



# Fluorophore-modified Fe<sub>3</sub>O<sub>4</sub>-magnetic-nanoparticles for determination of heavy metal ions in water

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## ABSTRACT

A prototype of fluorescence sensor, based on 1,4-dihydroxyanthraquinone (1,4-DHAQ) derivative and 9-fluorenylmethyl chloroformate (Fmoc-Cl) co-modified Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) (denoted as 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs), has been achieved via solvothermal synthesis of amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs and subsequent surface co-modification of 1,4-DHAQ derivative and Fmoc-Cl onto the Fe<sub>3</sub>O<sub>4</sub> MNPs. The 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs can be used for not only simple rapid qualitative detection of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> in aqueous solution, but also quantitative analysis of the above four heavy metal ions with lower detection limits of  $8 \times 10^{-9}$ ,  $1.5 \times 10^{-8}$ ,  $10^{-8}$  and  $10^{-8}$  M, respectively. This is the first prototype of fluorescence sensor that has potentials in the detection of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> in aqueous solutions and even in drinking water. The sensor designing idea might be extended to other multifunctional chemosensors.

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## 1. Introduction

Detecting heavy transitional metal ions, especially Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>, has received considerable attention, owing to the demands for environmental and biological monitoring and related applications [1–6]. Cu<sup>2+</sup> and Zn<sup>2+</sup> play important roles in life processes [1,2], and disruptions of both Cu<sup>2+</sup> and Zn<sup>2+</sup> homeostasis can induce health disorders [1–4]. On the contrary, Cd<sup>2+</sup> and Hg<sup>2+</sup> are highly toxic and common pollutants in our environment [5,6]. Therefore, the above-mentioned four heavy metal ions may affect our life and health severely, and exploiting highly sensitive and selective probes for trace amount of these heavy metal ions in water systems is important and exigent.

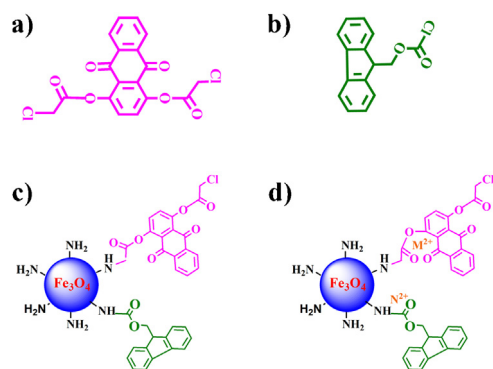
In view of the current in situ and real time detection approaches to specific metal ions, fluorescence spectroscopy approach has received special attention for its rapidity, simplicity, high sensitivity and selectivity. Meanwhile, fluorophores immobilized on nanomaterials exhibit much higher sensitivity than that of the

bare fluorophores dissolved in solutions, and have been widely used as fluorescence sensors [5–18]. So far, several nanomaterial-based fluorescence sensors for Cu<sup>2+</sup>, such as N-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide modified silicon nanowires [8], 1,4-dihydroxyanthraquinone doped cellulose microporous nanofiber films [10], 1,8-naphthalimide-based receptor in mesoporous silica material [11], 9,10-diphenylanthracene modified polymer nanoparticles [12], glutathione-capped gold nanoparticles [13], and CdS Quantum Dots [14], have been developed. As for the nanomaterial-based fluorescence sensors for Zn<sup>2+</sup>, CdS Quantum Dots [14] and 8-hydroxyquinoline imprinted mesoporous silica [15] have been reported. For the fluorescence detection of Cd<sup>2+</sup>, 8-hydroxyquinoline imprinted mesoporous silica [15] has been fabricated. And for the nanomaterial-based fluorescence sensors for Hg<sup>2+</sup>, porphyrin-functionalized Au@SiO<sub>2</sub> core/shell nanoparticles [5], 1,8-naphthalimide immobilized gold nanoparticles [16], bovine serum albumin functionalized fluorescent gold nanoparticles [17], and hydrophobic fluorescein derivative (FLS-C12) incorporated in a kind of micelle core [18], have been developed, respectively. However, most of them [8,10–13,15,16–18] can detect only one kind of metal ions, except that CdS Quantum Dots and 8-hydroxyquinoline imprinted mesoporous silica can detect two kinds of metal ions simultaneously [14,15], and none of these fluorescence sensors can detect more than three heavy metal ions, and none of them can be reclaimed from the detected samples after fluorescence

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**Fig. 1.** Structural illustration of (a) 1,4-DHAQ derivative, (b) Fmoc-Cl, (c) the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs, and (d) the coordination of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs with Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>, respectively. (M<sup>2+</sup> = Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>; N<sup>2+</sup> = Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>).

monitoring. Therefore, it is really a big challenge to develop nanomaterial-based fluorescence sensors that can be used to detect these four heavy metal ions in aqueous solutions.

Previously, we successfully assembled 1,4-dihydroxyanthraquinone (1,4-DHAQ) into the microporous nanofiber films for the fluorescence detection of Cu<sup>2+</sup> and Cr<sup>3+</sup> [10]. In that work, 1,4-DHAQ was found to be highly fluorescent and have good complexation ability with metal ions, thus it can act as a good reporter in fluorescence sensors. By simply derivation, 1,4-DHAQ is expected to be useful in fluorescence sensing for other heavy metal ions. On the other hand, we also reported a 9-fluorenylmethanol (Fmoc-OH) doped silica xerogel thin film for fluorescence detection of pentachlorophenol (PCP) [19], where Fmoc-OH worked as reporter of PCP with high sensitivity (with lower detection limit of 10 nM). Thus high sensitivity might be achieved if this fluorophore (Fmoc-) could be used for the fluorescence detection of heavy metal ions. Furthermore, 1,4-DHAQ and 9-fluorenylmethyl chloroformate (Fmoc-Cl) have well resolved emissions (with emission peaks of 530 and 307 nm respectively), therefore, a multifunctional fluorescence sensor might be achieved if both 1,4-DHAQ and Fmoc- could be conjugated onto one kind of nanomaterials at the same time.

Herein, the 1,4-DHAQ derivative (structure shown in Fig. 1a) and Fmoc-Cl (structure shown in Fig. 1b) with well-resolved emissions, were tentatively conjugated onto the environmental friendly and bio-safe amine-functionalized Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) [20], to achieve 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs (Fig. 1c) for the detection of four heavy metal ions of Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> in aqueous solutions. As expected, when excited with 250 and 450 nm, the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs exhibit two well-resolved emission peaks of 395 (from Fmoc-Cl on Fe<sub>3</sub>O<sub>4</sub> MNPs) and 530 (from 1,4-DHAQ on Fe<sub>3</sub>O<sub>4</sub> MNPs) nm respectively, both of which show different fluorescence changes with [Cu<sup>2+</sup>], [Zn<sup>2+</sup>], [Cd<sup>2+</sup>] and [Hg<sup>2+</sup>] in aqueous solution. The differences in fluorescence signal responses to different heavy metal ions endow the new 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs good fluorescence sensor for Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> in a single metal ion polluted aqueous solution. The sensor designation and experimental results presented here may open a new door for the building of highly selective and multifunctional chemosensors.

## 2. Experimental

### 2.1. Materials and instruments

All reagents used in this work (analytical reagent grade) were purchased from Aladdin, and used as received without further

purification. The morphologies of the Fe<sub>3</sub>O<sub>4</sub> MNPs were characterized by using scanning electron microscopy (FE-SEM, Sirion 200) and transmission electron microscopy (TEM, JEM-2010). UV-vis spectra were recorded on a CARY-5E spectrophotometer, and infrared spectra were measured with a Perkin-Elmer Fourier transform infrared (FTIR) spectrometer. The fluorescence spectra were obtained on a FluoroMax-4 fluorescence spectrometer (Horiba Jobin Yvon Inc., France). De-ionized water (DI-water) and 0.02 M HEPES buffer solution were used throughout, and NaOH was used to control the pH of the solutions.

### 2.2. Synthesis of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs

The amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs were obtained via a simple thermal decomposition method. Briefly, 1 g FeCl<sub>3</sub>·6H<sub>2</sub>O as ferric source, 2 g anhydrous sodium acetate and 10 ml 1,6-hexanediamine were added to 30 ml glycol, the mixture was vigorously stirred until a transparent solution was obtained. Then the solution was transferred into a teflon-lined autoclave, and reacted for 6 h at 200 °C. Then the two kinds of fluorophores, 1,4-DHAQ derivative (Fig. 1a, detailed synthesis and <sup>13</sup>CNMR spectrum evidence can be found in Part S1 and Fig. S1 in the supporting information) and Fmoc-Cl (Fig. 1b), were sequentially conjugated onto the amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs via covalent bonding (the synthesis scheme can be found in Fig. S2 in the supporting information).

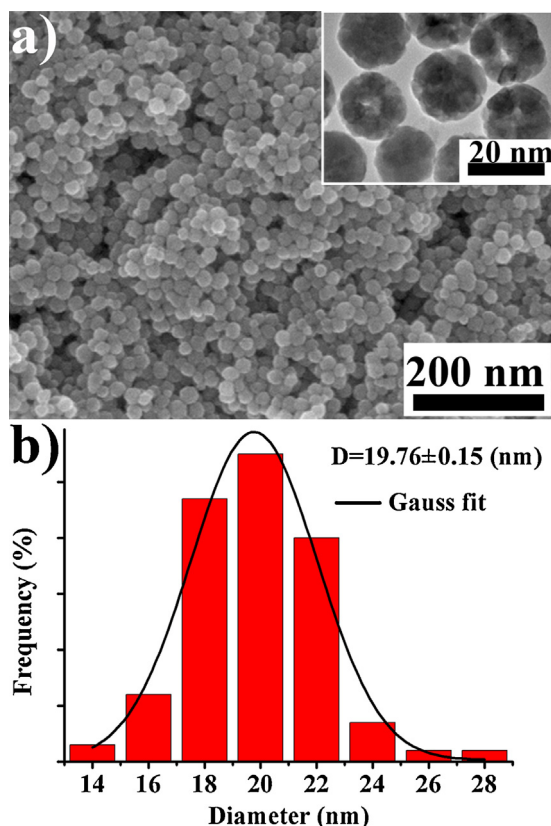
Specifically, a mixture of the as-prepared amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs (50 mg) and Na<sub>2</sub>CO<sub>3</sub> (0.1 g) was added to 1,4-DHAQ derivative (20 mg) in 150 ml CH<sub>3</sub>CN solution under stirring and refluxed for 4 h under N<sub>2</sub>. The product of the 1,4-DHAQ-modified Fe<sub>3</sub>O<sub>4</sub> MNPs was separated by an external magnet and repeatedly washed with ethanol and DI-water to remove any unreacted molecules. The above-obtained 1,4-DHAQ-modified Fe<sub>3</sub>O<sub>4</sub> MNPs were dispersed in 200 ml DMF by ultrasonic agitation. Then, 32.5 mg Fmoc-Cl was added and the mixture was reacted for another 2 h under stirring at room temperature. The final product was separated by an external magnet and repeatedly washed with ethanol and DI-water to remove any unreacted molecules.

## 3. Results and discussions

### 3.1. Morphological and spectral characterizations of amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs and the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs

Typical SEM (Fig. 2a) and TEM observations (inset in Fig. 2a) reveal that the as-prepared amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs have uniform diameter of about 20 nm (Fig. 2b). The Fe<sub>3</sub>O<sub>4</sub> phase purity is confirmed by powder X-ray diffraction (Fig. S3), and two peaks at 1054 and 1640 cm<sup>-1</sup> in the IR spectrum (Fig. S4) verify the successful amine-functionalization of the Fe<sub>3</sub>O<sub>4</sub> MNPs.

The IR spectrum of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs (Fig. 3) exhibits a broad amine stretching vibration at 3442 cm<sup>-1</sup> and an acyl amide bending vibration at 1570 cm<sup>-1</sup>, verifying the successful conjugation of the two fluorophores onto the surface of the amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs. Additionally, the bands at 1265, 1455, 792 cm<sup>-1</sup> from the 1,4-DHAQ derivative and the band at 1143 cm<sup>-1</sup> from Fmoc-Cl can be found in the IR spectrum of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs, also verifying that both 1,4-DHAQ derivative and Fmoc-Cl were covalently bonded onto the Fe<sub>3</sub>O<sub>4</sub> MNPs successfully. Importantly, the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs can be uniformly dispersed in water, as TEM image shown in Fig. S5, ensuring its



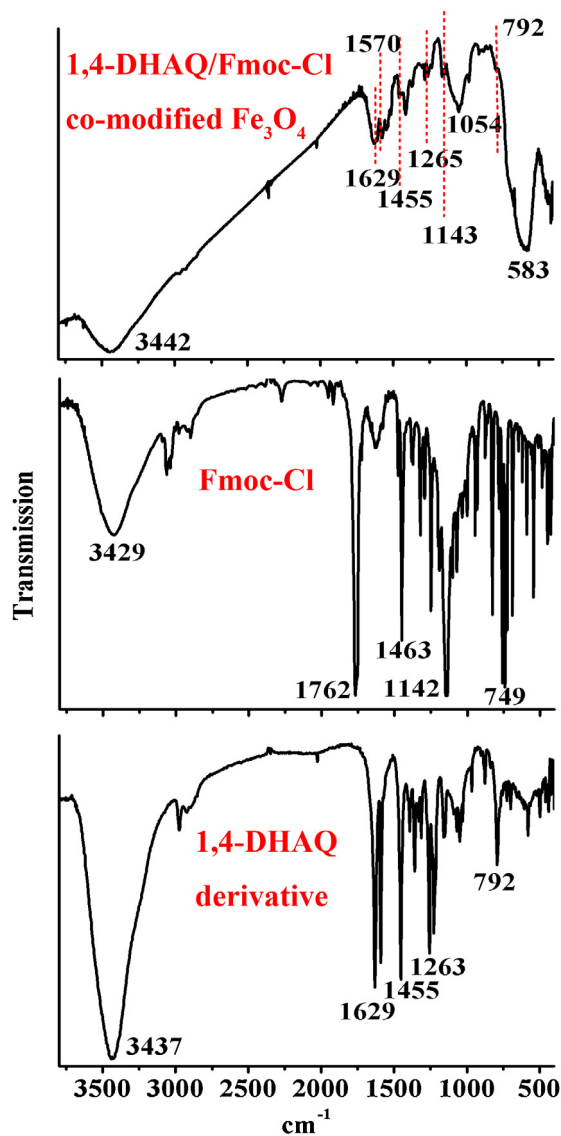
**Fig. 2.** (a) SEM and TEM (inset) images of the amine-functionalized  $\text{Fe}_3\text{O}_4$  MNPs, and (b) the size distribution of the  $\text{Fe}_3\text{O}_4$  MNPs.

reliability and practicability as fluorescence sensor materials in aqueous solutions.

### 3.2. Sensitivity and selectivity of the 1,4-DHAQ/Fmoc-Cl co-modified $\text{Fe}_3\text{O}_4$ MNPs to $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Hg}^{2+}$

The two well-resolved emission peaks of 395 and 530 nm from the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs show different fluorescence responses to  $[\text{Cu}^{2+}]$ ,  $[\text{Zn}^{2+}]$ ,  $[\text{Cd}^{2+}]$  and  $[\text{Hg}^{2+}]$  in aqueous solution, endowing fluorescence detection of these metal ions. The fluorescence titration experiments for each metal ion were conducted using 50  $\mu\text{g}/\text{mL}$  1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs in 0.02 M HEPES buffer solution, with successive addition of different concentrations of metal ions. All experiments were done in 0.02 M HEPES buffer solution (pH = 7, pH value was controlled using NaOH). Fluorescence measurements were conducted in a cuvette and the fluorescence spectra were recorded on the fluorescence spectrometer. When the system is excited with 250 nm, the emission peak at 395 nm (from Fmoc-Cl conjugated on the  $\text{Fe}_3\text{O}_4$  MNPs) enhances with  $[\text{Cu}^{2+}]$  and  $[\text{Hg}^{2+}]$  (Fig. 4a and b), while decreases with  $[\text{Zn}^{2+}]$  (Fig. 4c), but it doesn't change much with  $[\text{Cd}^{2+}]$  (Fig. 4d). However, when the system is excited with 450 nm, the intensity of the emission band around 530 nm (from 1,4-DHAQ derivative conjugated on the  $\text{Fe}_3\text{O}_4$  MNPs) decreases with  $[\text{Cu}^{2+}]$ ,  $[\text{Zn}^{2+}]$  and  $[\text{Cd}^{2+}]$  (Fig. 4a, c and d), while it doesn't change much with  $[\text{Hg}^{2+}]$  (Fig. 4b). As can be seen from Fig. 4, even for concentrations of heavy metal ions (whichever of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ ) as low as  $10^{-8}$  M, the changes of fluorescence intensity can still be clearly distinguished.

To show good selectivity of the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs to  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ , fluorescence titration experiments with other 10 metal ions ( $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,

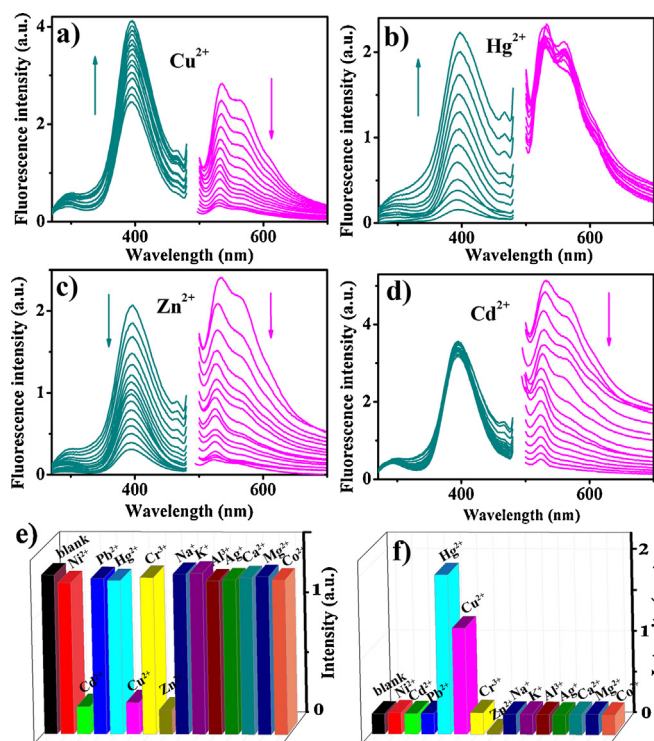


**Fig. 3.** IR spectra of the 1,4-DHAQ derivative, Fmoc-Cl, and the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs.

$\text{Al}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Co}^{2+}$ ) were performed respectively, and the results are summarized in Fig. 4e and f. When the system was excited with 450 nm, even  $10^{-7}$  M  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  can quench the emission band around 530 nm significantly, while all other metal ions have almost no impact. However, when excited with 250 nm, the peak at 395 nm is sharply enhanced with  $10^{-7}$  M  $\text{Hg}^{2+}$ . For  $\text{Cu}^{2+}$ , the fluorescence peak at 395 nm is obviously enhanced too, although not as sharp as that for  $\text{Hg}^{2+}$ . But for the same concentration of  $\text{Zn}^{2+}$ , the fluorescence at 395 nm (from Fmoc-Cl) of the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs is remarkably quenched. However, the addition of any other of the above-mentioned metal ions has no impact on the peak at 395 nm. Thus the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs show unique characteristic ratiometric fluorescence responses to  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ . On the basis of the above simple fluorescence phenomena, it can be reasonably concluded that, for single metal ion polluted solution, the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs can be used for very simple and rapid qualitative detection of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ .

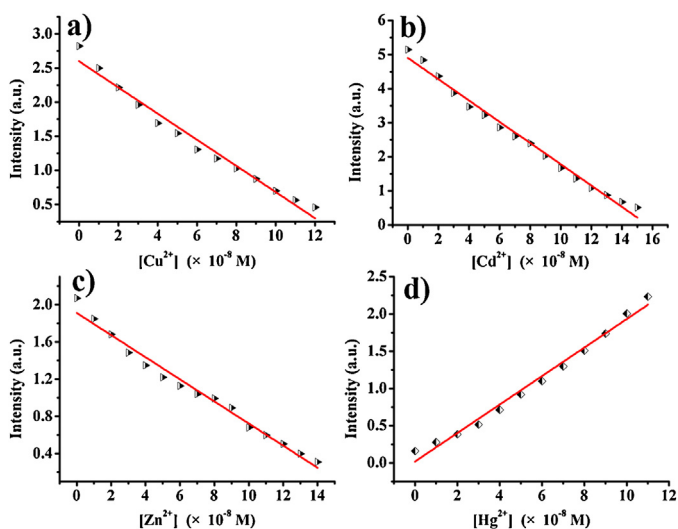
For single metal ion polluted solution, except for simple and rapid qualitative analysis of the four heavy metal ions, quantitative



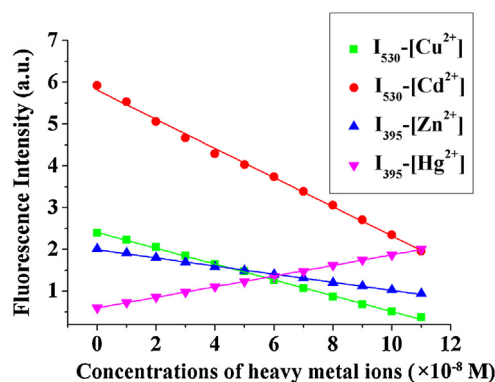


**Fig. 4.** Fluorescence spectra of the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs solution with successive addition of (a)  $1\text{--}14 \times 10^{-8}$  M  $\text{Cu}^{2+}$ , (b)  $1\text{--}11 \times 10^{-8}$  M  $\text{Hg}^{2+}$ , (c)  $1\text{--}15 \times 10^{-8}$  M  $\text{Zn}^{2+}$ , and (d)  $1\text{--}15 \times 10^{-8}$  M  $\text{Cd}^{2+}$ , respectively. ( $\lambda_{\text{ex}} = 250, 450$  nm) Relative fluorescence intensity histograms of the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs in  $10^{-7}$  M different metal ion solutions with excitation of (e) 450 nm and (f) 250 nm, respectively.

analysis of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  has also been achieved, and there exist linear relationships (Fig. 5 and Eqs. (1)–(4) in the following text) between the fluorescence intensities and  $[\text{Cu}^{2+}]$ ,  $[\text{Cd}^{2+}]$ ,  $[\text{Zn}^{2+}]$  and  $[\text{Hg}^{2+}]$ , with excitations of 450 nm (for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) and 250 nm (for  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ ), respectively. It should be mentioned that different emission peaks were used to achieve better linear relationships and larger linear ranges for quantitative analysis of different metal ions. The detailed linear relationships between the fluorescence intensity ( $I$ ) and the concentration of metal ions



**Fig. 5.** Titration curves of the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs to (a)  $\text{Cu}^{2+}$  (530 nm), (b)  $\text{Cd}^{2+}$  (530 nm), (c)  $\text{Zn}^{2+}$  (395 nm), and (d)  $\text{Hg}^{2+}$  (395 nm), respectively.



**Fig. 6.** Titration curves of the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs in heavy metal ion polluted lake water solutions.

are as follows.

$$I_{530} = 2.59 - 10^7[\text{Cu}^{2+}]$$

( $[\text{Cu}^{2+}]$  in the range of  $10^{-8} - 1.1 \times 10^{-7}$  M)

(1)

$$I_{530} = 4.9 - 3.12 \times 10^7[\text{Cd}^{2+}]$$

( $[\text{Cd}^{2+}]$  in the range of  $10^{-8} - 1.4 \times 10^{-7}$  M)

(2)

$$I_{395} = 1.91 - 1.1 \times 10^7[\text{Zn}^{2+}]$$

in the range of  $10^{-8} - 1.3 \times 10^{-7}$  M

(3)

$$I_{395} = 0.01 + 1.9 \times 10^7[\text{Hg}^{2+}]$$

in the range of  $10^{-8} - 10^{-7}$  M

(4)

Here,  $I_{530}$  and  $I_{395}$  refer to fluorescence intensities at 530 and 395 nm, respectively. Eqs. (1)–(4) can be served as the basis for the quantitative analysis of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  in single metal ion polluted aqueous solutions. Under this condition, detection lower limits of  $8 \times 10^{-9}$ ,  $1.5 \times 10^{-8}$ ,  $10^{-8}$  and  $10^{-8}$  M have been achieved for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ , respectively (based on the 10% fluorescence quenching or enhancement method). Therefore, the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs can be used not only for simple rapid qualitative analysis of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ , but also for quantitative analysis of the above four metal ions in single metal ion polluted solutions and even in drinking water (the drinking water health standards for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  are  $3.1 \times 10^{-5}$ ,  $4.5 \times 10^{-8}$ ,  $7.7 \times 10^{-5}$  and  $10^{-8}$  M, respectively). To prove this, the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs have been explored to the possible fluorescence detection of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  in heavy metal ion polluted lake waters, and the results were shown in Fig. 6 and Fig. S6 in the supporting information. As the titration curves shown in Fig. 6, the 1,4-DHAQ/Fmoc-Cl co-modified  $\text{Fe}_3\text{O}_4$  MNPs can be used for quantitative analysis of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  in heavy metal ion polluted lake waters in proper concentration ranges (from  $10^{-8}$  M to  $1.1 \times 10^{-7}$  M), insuring their practicability for fluorescence detection of environmental heavy metals. And fluorescence changes are still obvious even for  $10^{-8}$  M heavy metal ions (Fig. S6), indicating their high sensitivity as fluorescence sensors.

### 3.3. Superiority of the 1,4-DHAQ/Fmoc-Cl co-modified $\text{Fe}_3\text{O}_4$ MNPs

Assuming that bare 1,4-DHAQ derivative and Fmoc-Cl in solution have similar fluorescence quantum efficiency to those

modified onto the Fe<sub>3</sub>O<sub>4</sub> MNPs, then the average coverage of 1,4-DHAQ derivative and Fmoc-Cl can be calculated based on Eq. 5 and the Beer-Lambert Law (Eq. (6)) according to a previous report [9].

$$\eta_1 A_1 I_2 = \eta_2 A_2 I_1 \quad (5)$$

$$A = \epsilon bc \quad (6)$$

where  $\eta$ ,  $A$  and  $I$  refer to the fluorescence quantum efficiency, absorbance at the excited wavelength and the integral fluorescence intensity, respectively. Therefore, 50  $\mu\text{g}/\text{mL}$  1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs used in the experiments correspond to  $3.5 \times 10^{-6}$  M 1,4-DHAQ derivative and  $4.6 \times 10^{-6}$  M Fmoc-Cl, respectively. Thus the average coverage of dye molecules on Fe<sub>3</sub>O<sub>4</sub> MNPs, i.e., the number of dye molecules in per microgram of Fe<sub>3</sub>O<sub>4</sub> MNPs can be calculated to be  $7 \times 10^{-5}$  and  $9.2 \times 10^{-5}$  mol for 1,4-DHAQ derivative and Fmoc-Cl, respectively. To verify the superiority of our 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs, control experiments between 50  $\mu\text{g}/\text{mL}$  1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs in aqueous solution and equivalent concentrations of bare 1,4-DHAQ derivative in solution were conducted. And the results indicate that the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs show superior sensing property to the bare 1,4-DHAQ derivative and Fmoc-Cl in solutions. Take Cu<sup>2+</sup> as an example, when excited with 450 nm, the Stern-Volmer constant of the 50  $\mu\text{g}/\text{mL}$  1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs ( $K_{sv} = 2.6 \times 10^7 \text{ M}^{-1}$ , Fig. S7) is enhanced by almost two orders of magnitude than those of the bare 1,4-DHAQ derivative and Fmoc-Cl in solution ( $\sim 10^5 \text{ M}^{-1}$ , see Fig. S8). This might be attributed to the better contacts and interactions between the fluorophores and the metal ions after the fluorophores being conjugated onto the Fe<sub>3</sub>O<sub>4</sub> MNPs. Moreover, our experiments indicate that both the bare 1,4-DHAQ derivative and Fmoc-Cl in solutions are less selective than that of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs in solution to whichever of Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> or Hg<sup>2+</sup> (see Fig. S9 and Part S2 in the supporting information), being similar to that of the previously reported 8-aminoquinoline-modified silicon nanowires to Cu<sup>2+</sup> [8]. Furthermore, the fluorescence detection using the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs may be coupled with the magnetic separation capability of the Fe<sub>3</sub>O<sub>4</sub> MNPs (Fig. S10), thus the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs may be reclaimed from the detected samples. Therefore, samples being detected by this 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs will not be contaminated by the sensor materials.

### 3.4. Possible sensing mechanism of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs to Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>

In order to illustrate that fluorescence resonance energy transfer between 1,4-DHAQ and Fmoc-Cl can be neglected, UV-vis absorption spectrum of 1,4-DHAQ and emission spectrum of Fmoc-Cl are recorded (Fig. S11), indicating that the absorption of 1,4-DHAQ is too weak to be considered in the fluorescence wavelength range of Fmoc-Cl (290–370 nm). And this ensures that fluorescence changes of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs are uniquely induced by heavy metal ions. As for the possible sensing mechanism, our experiments reveal that the fluorescence sensing of the 1,4-DHAQ derivative to Cu<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> can be ascribed to the coordination of the 1,4-DHAQ derivative with Cu<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>. In the presence of Cu<sup>2+</sup>, Cd<sup>2+</sup> or Zn<sup>2+</sup>, the characteristic UV-vis absorption band of 1,4-DHAQ derivative around 470 nm decreases, while a new absorption band around 545 nm appears and increases with [Cu<sup>2+</sup>], [Cd<sup>2+</sup>] and [Zn<sup>2+</sup>] (Fig. S12a, b and c), together with clear isosbestic points at 496, 501 and 485 nm respectively, indicating the complex formation between 1,4-DHAQ derivative and the metal ions. For Fmoc-Cl, in the presence of Cu<sup>2+</sup> and Hg<sup>2+</sup>, the characteristic absorption at 255 nm increases (Fig. S12d and f);

however, in the presence of Zn<sup>2+</sup> the variation of the UV/vis absorption is not obvious (Fig. S12e). As the emission peak of Fmoc-Cl red-shifts about 90 nm (from 307 to 395 nm, see Fig. S9b and Fig. 4a, b, c, d) after being conjugated onto the amine-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs via amido, the emission peak at 395 nm may come from a newly appeared intra-molecular charge-transfer state [21] after being conjugated onto the Fe<sub>3</sub>O<sub>4</sub> MNPs via amido. Moreover, as Hg<sup>2+</sup> and Cu<sup>2+</sup> quench the fluorescence at 307 nm (Fig. S9g and i), while enhance that at 395 nm (Fig. 4a and b), we conclude that the presence of Hg<sup>2+</sup> and Cu<sup>2+</sup> probably promotes this intra-molecular charge-transfer process. The fluorescence quenching at 395 nm caused by Zn<sup>2+</sup> might be attributed to the photo-induced energy or electron transfer induced by Zn<sup>2+</sup> [8]. As the sensing mechanism of the 1,4-DHAQ derivative to Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> is based on static quenching, the formation constants  $K$  of the four heavy metal ions equivalent to their Stern-volmer constants (Fig. S13 for Zn<sup>2+</sup> with Fmoc-Cl and Fig. S8 for others,  $\sim 10^5 \text{ M}^{-1}$ ). The high  $K$  values ensures the high sensitivity of the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs to Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> as fluorescence sensors. It should be mentioned that as there exists competitions between different metal ions and the fluorophores, the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs are not suitable to solutions contaminated by several heavy metal ions so far.

## 4. Conclusion

In summary, a prototype of highly sensitive and selective fluorescence sensor, based on 1,4-DHAQ derivative and Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs, has been achieved for not only simple rapid qualitative analysis of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup>, but also quantitative analysis of these heavy metal ions in single metal ion polluted aqueous solutions with linear detection ranges of  $10^{-8}$ – $1.1 \times 10^{-7}$ ,  $10^{-8}$ – $1.4 \times 10^{-7}$ ,  $10^{-8}$ – $1.3 \times 10^{-7}$  and  $10^{-8}$ – $10^{-7}$  M, respectively. Furthermore, coupled with the magnetic separation capability of the Fe<sub>3</sub>O<sub>4</sub> MNPs, the 1,4-DHAQ/Fmoc-Cl co-modified Fe<sub>3</sub>O<sub>4</sub> MNPs may be reclaimed from the detected samples. This is the first reported fluorescence sensor that can detect four heavy metal ions in single metal ion polluted aqueous solutions, opening a new door to the development of multifunctional probes in aqueous solutions.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.04.086>.

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