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ARTICLE

## Fluorescent magnetic nanosensors for Zn<sup>2+</sup> and CN<sup>-</sup> in aqueous solution prepared by adamantane-modified fluorescein and $\beta$ -cyclodextrin-modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> via Host-Guest interaction

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### Abstract

A novel multifunctional fluorescent chemosensor has been constructed with highly selective “off-on” behavior, recoverable and recycled property based on  $\beta$ -CD/AD (adamantane) Host-Guest self-assembly interactions. Adamantane-modified fluorescein/cyclodextrin-modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> inclusion complex magnetic nanoparticles (FFIC MNPs), which can provide a specific green fluorescence enhancement in response to Zn<sup>2+</sup>, have a detection limit of 4.5×10<sup>-7</sup> mol/L in CH<sub>3</sub>CN: H<sub>2</sub>O (1:4, v/v). The spirolactam ring in fluorophore moiety would be open with the induction of Zn<sup>2+</sup>, while it could recover as long as the complex zinc is taken off. Meanwhile, one gram of FFIC MNPs can adsorb 6.1mg zinc. Therefore the derivative chemosensors FFIC MNPs-Zn are available to respond to CN<sup>-</sup> due to the fluorescence quenching under UV (ultraviolet) with a detection limit of 7.7×10<sup>-7</sup> mol/L. Furthermore, the FFIC MNPs exhibit great reusability and recyclability in aqueous solution on account of its magnetism and reproducibility. We recycle the residual MNPs to detect Zn<sup>2+</sup> repeatedly for at last 4 times, after adsorbing the complex zinc with superfluous CN<sup>-</sup> extravagantly, and the same principle also works in reverse. If the fluorophore moiety is out of action, we could also wash out the useless fluorescent molecules from MNPs (Host), then reassemble new fluorescent small-molecule (Guest) to stay probes' efficient properties in responding to Zn<sup>2+</sup> and CN<sup>-</sup> for at last 7 times.

**Keywords:** Fluorescence Chemosensor; Host-guest self-assembly interactions; Magnetic microspheres; Reusability and Recyclability;

### Introduction

Zinc, which plays an important role in life activity, is an abundant heavy metal just like iron and copper and essential as a catalytic co-factor in hundreds of metalloenzymes like carbonic anhydrase, DNA polymerase and pancreatic carboxypeptidase. Excessive zinc can result in poison gastrointestinal and immunological toxicity. And trace cyanide

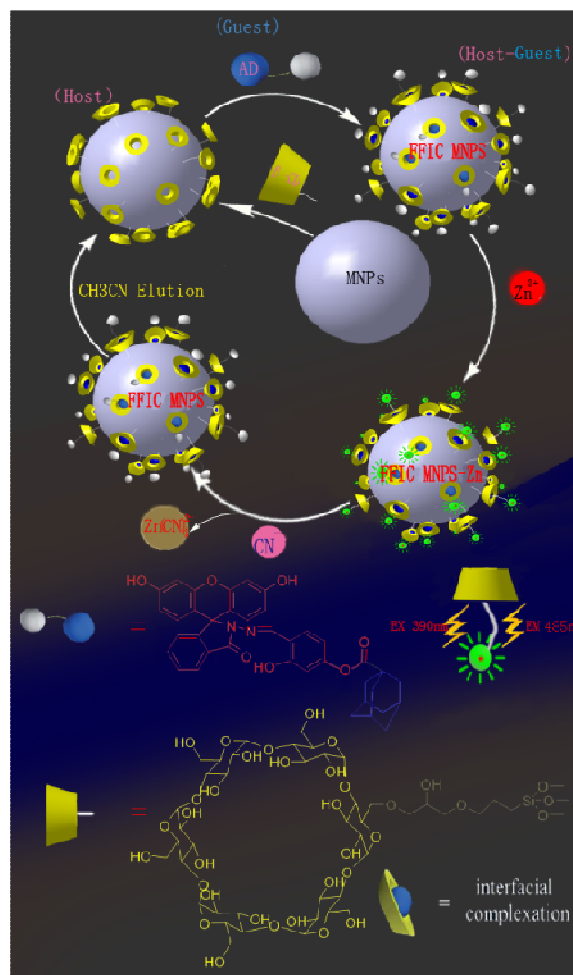
to living creatures is highly toxic, which should not be ignored as well. So it is significant to rapidly and quantitatively monitor trace amount of zinc ion in vitro and in vivo or CN<sup>-</sup> in aqueous environment. Thus in recent decades, efficient detection, removal and recovery of zinc or cyanide in chemosensor applications have gained considerable attention,

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which could solve technological challenging and ecological urgent question. Up to now, numerous superior fluorescent molecule chemosensors for detection and recognition of  $Zn^{2+}$  or  $CN^-$  have been developed due to their high selectivity, sensitivity, kind examination conditions and short response time by many research groups. But these small-molecule sensors have many disadvantages, such as that they cannot be reused repeatedly or be separated after detecting. Therefore we have utilized the 'host-guest'  $\beta$ -CD/AD self-assembly interactions to construct a multifunctional fluorescent chemosensor the FFIC MNPs, which can respond to  $Zn^{2+}$ , be separated and be reused repeatedly with high selectivity and sensitivity. In these  $\beta$ -CD/AD host-guest supramolecular inclusion complexation, adamantane can be specificity identified and well included by  $\beta$ -CD, cause it has numbers of hydrophilic oxyhydril on the external and a hydrophobic internal cavity, in which it can accommodate suitable micromolecule. On the contrary, the exclusion is easy to control in acetonitrile and ethanol.

It is shown from the measurement results that FFIC MNPs can adsorb zinc approach to 6.1mg/g and when  $CN^-$  takes off the  $Zn^{2+}$  combined with FFIC MNPs, the spirolactam ring in fluorophore moiety will close again accompanied with fluorescence quenching that is why the FFIC MNPs-Zn can effectively respond to  $CN^-$ . Another reason is that the higher association constant between zinc and  $CN^-$  than zinc and other anions according to the literature [11] those nearly have no influence on the probing, such as  $Cl^-$ ,  $I^-$ ,  $SCN^-$ ,  $Br^-$ ,  $HPO_4^{2-}$ ,  $F^-$ ,  $HSO_3^-$ , and  $S_2O_3^{2-}$ , certainly including FFIC MNPs as well. This method solves complicated action modes of the direct cyanide chemosensors which is based on hydrogen-bonding, bond-forming

reaction .Because we know much about the rules of coordination chemistry between ligands of sensors and cations but have poor knowledge of the interactions between compounds and anions. In brief, the probe can be reused for many times either FFIC MNPs or FFIC MNP-Zn with high selectivity and sensitivity.



**Scheme 1** Chemical and schematic illustration of the preparation of FFIC MNP and FFIC MNP-Zn fluorescent sensors for  $Zn^{2+}$  ions.

## Materials and methods

### Apparatus

Fluorescence measurements were performed on a HitachiF-4500 spectrofluorimeter (Japan), 10×10 mm conventional quartz cuvette, the slit width was 2.5nm. 1H NMR spectras were measured on a Bruker AV-400 spectrometer at 400MHz in DMSO and  $CDCl_3$  with tetramethylsilane as the internal standard(US). Mass spectra were measured with Axima CFR MALDI-TOF(US). The absorption spectra were recorded with a Bruker Vector-22 infrared and Hitachi U-3010 UV-Vis spectrophotometer(US). A model Mettler-Toledo Instruments DELTA 320 pH pH-meter was used for pH measurements. Scanning electron microscope (SEM) was SII: SPI3800N (Japan).

### Materials and reagents

Fluorescein, hydrazine hydrate (80%) and other organic reagents are all used as deliver from Aladdin .the rest

chemicals used were all of analytical grade. Distilled–deionized water was used throughout. Stock solutions (10–3mol/L) of various ions ( $\text{CaCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{BaCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{SnCl}_4$ ,  $\text{NiCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{KCl}$ ,  $\text{FeCl}_3$ ,  $\text{CuSO}_4$ ;  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{Br}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{HSO}_3^-$ , and  $\text{S}_2\text{O}_3^{2-}$ ) were prepared by dissolving their salts in buffer Tris-HCl(0.05 mol/L) to keep pH value (pH=7.20), and to maintain the ionic strength of all solutions in experiments.

#### Preparation of FFIC MNPs and FFIC MNPs-Zn

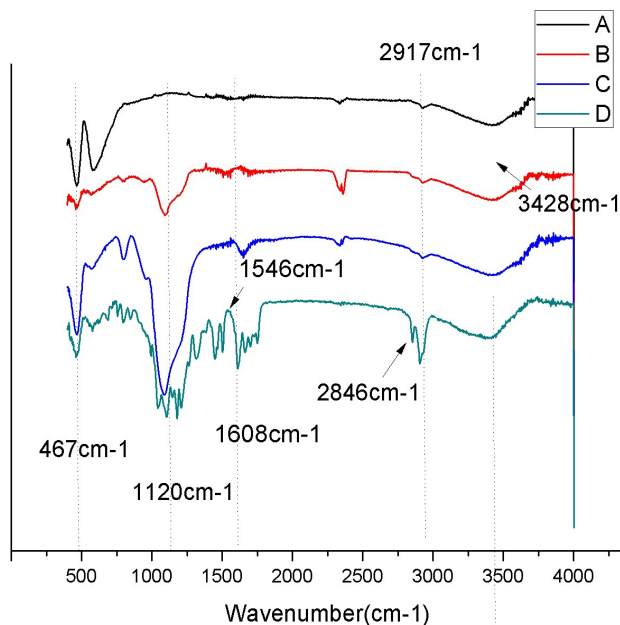
The Fluor-Ad/ $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\beta$ -CD inclusion complex magnetic nanoparticles (FFIC MNPs) were facilely prepared from cyclodextrin-functionalized magnetic silica microspheres (denoted as  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\beta$ -CD MNPs) (Host) and Fluor -Ad (Guest) by a self-assembly technique. The  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\beta$ -CD MNPs were prepared by two steps as scheme 2(see ESI<sup>†</sup>). One, monodisperse superparamagnetic  $\text{Fe}_3\text{O}_4$ -silica spheres were prepared, and then  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  MNPs were reacted with  $\beta$ -cyclodextrin that had been linked with silane coupling agent by a sol–gel grafting reaction on the surface of the  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  nanoparticles. The preparation of the Fluor -Ad moiety was described in scheme 1(see ESI<sup>†</sup>), and detailed procedures can be found too. The synthetic product was well characterized by FTIR, SEM, TEM, XRD, superconducting quantum interference measurement device (SQUID), UV-vis spectroscopy and  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR (see Fig S3 ESI<sup>†</sup>). FFIC MNPs-Zn was prepared according to the following Langmuir isotherm that per gram of FFIC MNPs can adsorb 6.1mg  $\text{Zn}^{2+}$ , and then be separated magnetically.

## Results and discussion

### Morphology of the FFIC MNPs

SEM imaging shows that the  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  nanoparticles have an average diameter of about 270nm and obviously possess smooth surfaces. It is found that the  $\text{Fe}_3\text{O}_4$  nanoparticles possess the diameter about 200nm indicating the shell thickness is about 35nm.  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  nanostructures are quite uniform in size with an average diameter and no aggregation. As shown in Fig.S1b (see ESI<sup>†</sup>) that only few nanoparticles deformed or cracked structures are observed, it is because the silica nanocomposites possess a solid structure that is seen from the TEM Fig.S1a (see ESI<sup>†</sup>), therefore it is hard to be fractured mechanically.

### Fourier transform IR spectroscopy analysis



**Fig.1** exhibits the FTIR spectra of  $\text{Fe}_3\text{O}_4$  (A),  $\text{SiO}_2$ @ $\text{Fe}_3\text{O}_4$  (B),  $\beta$ -CD/ $\text{SiO}_2$ @ $\text{Fe}_3\text{O}_4$  (C) and FFIC MNPs (D)

We use the FTIR to further confirm the fluorescein-AD moiety is successfully loaded on the surface of  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ / $\beta$ -CD. Fig.1 exhibits the FTIR spectra of  $\text{Fe}_3\text{O}_4$ (A), $\text{SiO}_2$ @ $\text{Fe}_3\text{O}_4$  (B), $\beta$ -CD/ $\text{SiO}_2$ @ $\text{Fe}_3\text{O}_4$  (C) and FFIC MNPs (D).The broad band at 3300–3500  $\text{cm}^{-1}$  (A, B, C, D) is ascribed to O-H stretching vibration of water in  $\text{Fe}_3\text{O}_4$  crystal. In particular, the broad band centered at 467  $\text{cm}^{-1}$ (simple A, B, C,D)and the band at 1120  $\text{cm}^{-1}$ (B,C,D)are ascribed to the Fe-O and Si-O stretching vibration, symmetric Si-O-Si stretching and asymmetric Si-O-Si stretching of silane. Therefore, we confirm that  $\text{SiO}_2$  is successfully wiped on the surface of  $\text{Fe}_3\text{O}_4$  MNPs. In addition, simple D shows that the characteristic bands 1546  $\text{cm}^{-1}$ (secondary amide N-N bending), 1100–1296  $\text{cm}^{-1}$  (aromatic C-N stretching), 1608 $\text{cm}^{-1}$ (C=N stretching), 1693  $\text{cm}^{-1}$  (C=O stretching vibration) can also be achieved. Based on these data from FT-IR, it can be concluded that the attachment of fluorophore moieties to the surface of  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\beta$ -CD MNPs has indeed taken place via host–guest self-assembly interaction.

### Magnetic property

The magnetic hysteresis loop of the FFIC MNPs measured at  $T=300$  K (close to room temperature).It demonstrated that the samples have low coercivity and no obvious hysteresis, which indicates that the FFIC MNPs have superparamagnetism (Fig.S2a. ESI<sup>†</sup>) Superparamagnetism means that when the outer magnetic field withdraws, there is no residual magnetism in nanoparticles. If the nanoparticles have residual magnetism, it is highly possible for these nanoparticles to aggregate irreversibly. The saturation magnetization ( $M_s$ ) values for  $\text{Fe}_3\text{O}_4$  nanoparticles and FFIC MNPs are 80.33 and 28.26  $\text{emu/g}$ , respectively. The decrease in  $M_s$  of magnetic

nanoparticles could be attributed to the increasing amount of the nonmagnetic material (organic ligands and silica shell) on the particle surface, which makes up a larger percentage of the nonmagnetic fraction. The binding of silica and moleculeS3 on the particle surface might have quenched the magnetic moment. In addition, organic molecules on the surface lack complete coordination thus increase the surface spin disorientation. This disordered structure in the amorphous materials and at the interface might have caused a decrease in the effective magnetic moment. However, the FFIC MNPs inherit the strong magnetic property from the  $\text{Fe}_3\text{O}_4$  nanoparticles. Complete magnetic separation of FFIC MNPs was achieved in 60 s by placing a magnet near the vessels containing the  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  dispersion of the nanoparticles. The magnetic separation capability of FFIC MNPs in this detection method can also offer a simple and efficient route for separation and extraction of toxic metal ions from various environments.

#### X-ray powder diffraction pattern analysis

The crystal structure of the as-synthesized  $\text{Fe}_3\text{O}_4$  nanocrystals and FFIC MNPs was investigated using X-ray diffraction (XRD) - (Fig.S4.ESI†). XRD patterns of the synthesized  $\text{Fe}_3\text{O}_4$  and FFIC MNPs display several relatively strong reflection peaks in the  $2\theta$  region of  $10-80^\circ$ . The discernible six diffraction peaks in Fig.S4a can be indexed to (220), (311), (400), (422), (511) and (440), which match well with the database of magnetite in the JCPDS file. This result shows that the embedded  $\text{Fe}_3\text{O}_4$  MNPs retain their magnetite crystalline structure after template extraction. Besides the peak of iron oxide, the XRD pattern of iron-oxide- $\text{SiO}_2$  core-shell nanoparticles presented a broad featureless XRD peak at a low diffraction angle, which corresponds to the amorphous state  $\text{SiO}_2$  shells. This result shows that the  $\text{Fe}_3\text{O}_4$  MNPs were successfully coated and passivated by the  $\text{SiO}_2$  shell. To further confirm the components of the products, TEM is shown in Fig.S1a (see ESI).

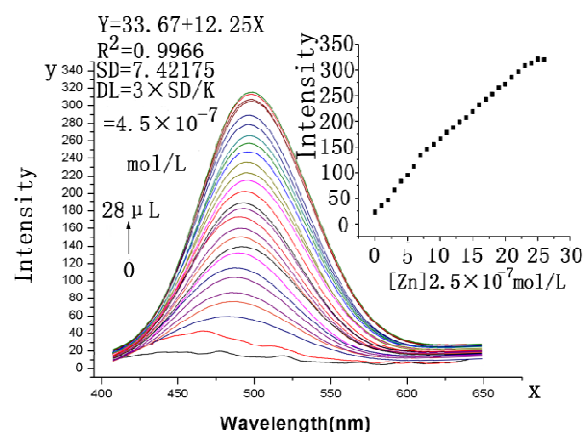
#### The responsive pH range appropriately

Fluorophores are usually disturbed by the protons during the detection of metal ions, not only the structure of molecule was broken easily, but the hydrolysis of metal ions must be considered in various pH, so their low sensitivity to the operational pH value was expected and investigated. The Fig.S6 (see ESI†) reveals that FFIC MNPs could respond to  $\text{Zn}^{2+}$  ions in a pH range from 6 to 10 with little changes of the fluorescent intensity. More than 10, the  $\text{Zn}^{2+}$  was hydrolyzed severely along with the fluorescent response decline. But when the pH was below 6, the fluorescence intensity was distinctly decreased. What is more, no matter how pH changed from 3 to 6, the intensity had almost no enormous variety, because of the structure of molecule on the surface of  $\text{SiO}_2@-\text{Fe}_3\text{O}_4$  MNPs had been destroyed by the formation of the open-ring state from the strong protonation. In consideration of most samples for the FFIC MNPs analysis of  $\text{Zn}^{2+}$  ions being neutral, the medium for  $\text{Zn}^{2+}$  ion quantification was buffered at pH 7.10.

#### Fluorescence property detecting $\text{Zn}^{2+}$

In order to gain insight into the signalling properties of the FFIC

MNPs, fluorescence titrations were conducted. The most appropriate proportion of  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  was found as the Fig.S8, showing 1/4(v/v) (see ESI†). The fluorescence titration of  $\text{Zn}^{2+}$  was carried out using a solution of FFIC MNPs 0.1 g/L in buffered (Tris-HCl, pH=7.1)  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (1/4, v/v). Excitation wavelength was 390 nm and the fluorescence emission intensity was recorded at 485nm. Before dropping  $\text{Zn}^{2+}$  the fluorescence intensity of FFIC MNPs was extremely weak. It was attributed to the spirolactam form. The fluorescence spectra of different concentrations of  $\text{Zn}^{2+}$  solution are shown at Fig.2. Upon addition of increasing concentrations of  $\text{Zn}^{2+}$  ions, an apparent enhancement of the characteristic fluorescence emerges at 485nm, accompanied by an obvious green fluorescence under UV. It is because that the  $\text{Zn}^{2+}$  ions could chelate with the imine N, carbonyl O and phenol O atoms with ring opening of the spirolactam in fluorescein moiety taking place instantaneously according to literature [8]. When concentration of  $\text{Zn}^{2+}$  reached to  $62.5 \times 10^{-7}$  mol/L, the fluorescence increased smoothly until saturation and maximum fluorescence intensity was retained. A linear relationship existed between the fluorescence intensity of FFIC MNPs and concentration of  $\text{Zn}^{2+}$  over the range  $2.5 \times 10^{-7}$  mol/L to  $62.5 \times 10^{-7}$  mol/L. The correlation coefficient was  $R^2 = 0.9966$ . The detection limit was  $4.5 \times 10^{-7}$  mol/L.

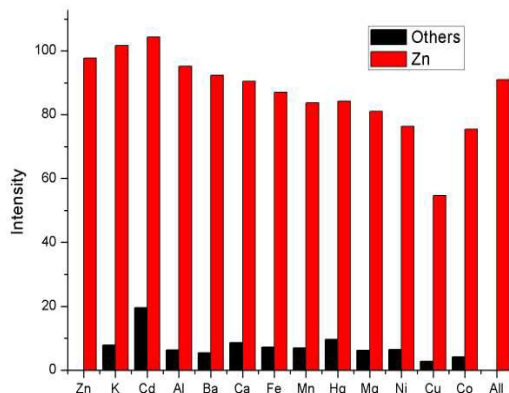


**Fig.2.** Fluorescent spectra of the FFIC MNPs (0.1 g/L) in the absence and presence of  $\text{Zn}^{2+}$  ( $2.5 \times 10^{-7}$  to  $6.25 \times 10^{-6}$  mol/L). The inset exhibits fluorescence intensity as concentration of  $\text{Zn}^{2+}$  ( $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ , 1: 4, v/v, buffered at pH=7.1 with Tris-HCl(0.1M), Excitation was at 390 nm, Emission was monitored at 485 nm). Slit: 2.50x5.00mm

#### Metal ion competition studies

To evaluate the utility of FFIC MNPs as an ion-selective fluorescence probe for  $\text{Zn}^{2+}$  ions, the fluorescence emission response of FFIC MNPs upon addition of various biologically and environmentally relevant metal ions, including  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,

$\text{Fe}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions, each concentration was  $50\mu\text{mol/L}$  (blue bars in Fig.3). As we expected, the above-mentioned metal ions show a weak effect on the fluorescence intensity of the nanosensor. However, compared with the marked enhancement provoked by  $\text{Zn}^{2+}$  ions  $1.0\mu\text{mol/L}$ , the influence of the above-mentioned metal ions is negligible. Although the fluorescence was affected to some extent in the solutions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , we increased  $\text{Zn}^{2+}$  from  $1\mu\text{mol/L}$  to  $5\mu\text{mol/L}$  and experimental results indicated that the proportion of other ions showed no obvious interference in the  $\text{Zn}^{2+}$  detection completely. Thus, the FFIC MNPs exhibit excellent selectivity toward  $\text{Zn}^{2+}$ , which makes their practical application feasible.



**Fig.3** Black bars: fluorescent emission response of FFIC MNPs  $0.1\text{ g/L}$  in the presence of different metal ions  $50\mu\text{mol/L}$  in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  solution. Red bars: fluorescent response of FFIC MNPs upon addition of  $1.0\mu\text{mol/L}$   $\text{Zn}^{2+}$  ions in the presence of each interference metal ions ( $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ , 1:4, v/v, buffered at  $\text{pH}=7.1$  with  $\text{Tris-HCl}(0.1\text{M})$ , excitation was at  $390\text{ nm}$ , emission was at  $485\text{ nm}$ ).

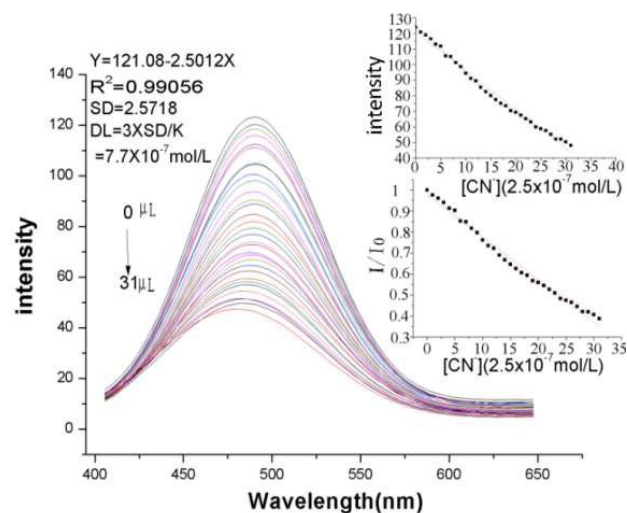
#### Adsorption kinetics of $\text{Zn}^{2+}$ onto FFIC MNPs

Almost all current  $\text{Zn}^{2+}$  sensors can only detect the heavy metal ions, but not remove them from solution. In this work, we endowed the FFIC MNPs with adsorptive and separable properties to remove the  $\text{Zn}^{2+}$  ions from aqueous solution. The FFIC MNPs were added to an aqueous solution containing different concentrations of  $\text{Zn}^{2+}$  ions and were thoroughly removed by a magnet ( $[\text{FFIC}] = 1\text{ g/L}$ ,  $[\text{Zn}^{2+}] = 0-14\text{ mg/L}$ ). It was found that the adsorption of  $\text{Zn}^{2+}$  enhanced initially with the increasing concentration and then would level off showing  $q_e=6.1\text{mg/g}$  in Fig.S11(see ESI). The initial enhancement in metal adsorption might be due to many available chelating sites on the FFIC MNPs. The concentration of  $\text{Zn}^{2+}$  ions left in

aqueous solution was measured by inductively coupled plasma mass spectrometry (ICP-MS). The experimental adsorption equilibrium data of  $\text{Zn}^{2+}$  were analyzed according to the Langmuir adsorption equation, which is given as follows:  $C_e/q_e = 1/K_L q_m + C_e/q_m$  [1], where  $q_e$  is the equilibrium quantity of the metals ions adsorbed onto the FFIC MNPs (mg/g),  $C_e$  is the equilibrium concentration (mg/L), and  $q_m$  (mg/g)=7.19 and  $K_L$  (L/mg)=0.364 are the Langmuir constants related to the saturation adsorption capacity and binding energy (affinity), respectively. Fig.S12 (see ESI) shows the Langmuir  $C_e/q_e$  versus  $C_e$  plot and a good linear relationship ( $R^2=0.9503$ ) was found. The basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent and once a metal ion occupies a reaction site, no further adsorption occurs at that location. Thus, monolayer adsorption occurred on the FFIC MNPs. The values of  $q_e=6.1\text{mg/g}$ ,  $q_m$  and  $K_L$  have calculated from the slope and intercept of the  $C_e/q_e$  versus  $C_e$  plot in Fig.S11. The linear plot indicates that  $\text{Zn}^{2+}$  ion adsorption followed the Langmuir isotherm. The adsorption capacity was  $6.1\text{ mg}$  of  $\text{Zn}^{2+}$  ions per gram of FFIC MNPs.

#### Fluorescence property detecting $\text{CN}^-$

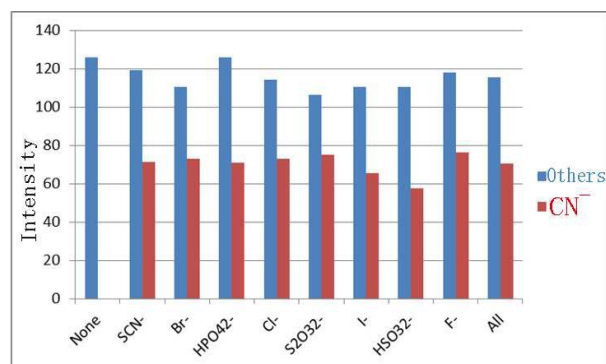
$2\text{g/L}$  FFIC MNPs- $\text{Zn}$  solution was prepared in advance. Fluorescence titrations were conducted with  $\text{CN}^-$  ( $1\times 10^{-3}\text{ mol/L}$ ) and the experiment conditions are the same as Fig.2. Fig.4 shows the fluorescence intensity of FFIC MNPs- $\text{Zn}$  quenched from initial 121 to ultimate 43 as the increasing concentration of  $\text{CN}^-$ . After  $77.5\times 10^{-7}\text{ mol/L}$ , the linearity would mainly stay smooth. A linear relationship existed between the fluorescence intensity of FFIC MNPs- $\text{Zn}$  and concentration of  $\text{CN}^-$  over the range  $2.5\times 10^{-7}\text{ mol/L}$  to  $77.5\times 10^{-7}\text{ mol/L}$ . The correlation coefficient was  $R^2=0.9906$ . The detection limit was  $7.7\times 10^{-7}\text{ mol/L}$ . Therefore FFIC MNP- $\text{Zn}$  can be used to respond to  $\text{CN}^-$  efficiently and specifically, just as the chemosensor in reference[18], due to that the complex constants of  $\text{CN}^-$  and  $\text{Zn}^{2+}$  is larger than that of FFIC MNPs and  $\text{Zn}^{2+}$  with the decrease of fluorescence intensity.



**Fig.4** Fluorescent spectra of the FFIC MNPs-Zn 0.1g/L in the absence and presence of  $\text{CN}^-$  from 0 to  $77.5 \times 10^{-7} \text{ mol/L}$ . The inset shows fluorescence intensity as concentration of  $\text{CN}^-$  ( $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ , 1: 4, v/v, buffered at  $\text{pH}=7.1$  with  $\text{Tris-HCl}$ , excitation was at 390 nm, emission was monitored at 485 nm). Slit  $2.50 \times 5.00 \text{ mm}$

#### Anion competition studies

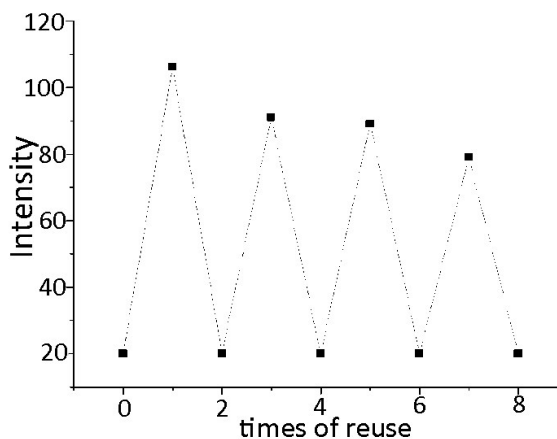
The sensitivity of the fluorescence turn-on response to other biologically relevant anions was examined. Aqueous solutions of  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{Br}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{HSO}_3^-$ , and  $\text{S}_2\text{O}_3^{2-}$  were titrated into suspension solution of FFIC MNPs-Zn and change to the emission and absorbance spectra were monitored. Interfering ions were tested at  $25 \mu\text{mol/L}$ , while the target analyte  $\text{CN}^-$  was tested at  $5 \mu\text{mol/L}$ . As Fig.5 shows that the changes of fluorescence intensity caused by other anions and  $\text{CN}^-$ , it can be seen that there is slight fluorescence quenching after dropwise adding interfering ion, only  $\text{CN}^-$  can change the fluorescence intensity obviously, which means other anions remain entirely silent at the same conditions. As a result, the selectivity of FFIC MNPs-Zn toward  $\text{CN}^-$  ions over other anion ions is remarkably high.



**Fig.5** Blue bars: fluorescent emission of FFIC MNPs-Zn (0.1 g/L) in the presence of different anions  $25 \mu\text{mol/L}$ . Red bars: fluorescent response of FFIC MNPs-Zn upon addition of  $\text{CN}^-$  ions  $5 \mu\text{mol/L}$  ( $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ , 1:4, v/v, buffered at  $\text{pH}=7.1$  with  $\text{Tris-HCl}$  (0.1M), excitation was at 390 nm, emission was at 485 nm).

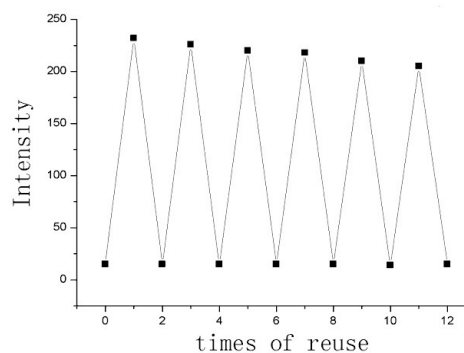
#### Regeneration property

Recycling of the switchable FFIC MNPs was conducted for response to zinc ions. After responding, we made the residual MNPs saturatedly adsorb zinc, be magnetically separated, dry under vacuum and be reused to detect  $\text{CN}^-$ . After that we made EDTA chelate and adsorb residual  $\text{Zn}^{2+}$  on the surface of MNPs-Zn, then the MNPs regain the capacity to respond to  $\text{Zn}^{2+}$ . This circulation exhibits the same FFIC MNPs possess the capacity to respond to  $\text{Zn}^{2+}$  and  $\text{CN}^-$  repeatedly as Fig.6 shows.



**Fig.6** Recycling and reusing of the same FFIC MNPs sensors that fluorescence enhancement for  $\text{Zn}^{2+}$ , fluorescence quenching for  $\text{CN}^-$ . Slit  $2.50 \times 5.00 \text{ mm}$ .

off fluorescent functional molecules from assembled MNPs in  $\text{CH}_3\text{CN}$  by ultrasonic, then reassemble with new fluorescent functional molecules to detect zinc again. The recycling was easy and high yielding. Fig.7 illustrates the fluorescent intensity of the FFIC MNPs after each cycle. After 7 cycles, the ability to respond to  $\text{Zn}^{2+}$  ion is still active and efficient. Therefore the MNPs have outstanding reproducibility and practicability.



**Fig.7** The same "Host" (MNPs), we change the "Guest" (fluorescent molecules). Slit  $2.50 \times 5.00 \text{ mm}$ .

#### Conclusions

In summary, we have prepared novel and functionalized solid magnetic nanoparticles which act as a new type of colorimetric and switchable chemosensor for sensing and separating  $\text{Zn}^{2+}$  and  $\text{CN}^-$  efficiently in aqueous solutions. These multifunctional

nanoparticles exhibit high selectivity and sensitivity for targeting  $\text{Zn}^{2+}$  and  $\text{CN}^-$  over a number of other metal ions and anions tested, with the detection limit of  $4.5 \times 10^{-7}$  mol/L for  $\text{Zn}^{2+}$ ,  $7.7 \times 10^{-7}$  mol/L for  $\text{CN}^-$ . The FFIC MNPs show good ability of adsorption for  $\text{Zn}^{2+}$  ions and can separate zinc ions from aqueous solution with a commercial magnet easily and quickly. Furthermore, the switched FFIC MNPs-Zn could be separated and collected after responding to  $\text{CN}^-$  within 60 s. The recycling of the FFIC MNPs or FFIC MNPs-Zn is easy and high-yielding as the described approach (based on sol-gel grafting reaction and simple self-assembly techniques). We believe that this technique would provide a very promising alternative for developing high-performance magnetic sensing materials for  $\text{Zn}^{2+}$  and  $\text{CN}^-$  detection and separation from aqueous solution.

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