intensities. However, the diffraction peaks of DTH-Fe₃O₄@SiO₂ still maintain the same position as the magnetite core (Figure S1 in Additional file 1) [52]. The six characteristic diffraction peaks in Figure 3 can be indexed to (220), (311), (400), (422), (511), and (440), which well agree with the database of magnetite in the

Figure 2 TEM image (A) and the particle size histogram from DLS (B) of DTH-Fe₃O₄@SiO₂.
Joint Committee on Powder Diffraction Standards [JCPDS] (JCPDS card: 19-629) file [42,46,53,54]. Also, the broad XRD peak at a low diffraction angle of 20° to 30° corresponds to the amorphous-state SiO₂ shells surrounding the Fe₃O₄ NPs [53].

The successful conjugation of DTH onto the surface of the Fe₃O₄@SiO₂ NPs can be confirmed by DRIFT (Figure 4). The bands at 3,400 to 3,500 cm⁻¹ and 1,000 to 1,250 cm⁻¹ are due to -OH stretching on silanol [55]. It indicates that not all the silanol on Fe₃O₄@SiO₂ NPs...
have been covalently modified. The band at 1,630 cm\(^{-1}\) represents the bending mode of -OH vibrations [56]. DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) (see Figure 1) has additional peaks at 2,918 and 2,850 cm\(^{-1}\) that correspond to the -CH vibration of aliphatic and aromatic groups [28,57,58]. The bands at 1,473 and 1,463 cm\(^{-1}\) of DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) are probably due to the bending vibrations of -CH\(_3\), which come from the DTH part [59]. According to the spectra of Fe\(_3\)O\(_4\)@SiO\(_2\) and DTH-Fe\(_3\)O\(_4\)@SiO\(_2\), the bands which appear as broad and strong and are centered at 1,102 (\(\nu_{as}\)) and 800 cm\(^{-1}\) can be attributed to the siloxane (-Si-O-Si-) [60]. These results support the presence of the organic DTH-APTES in the magnetic material DTH-Fe\(_3\)O\(_4\)@SiO\(_2\).

The UV-visible [UV-Vis] spectra of DTH-APTES (1.0 \(\times\) 10\(^{-5}\) M), Fe\(_3\)O\(_4\)@SiO\(_2\) (0.3 g/L), and DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) (0.3 g/L) can provide further evidence on the grafting of DTH onto the surface of the Fe\(_3\)O\(_4\)@SiO\(_2\) NPs (Figure 5). Compared to Fe\(_3\)O\(_4\)@SiO\(_2\) (b), a new absorption band centered at about 330 nm of DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) can be attributed to the typical electronic transition of an aromatic ring and -C = N- conjugate system in a Schiff base molecule [29]. This result can also imply the successful immobilization of DTH-APTES onto the magnetic core/shell NPs.

The superparamagnetic property of the magnetic NPs plays a vital role for its biological application. Figure 6 shows the magnetization curves of the Fe\(_3\)O\(_4\)@SiO\(_2\) and DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) which were investigated with a vibrating sample magnetometer tuned from -15,000 to 15,000 Oe at 300 K. The result was consistent with the conclusion that magnetic Fe\(_3\)O\(_4\) NPs smaller than 30 nm are usually superparamagnetic at room temperature [47]. The saturation magnetization value for synthesized DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) is about 3.96 emu/g. The saturation magnetization value for Fe\(_3\)O\(_4\)@SiO\(_2\) support was measured to be 4.24 emu/g. Considering the grafting rate of 7.64% (according to TGA, Figure S2 and Table S1 in Additional file 1), the difference of saturation magnetization values between DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) and its support could be due to the decreased weight ratio of magnetic support after grafting. More importantly, from the hysteresis loops of Fe\(_3\)O\(_4\)@SiO\(_2\) NPs and the DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) NPs, it can be found that both exhibited superparamagnetic properties for no remanence was observed when the applied magnetic field was removed. These phenomena were due to the fact that the magnetite core is smaller than 30 nm in core/shell NPs (Figure 2A). As a result of this superparamagnetic property, DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) had a reversal magnetic responsivity. It could be easily separated from dispersion after only 5 min using a magnet (Figure 6, inset) and then redispersed by mild agitation when the magnet was removed. The reversal magnetic responsivity of DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) would be a key factor when evaluating their recoverability [61]. The magnetic separation capability of DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) NPs and the reversibility of the combination between DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) and Zn\(^{2+}\) could also provide a simple and efficient route to separate Zn\(^{2+}\) rather than through filtration approach (see Figure 6 inset).
Fluorescence response of DTH-Fe₃O₄@SiO₂

To verify its fluorescence response towards various metal ions, we investigated fluorescence properties of DTH-Fe₃O₄@SiO₂ NPs (0.3 g/L, containing 5.2 × 10⁻⁵ M DTH-APTES according to TGA in Figure S2 and Table S1 in Additional file 1) towards various metal ions Ag⁺, Ca²⁺, Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Hg²⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, and Zn²⁺ in ethanol solution (all as perchlorates, 1.0 × 10⁻⁴ M). As shown in Figure 7A, DTH-Fe₃O₄@SiO₂ NPs exhibited significant ‘off-on’ changes in fluorescence emission only for Zn²⁺, but not for the others. It is noted that Cd²⁺ with a d¹⁰ electron configuration, which often exhibited coordination properties similar to Zn²⁺ [19], do not influence the fluorescence intensity of DTH-Fe₃O₄@SiO₂ NPs significantly.

As a comparison, DTH (1.0 × 10⁻⁵ M) exhibited fluorescence response towards both Zn²⁺ and Mg²⁺ ions (1.0 × 10⁻⁴ M) in the same solution, which is not as selective as DTH-Fe₃O₄@SiO₂ for Zn²⁺ detection (Figure 7B). Compared to the single aldehyde DTH, the origin of selectivity for DTH-Fe₃O₄@SiO₂ may come from its Schiff base structure, which prefers to coordinate with Zn²⁺ under the interference of Mg²⁺.

The remarkable increase of fluorescence intensity can be explained as follows: DTH-Fe₃O₄@SiO₂ is poorly fluorescent due to the rotation of the N-C bond of DTH-APTES part. When stably chelated with Zn²⁺, the N-C rotation of DTH-APTES part is restricted and the rigid plane with conjugation is formed and the fluorescence enhanced, which consists of our previous work [62]. The emission spectra of DTH-Fe₃O₄@SiO₂, which is excited at 397 nm, exhibit the emission maximum at 452 nm with a low quantum yield (Φ = 0.0042) at room temperature in ethanol. Upon the addition of excess Zn²⁺, the fluorescence intensity of DTH-Fe₃O₄@SiO₂ increased by more than 25-fold, the emission maximum shifts from 452 to 470 nm, and the quantum yield (Φ = 0.11) results in a 26-fold increase.

As illustrated in Figure 8A, the fluorescence emission of DTH-Fe₃O₄@SiO₂ (0.3 g/L) increases gradually when adding various concentrations (0 to 30 μM) of Zn²⁺ in ethanol, indicating that Zn²⁺ is quantitatively bound to the Schiff base moiety attached to the NPs. Fluorescence titration experiment suggests that the association constant (Kₐ) for Zn²⁺ binding to DTH-Fe₃O₄@SiO₂ is calculated to be 51.08 M⁻² (log K = 1.71; Figure 8A). Job’s plot suggested a 1:2 binding ratio for Zn²⁺ with DTH-APTES (Figure 8B).

The competition experiments indicated that the presence of most metal ions, especially Na⁺, K⁺, Ca²⁺, and Mg²⁺, which are abundant in the biological environment, had a negligible effect on Zn²⁺ sensing (Figure 9A). Since Cr³⁺, Cu²⁺, Fe³⁺, and Hg²⁺ also appeared to bind DTH-Fe₃O₄@SiO₂ sensors (Figure S3 in Additional file 1), they quenched the fluorescence of the Zn²⁺-DTH-Fe₃O₄@SiO₂, owing to an electron or energy transfer between the metal.
cation and fluorophore known as the fluorescence quenching mechanism [63-66]. The fluorescence enhancement that occurred upon exposure to Zn\(^{2+}\) was fully reversible as the addition of EDTA (2.5 × 10\(^{-4}\) M; Figure 9B and inset) restored the emission band. Combined with its magnetic property, the results above implied that DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) was considerably applicable to some field as a new inorganic-organic hybrid sensor for the Zn\(^{2+}\) ion.

Figure 10A depicts the UV-Vis spectra of DTH-APTES (10 \(\mu\)M), DTH-APTES (10 \(\mu\)M) + Zn\(^{2+}\) (100 \(\mu\)M), DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) (0.3 g/L), and DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) (0.3 g/L) + Zn\(^{2+}\) (100 \(\mu\)M). It can be seen that the absorbance peaks at around 390 nm are formed when Zn\(^{2+}\) is added in both DTH-APTES and DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) systems. The absorption spectra of DTH-Fe\(_3\)O\(_4\)@SiO\(_2\) systems.
of Zn$^{2+}$ (0 to 240 μM) were investigated in ethanol at room temperature, as shown in Figure 10B. When Zn$^{2+}$ was added gradually, the absorbance of DTH-Fe$_3$O$_4$@SiO$_2$ at 390 nm gradually increases, which indicated that DTH-Fe$_3$O$_4$@SiO$_2$ NPs coordinated with Zn$^{2+}$ gradually.

**Figure 8 Fluorescence titrations and Job’s plot**  
(A) Fluorescence titrations of DTH-Fe$_3$O$_4$@SiO$_2$ with Zn$^{2+}$.  
(B) Job’s plot of DTH-APTES with Zn$^{2+}$. Spectra were recorded every 25 min after adding Zn$^{2+}$.

**Conclusions**  
In summary, we have successfully designed and synthesized functionalized magnetic core/shell Fe$_3$O$_4$@SiO$_2$ NPs (DTH-Fe$_3$O$_4$@SiO$_2$ NPs) which could act as a new type of fluorescent chemosensor for efficient sensing and
separation of $\text{Zn}^{2+}$ in ethanol. The inorganic-organic hybrid fluorescent chemosensor DTH-Fe$_3$O$_4$@SiO$_2$ was able to recognize and adsorb $\text{Zn}^{2+}$ with a selective and sensitive fluorescence response in ethanol. The magnetic separation capability of Fe$_3$O$_4$@SiO$_2$ NPs and the reversibility of the combination between DTH-Fe$_3$O$_4$@SiO$_2$ and $\text{Zn}^{2+}$ would also provide a simple route to separate $\text{Zn}^{2+}$ from the environment (Figure 6, inset).

Figure 9 Competition of DTH-Fe$_3$O$_4$@SiO$_2$ towards cations and reversibility of DTH-Fe$_3$O$_4$@SiO$_2$ towards $\text{Zn}^{2+}$. (A) Fluorescent emission changes of DTH-Fe$_3$O$_4$@SiO$_2$ (0.3 g/L) upon addition of 1, blank; 2, $\text{Zn}^{2+}$; 3, $\text{Na}^+$; 4, $\text{Na}^+$ + $\text{Zn}^{2+}$; 5, $\text{K}^+$; 6, $\text{K}^+$ + $\text{Zn}^{2+}$; 7, $\text{Ca}^{2+}$; 8, $\text{Ca}^{2+}$ + $\text{Zn}^{2+}$; 9, $\text{Mg}^{2+}$; and 10, $\text{Mg}^{2+}$ + $\text{Zn}^{2+}$ (each metal ion is 100 $\mu$M) in ethanol at room temperature. (B) Fluorescence spectra of DTH-Fe$_3$O$_4$@SiO$_2$ (0.3 g/L) in (a) without, (b) with $\text{Zn}^{2+}$ (1.0 $\times$ 10$^{-4}$ M), and (c) after treatment with EDTA (2.5 $\times$ 10$^{-4}$ M) in (b) solution. The inset picture shows the photograph of DTH-Fe$_3$O$_4$@SiO$_2$ with $\text{Zn}^{2+}$ by treatment of EDTA (2.5 $\times$ 10$^{-4}$ M) under a 365-nm UV light.
Figure 10 UV-Vis spectra. (A) Absorption spectra of (a) DTH-APTES (1.0 × 10^{-5} M), (b) DTH-APTES + Zn^{2+} (1.0 × 10^{-4} M), (c) DTH-Fe_3O_4@SiO_2 (0.3 g/L), and (d) DTH-Fe_3O_4@SiO_2 (0.3 g/L) + Zn^{2+} (1.0 × 10^{-4} M) in ethanol. (B) UV-Vis spectra of DTH-Fe_3O_4@SiO_2 (0.3 g/L) in ethanol in the presence of different amounts of Zn^{2+} (0 to 240 μM).
Additional material

Additional file 1: Characterization and properties of DTH-Fe3O4@SiO2. Figure S1, XRD patterns of Fe3O4 core: Figure S2, TGA curves of Fe3O4@SiO2 (a) and DTH-Fe3O4@SiO2 (b); Figure S3, selectivity of DTH-Fe3O4@SiO2 for Zn(II) in the presence of other metal ions in ethanol; and Table S1, the loading of DTH-APTES in the Fe3O4@SiO2 NPs as estimated by different methods.

Abbreviations

APTES: (3-aminopropyl)triethoxysilane; DLS: dynamic light scattering; DRIFT: diffuse-reflectance infrared Fourier transform; DTH: 3,5-di-tert-butyl-2-hydroxybenzaldehyde; DTH-Fe3O4@SiO2: 2,4-di-tert-butyl-6-(3-(triethoxysilyl)propylamino)methylphenol; EDX: energy-dispersive X-ray spectrometer; NPs: nanoparticles; TEM: transmission electron microscopy; TRES: tetraethyl orthosilicate; TGA: thermal gravimetric analysis; XRD: X-ray powder diffraction.

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Authors’ contributions

YW supervised and participated in all the studies and wrote this paper. XP conceived the study and participated in its design. JS participated in the revision of the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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