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## PAPER

## Differentiation of multi-metal ions based on Fluorescent Dual-Emission Carbon Nanodots

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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A new fluorescence nanosensor for selective determination and differentiation of Fe<sup>3+</sup>, Bi<sup>3+</sup> and Al<sup>3+</sup> were reported based on dual-emission carbon nanodots (DECNDs), which contained the blue emitters ( $\lambda_{\text{ex}} = 315 \text{ nm}$ ,  $\lambda_{\text{em}} = 386 \text{ nm}$ ) and the yellow emitters ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\lambda_{\text{em}} = 530 \text{ nm}$ ). In this assay, Fe<sup>3+</sup> could quench the fluorescence of the blue emitters; Bi<sup>3+</sup> and Al<sup>3+</sup> could be differentiated by the yellow emitters, such as fluorescence dropping for Bi<sup>3+</sup>, and the blue-shifted emission upon addition of Al<sup>3+</sup> with signal amplification. The different responses were considered to be associated with the various ligands on the two emitters. Moreover, this sensing system also exhibited good sensitivity and selectivity. Finally, the present method was used to detect Fe<sup>3+</sup>, Bi<sup>3+</sup> and Al<sup>3+</sup> in common drugs.

### 1. Introduction

Metal ions are ubiquitous and play essential roles in chemistry, electronics, environment, biology, and medicine. Too much or too little metal ions will affect normal life activities. For example, Fe<sup>3+</sup> is important for binding with the transport protein transferrin in sera,<sup>1</sup> and both of its deficiency and overload can influence the balance of cellular homeostasis and induce various biological diseases.<sup>2</sup> Bi<sup>3+</sup> is also toxic, sometimes even causing nephropathy, osteoarthropathy, hepatitis and neuropathology.<sup>3</sup> While excess Al<sup>3+</sup> will do great damage to the central nervous leading to idiopathic Parkinson's disease, impairment of memory and Alzheimer's disease.<sup>4-6</sup> However, Fe<sup>3+</sup>, Bi<sup>3+</sup> and Al<sup>3+</sup> also play vital roles in common drugs, mainly in the treatment of hypoferric anemia and gastritis. In view of the importance of the detection of metal ions in drugs and physiological systems, many strategies have been proposed in the past decade, for example hydride generation-atomic fluorescence spectrometry,<sup>7</sup> anodic stripping voltammetry,<sup>8</sup> cold-vapor atomic absorption spectrometry,<sup>9</sup> and inductively coupled plasma-mass spectrometry.<sup>10</sup>

Recently carbon nanodots (CNDs), as new members of the carbon nanomaterials family, have attracted increasing attention because of their superior performances. Compared with conventional semiconductor quantum dots, the

advantages of CNDs are their low toxicity, high photo stability, good biocompatibility, tunable color emission, easy preparation, environmental friendliness, and so on.<sup>11-18</sup> Since advances in nano-materials greatly expand our understanding of nanoworld, numerous CNDs have been employed in sensing and analysis of metal ions based on fluorescence and ultraviolet-visible (UV-vis) spectrophotometer. For instance, Zhang et al. have developed a simple method for preparation of N-doped CNDs, which shows high quantum yield and good selectivity for Fe<sup>3+</sup>.<sup>19</sup> In the meantime, the CNDs, using pomelo peel as a carbon source, have been demonstrated for sensitive and selective detection of Hg<sup>2+</sup>.<sup>20</sup>

However, the intrinsic limitations of spectrophotometer, such as lack of the functions of separation and differentiation, have posed great difficulties for the further development of high-efficiency techniques and high-throughout assays, so most of literature reported the single-target responsive molecular sensor via spectrophotometer. As is the case with all new nanoparticles, the design criteria for differentiation sensing based on spectrophotometers are still being challenged. The development of nanomaterials consisting of several emitters, which exhibit different responses to the multi-targets, seems to be a robust approach for addressing these problems.

Our groups recently reported the design and synthesis of dual-emission carbon nanodots (DECNDs), which contained two types of CNDs due to the different modified ligands on their surfaces, such as ascorbic acid (AA) capped on the blue emitters ( $\lambda_{\text{ex}} = 315 \text{ nm}$ ,  $\lambda_{\text{em}} = 386 \text{ nm}$ ) and alcohol molecules capped on the yellow emitters ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\lambda_{\text{em}} = 530 \text{ nm}$ ).<sup>21</sup> Using DECNDs as a multi-responsive probe, Fe<sup>3+</sup>, Bi<sup>3+</sup> and Al<sup>3+</sup> could be differentiated and detected from other popular metal ions via fluorescent spectrophotometer. For example, Fe<sup>3+</sup> could quench the fluorescence of the blue emitters; the yellow emitters could distinguish Bi<sup>3+</sup> and Al<sup>3+</sup>, such as fluorescence

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<sup>†</sup>Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

dropping for  $\text{Bi}^{3+}$ , and the blue-shifted emission upon addition of  $\text{Al}^{3+}$  with signal amplification. Therefore, this new sensing model was of interest because it provided a novel sensing mechanism and a simple differentiation of metal ions with high selectivity and sensitivity, which could open a new design strategy for fluorescence sensor development.

## 2. Experimental section

### 2.1 Materials

Ascorbic acid (AA), methanol, ethanol, n-propanol, ethylene glycol, acetic acid, sodium acetate, citrate acid, sodium citrate, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), trihydroxymethyl aminomethane (Tris), NaOH, HCl,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{AgNO}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{CoCl}_2$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2$ ,  $\text{Ce}(\text{NO}_3)_3$ , NaCl, KCl,  $\text{BaCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{MnSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{Hg}(\text{NO}_3)_2$  and  $\text{Bi}(\text{NO}_3)_3$  were purchased from Aladdin (Shanghai, China). Ferrous succinate tablets, bismuth potassium citrate granules and aluminum magnesium carbonate tablets were purchased from local pharmacy. All chemicals were used as received without further purification. Ultrapure water was used throughout all the experiments.

### 2.2 Instruments

Fluorescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were obtained on a Tecnai G2 F20 electron microscope. The ultraviolet-visible (UV-vis) absorption spectra were obtained on a Cary 300 Bio UV-visible spectrophotometer. The Fourier transform infrared (FT-IR) spectra of the samples were analyzed by a WQF-520A FTIR spectrophotometer using KBr pellets.

### 2.3 Synthesis of DECNDs.

In a typical synthesis procedure, 0.8 g AA was dissolved in alcohol-water binary reaction media, respectively, including methanol-water, ethanol-water, n-propanol-water, and glycol-water, and all the volume fractions of alcohols were 50%. Subsequently, under vigorous stirring, the mixture was heated at 160 °C in a constant temperature drying oven for 70 min. After cooling to room temperature, the mixture was centrifuged at 12000 rpm for 10 min. Finally, a clear yellow aqueous dispersion containing DECNDs was obtained, and the DECNDs were stored at ambient environment.

### 2.4 Fluorescence Assay of $\text{Fe}^{3+}$ , $\text{Bi}^{3+}$ and $\text{Al}^{3+}$ .

Detection of  $\text{Fe}^{3+}$ : In a typical experiment, 0.4  $\mu\text{L}$  DECNDs, 200  $\mu\text{L}$  Tris-HCl buffer (0.1 M, pH 8.0) and a calculated amount of  $\text{Fe}^{3+}$  were mixed together with vigorous stirring, and then the fluorescent spectra of the mixture were recorded with the excitation wavelength at 315 nm.

Detection of  $\text{Bi}^{3+}$  or  $\text{Al}^{3+}$ : In brief, 5  $\mu\text{L}$  DECNDs, 200  $\mu\text{L}$  HAC-NaAC (0.2 M, pH 4.4), and different concentrations of  $\text{Bi}^{3+}$  or  $\text{Al}^{3+}$  were added into ultrapure water. After shaking, the

fluorescence spectra were recorded with the excitation wavelength at 365 nm.

Other metal ions were used to evaluate the selectivity of DECNDs, such as  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{2+}$ .

### 2.5 Real Sample Detection

In this assay, we detected  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  in common drugs. Detection of  $\text{Fe}^{3+}$ : First, one tablet of ferrous succinate (0.1 g) was powdered in a mortar; then 3 mL of 65% nitric acid was introduced into the powder to oxidize ferrous iron to ferric iron; after stirring thoroughly for a few seconds, the mixture reacted at ambient temperature for 15 min; subsequently, the solution was centrifuged at 45000 rpm for 10 min. The supernatant was separated and adjusted to pH 7.0 with NaOH. Finally, the mixture was diluted several folds before detection.

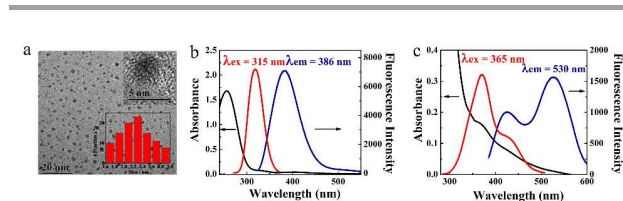
Detection of  $\text{Bi}^{3+}$ : A bag of bismuth potassium citrate granules, containing  $\text{Bi}^{3+}$  110 mg, was transferred into a beaker and added 10 mL ultrapure water. With stirring vigorously, a transparent solution was obtained. Then the solution was diluted several folds to ensure the concentration of  $\text{Bi}^{3+}$  in the linear range.

Detection of  $\text{Al}^{3+}$ : 0.1243 g of aluminum magnesium carbonate tablets was weighed into a beaker; then 1 mL of 65% nitric acid and 9 mL of ultrapure water were added; subsequently, the mixture was centrifuged at 45000 rpm for 10 min. The supernatant was separated and adjusted to pH 7.0 with NaOH before determination.

## 3. Results and discussion

### 3.1 Synthesis and Characterization of Fluorescent DECNDs.

Taking the DECNDs synthesized in n-propanol-water binary system as an example, Figure 1a displayed that the DECNDs were monodispersed and uniform in size with an average diameter of 2.3 nm. Fluorescence spectra in Figure 1b and 1c depicted the DECNDs containing two different emitters: the blue emitters exhibited the maximum emission at 386 nm when excited at 315 nm; the yellow emitters had the maximum excitation and emission wavelengths at 365 and 530 nm, respectively. Correspondingly, the UV-vis absorption spectra indicated that the DECNDs showed a strong peak at 256 nm and a weak peak at 370 nm (Figure 1b and 1c). The TEM images, UV-vis absorption spectra and fluorescence spectra of DECNDs prepared in other alcohol-water binary systems were displayed in the supporting information (Figure S1 and S2).



**Figure 1** TEM images (a); UV-vis absorption and fluorescence spectra of blue emitters (b) and yellow emitters (c) synthesized

in n-propanol-water binary system.

### 3.2 Fluorescence Differentiation of $\text{Fe}^{3+}$ , $\text{Bi}^{3+}$ and $\text{Al}^{3+}$ by DECNDs.

The fluorescence of DECNDs could be efficiently affected by  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , and the two emitters displayed different selectivity as shown as Figure 2 (DECNDs synthesized in n-propanol-water binary system). When  $\text{Fe}^{3+}$  was added into the solution, the first emission peak ( $\lambda_{\text{ex}} = 315 \text{ nm}$ ,  $\lambda_{\text{em}} = 386 \text{ nm}$ ) could quench obviously, while the fluorescence of yellow emitters was very stable. On the other hand, the second emission peak ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\lambda_{\text{em}} = 530 \text{ nm}$ ) selectively responded to  $\text{Al}^{3+}$  and  $\text{Bi}^{3+}$ . Adding  $\text{Al}^{3+}$ , the wavelength of the yellow emitters blue shifted to  $490 \text{ nm}$ , and the fluorescence increased greatly. However, with the addition of  $\text{Bi}^{3+}$ , the fluorescence intensity of yellow emitters reduced dramatically without the wavelength-shift (Figure 2b). In the meantime, the first emission peak was insensitive to  $\text{Al}^{3+}$  and  $\text{Bi}^{3+}$ . Hence, the fluorescence quenching, signal amplification and wavelength shift coexisted in the same sensing system, facilitating the differentiation of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Bi}^{3+}$  based on the different responses, which is ideal for the measurement of these three metal ions in applications. Furthermore, the photographs of DECNDs with addition of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Bi}^{3+}$  under UV light (Figure 2c) coincided with the variations of fluorescence spectra. The DECNDs exhibited a bright yellow fluorescence, which could not be observed after adding  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$ . However, when  $\text{Al}^{3+}$  was incorporated into the solution, the fluorescence color of DECNDs changed from yellow to green. More notably, the same phenomena could also be obtained by using the DECNDs synthesized in other alcohol-water binary systems as probes (Figure S3).

### 3.3 Optimizing Experimental Conditions.

In order to obtain a highly sensitive responses for the detection of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , the optimization of the different experimental conditions, such as the probe concentrations, the pH values and the reaction of time, were carried out in our experiment. Because the blue emitters could only be quenched by  $\text{Fe}^{3+}$  and the yellow emitters

under UV light at  $365 \text{ nm}$  (c). Concentrations: a,  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  were  $100 \mu\text{M}$ ; b and c,  $\text{Fe}^{3+}$  was  $100 \mu\text{M}$ , and  $\text{Bi}^{3+}/\text{Al}^{3+}$  was  $20 \mu\text{M}$ .

selectively responded to  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , we investigated the influence of experimental conditions to those metal ions respectively.

The sensitivity of detection depended on the probe concentration. A lower concentration of probe achieved lower detection limits of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ . Based on the different fluorescent properties of the two emitters, the optimal probe concentrations was  $0.4 \mu\text{L/mL}$  for  $\text{Fe}^{3+}$ , and  $5 \mu\text{L/mL}$  for  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , respectively (Figure S4).

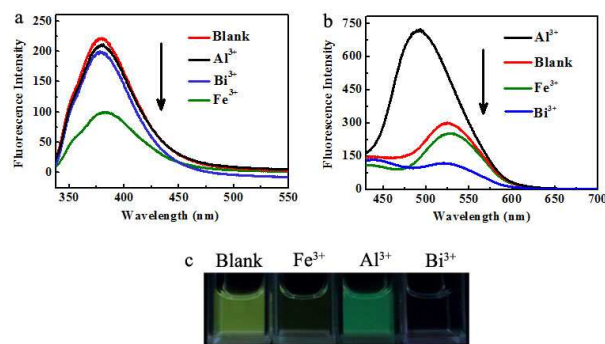
In the optimization of pH values, we first examined the influence of pH for DECNDs. As illustrated in Figure S5, the stable fluorescence was observed in the pH range 2–12 for the blue emitter and 4–9 for the yellow emitter without obvious wavelength shift of the two emitters. In the stable pH range, several buffer solutions were chose to investigate the pH influence on the detection of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , including Britton-Robinson (BR) buffers, HCl–NaAC, HEPES–NaOH buffers, citrate acid–sodium citrate buffers, Tris–HCl and HAC–NaAC buffers, in which Tris–HCl (pH 8.0) and HAC–NaAC (pH 4.4) were selected as the optimum buffers for the detection of  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}/\text{Al}^{3+}$ , respectively (Figure S6).

In addition, the reaction could complete within 1 min (Figure S7), indicating the rapid reaction rates between DECNDs and these metal ions, so the DECNDs could be employed as a new fluorescent probe for real-time tracking of these metal ions.

### 3.4 Sensitivity.

On the basis of the optimized conditions discussed above, the linear ranges and the detection limits of this sensing system were estimated by varying the concentrations of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ . The fluorescence intensities of DECNDs in the absence and presence of metal ions were denoted by  $F_0$  and  $F$ , respectively. Because of the fluorescence quenching producing by  $\text{Fe}^{3+}$  (for blue emitters) or  $\text{Bi}^{3+}$  (for yellow emitters), the quenching efficiency was expressed by  $(F_0 - F)/F_0$ , while the fluorescent enhancement with  $\text{Al}^{3+}$  was described by  $F/F_0$ .

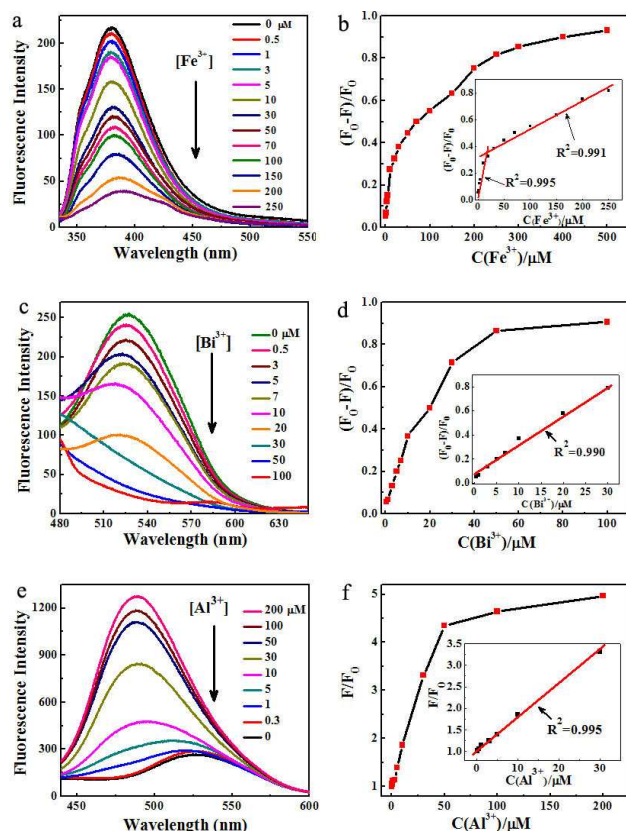
Taking the DECNDs synthesized in n-propanol-water binary system as an example, with the increase of  $\text{Fe}^{3+}$  or  $\text{Bi}^{3+}$  concentrations, gradual declines in fluorescence intensities at  $315 \text{ nm}$  (Figure 3a, the blue emitters) and  $365 \text{ nm}$  (Figure 3c, the yellow emitters) were observed, respectively. Good linear correlations were obtained over the concentration range from  $0.5$  to  $250 \mu\text{M}$  for  $\text{Fe}^{3+}$  (Figure 3b, inset), and  $0.5$  to  $30 \mu\text{M}$  for  $\text{Bi}^{3+}$ , respectively (Figure 3d, inset). The limits of detection (LOD) of  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$  were estimated to be  $200 \text{ nM}$  and  $150 \text{ nM}$ , respectively. In addition, with the increase of  $\text{Al}^{3+}$  concentrations from  $0.3$  to  $30 \mu\text{M}$ , the fluorescence at  $530 \text{ nm}$  gradually enhanced (Figure 3e, the yellow emitters) and finally reached to about 3.3-fold stronger than that of the initial probe solution (Figure 3f, inset). Meanwhile, the emission wavelength showed obvious blue-shift with increasing  $\text{Al}^{3+}$  concentrations and the detection limit could reach as low as  $100 \text{ nM}$ .



**Figure 2** Fluorescence spectra (a, blue emitters; b, yellow emitters) and the fluorescence color changes of DECNDs synthesized in n-propanol-water binary system with the addition of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Bi}^{3+}$



The fluorescence spectra and calibration curves of DECNDs prepared in other alcohol-water binary systems with the addition of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  were displayed in Figure S8.



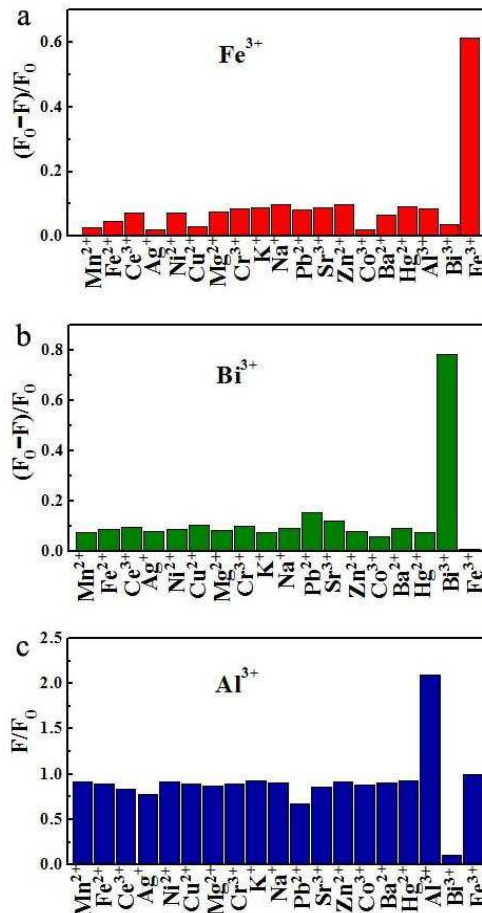
**Figure 3** Fluorescence spectra of DECNDs synthesized in n-propanol-water binary system in the presence of different concentrations of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  (a, c, and e) and the corresponding linear ranges (b, d, and f).

And the corresponding linear ranges and LODs were compared in Table S1, where the DECNDs prepared in methanol-water binary systems exhibited a better sensitivity for  $\text{Fe}^{3+}$  with LOD 150 nM; while DECNDs synthesized in n-propanol-water binary system was proper for the determination of  $\text{Bi}^{3+}$  with LOD 150 nM; besides, compared with  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$ , the DECNDs showed higher sensitivity for  $\text{Al}^{3+}$ , in which the DECNDs fabricated in ethanol-water was more appropriate to detect  $\text{Al}^{3+}$  with LOD 4 nM. Therefore, according to different requirements and analytes, we could choose proper DECNDs synthesized in different alcohol-water systems as probes, which was feasible and flexible in the applications.

### 3.5 Selectivity.

Based on the different selectivity of the two emitters for  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , we measured the fluorescence variations in the presence of the competition metal ions, including  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Fe}^{2+}$  under the same conditions (excitation at 315 nm for  $\text{Fe}^{3+}$  and 365 nm for  $\text{Bi}^{3+}$  /  $\text{Al}^{3+}$ ). In Figure 4, among various metal ions,  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$  led to the fluorescence quenching of

blue emitters and yellow emitters, respectively, and the distinctive effect of  $\text{Al}^{3+}$  on the second emission peak could be recognized by the remarkable enhancement of fluorescence.



**Figure 4** Selectivity of DECNDs synthesized in n-propanol-water binary system for detection of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ : a, the concentrations of all the metal ions were 100  $\mu\text{M}$ ; b, the concentrations of  $\text{Ce}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$  were 50  $\mu\text{M}$  and  $\text{Cr}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  were 100  $\mu\text{M}$ , except for 30  $\mu\text{M}$   $\text{Bi}^{3+}$ ; c, the concentration of  $\text{Al}^{3+}$  was 10  $\mu\text{M}$ ,  $\text{Bi}^{3+}$  30  $\mu\text{M}$ , and other metal ions were 100  $\mu\text{M}$ .

Therefore, the two types of CNDs exhibited an excellent selectivity to  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Al}^{3+}$ . Moreover, the good selectivity also displayed in the DECNDs synthesized in other alcohol-water binary systems (Figure S9).

### 3.6 Mechanism of Fluorescence Response of DECNDs to $\text{Fe}^{3+}$ , $\text{Bi}^{3+}$ and $\text{Al}^{3+}$ .

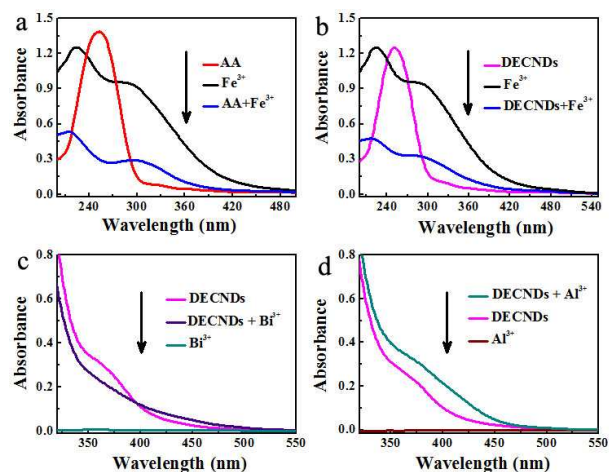
In this assay,  $\text{Fe}^{3+}$  could quench the fluorescence of the blue emitters; the yellow emitters could distinguish  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ . The differentiation of multi-metal ions was considered to be associated with the different ligands on DECNDs. The blue emitters and the yellow emitters were ascribed to two different species of CNDs: AA molecules act as the functional groups on the surfaces of particles leading to the formation of

blue emitters; at the same time, other DECNDs capped by alcohol molecules produced the yellow emitters in alcohol-water binary systems. The details of synthetic mechanism were reported in our previous literature.<sup>21</sup> Furthermore, some supplementary experiments were carried out to explore the recognition mechanism for  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , respectively.

First, we compared the UV-vis absorption spectra of  $\text{Fe}^{3+}$  and AA with those of  $\text{Fe}^{3+}$  and DECNDs. When  $\text{Fe}^{3+}$  was added in AA solution, a direct redox reaction occurred based on the oxidizing property of  $\text{Fe}^{3+}$  and reducing feature of AA, producing the absorbance of  $\text{Fe}^{3+}$  dropped dramatically (Figure 5a); similarly to these phenomena, the absorbance decrease was observed with the addition of DECNDs (Figure 5b), suggesting that the surfaces of blue emitters were indeed capped by AA, and the redox mechanism resulted in the fluorescence quenching of the first emission peak ( $\lambda_{\text{ex}} = 315 \text{ nm}$ ,  $\lambda_{\text{em}} = 386 \text{ nm}$ ). However, due to the absence of oxidation ability of  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , there was no effect on the blue emitters by adding  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ . Besides, we also investigated the influence of the species of Fe(III) on the fluorescence quenching of DECNDs. In order to obtain hydrated iron, NaOH (0.1 M) was used to prepare the standard stock solution of Fe(III). Hydrated iron instead of  $\text{Fe}^{3+}$  was used to prepare sample. As illustrated in Figure S10, when the concentrations of  $\text{Fe}^{3+}$  and hydrated iron were same (100  $\mu\text{M}$ ), hydrated iron induced the fluorescence quenching of DECNDs was inconspicuous comparing with the obvious fluorescence decline produced by  $\text{Fe}^{3+}$ , indicating that  $\text{Fe}^{3+}$ , rather than hydrated iron, quenched the fluorescence of DECNDs.

Meanwhile, the yellow emitters could differentiate  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , and the reason may be ascribed to two aspects: (1)  $\text{Bi}^{3+}$  possessed three accessible vacant orbits to form coordination complexes with alcoholic hydroxyl on the surfaces of yellow emitters, causing the fluorescence of yellow emitters dropping. Correspondingly, the characteristic absorption peak of yellow emitters at 370 nm disappeared (Figure 5c). (2) Besides, because  $\pi$ -conjugation of carbon atoms was considered to be weakened due to the large molecular curvature,<sup>22</sup> it seemed that the fluorescence enhancement was ascribed to more widespread formation of the  $\pi$ -conjugation system upon  $\text{Al}^{3+}$  binding,<sup>23</sup> and this would be supported by Figure 5d, in which the absorbance at 370 nm enhanced obviously by adding  $\text{Al}^{3+}$ . Moreover, the larger charge density affords strong coordination ability between  $\text{Al}^{3+}$  and yellow emitters, leading to blue-shifted emission.<sup>24</sup> Moreover, in FT-IR spectra (Figure S11), with the addition of  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , both of the strong peak at  $3500 \text{ cm}^{-1}$  associated with O-H stretching and a strong absorption peak at  $1716 \text{ cm}^{-1}$  associated with C=O decreased obviously, revealing that  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  indeed combined with hydroxyl and carbonyl groups on the surface of yellow emitters. Additionally, some literature also supported our theory that  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  could combine with hydroxyl and carbonyl groups: (1) Tiron, which contained hydroxyl groups, was used as a chelating agent to detect  $\text{Bi}^{3+}$  by fluorescence quenching method;<sup>25</sup> (2) the tridentate ligand o-phenolsalicylimine (PSI) was reported as a chemosensor, which exhibited enhanced fluorescence upon binding to  $\text{Al}^{3+}$ ;

the detection mechanism was that  $\text{Al}^{3+}$  could participate in complex formation with the hydroxyl groups of PSI;<sup>26</sup> (3)  $\text{Al}^{3+}$  could bind to the carbonyl group of anthraquinone, and by



**Figure 5** UV-vis spectra of AA and DECNDs in absence and presence of  $\text{Fe}^{3+}$  (a and b),  $\text{Bi}^{3+}$  (c), and  $\text{Al}^{3+}$  (d).

intramolecular charge transfer, the detection of  $\text{Al}^{3+}$  could be realized.<sup>27</sup>

Therefore, the differentiation of multi-metal ions by DECNDs was on the basis of different reaction mechanism, and the functional groups on the surfaces of DECNDs played a vital role in this assay.

### 3.7 Detection of $\text{Fe}^{3+}$ , $\text{Bi}^{3+}$ and $\text{Al}^{3+}$ in Real Samples.

With good selectivity and sensitivity, the present method was used to detect  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  in common drugs. For instance, bismuth potassium citrate and aluminum magnesium carbonate, containing  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$ , respectively, were usually used for gastritis; however, most drugs, for the prevention and treatment of iron deficiency anemia, contained iron element in Fe (II) state, so nitric acid was supplied to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

**Table 1** Detection of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  in drugs.

As shown in Table 1, the recoveries for these three drugs were 105% for  $\text{Fe}^{3+}$ , 95% for  $\text{Bi}^{3+}$ , 98% for  $\text{Al}^{3+}$ . The satisfactory results suggested that the  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  measurements based on DECNDs were sensitive, rapid, reliable, and promising to be potentially useful for drug quality control analysis.

#### 4. Conclusions

In this assay, we successfully utilized the different responses of DECNDs on  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  to develop analytical methods. For instance,  $\text{Fe}^{3+}$  could quench the fluorescence of blue emitters; for the yellow emitters,  $\text{Bi}^{3+}$  produced an obvious quenching effect, while a dramatic fluorescence enhancement with blue-shift of emission maximum depended on the concentration of  $\text{Al}^{3+}$ . The different responses were considered to be associated with the various ligands on the two emitters. With the present sensor, the determinations of  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Al}^{3+}$  have been realized in common drugs, indicating the DECNDs were promising candidates in applications of drug quantification.

#### Acknowledgements

Fei Qu and Shuai Wang contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Youth Fund Project) (21405093) and the Scientific Research Foundation of Qufu Normal University (BSQD20130117).

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Drug	Metal ions	Labeled amount ( $\mu\text{M}$ )	Found amount ( $\mu\text{M}$ )	Recovery (%)
Ferrous succinate tablets (oxidation of $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ )	$\text{Fe}^{3+}$	100	105	105
Bismuth potassium citrate granules	$\text{Bi}^{3+}$	20	19	95
Aluminum magnesium carbonate tablets	$\text{Al}^{3+}$	5	4.9	98

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