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# Ferric ion detection mechanism of a dicarboxylic cellulose nanocrystal and a 7-amino-4-methylcoumarin based fluorescent chemosensor

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As one of Earth's most widely distributed and abundant elements, iron impacts the natural environment and biological systems. Therefore, developing a simple, rapid, and accurate Fe<sup>3+</sup> detection method is vital. Fluorescent dicarboxylic cellulose nanocrystals (FDCN) with selective quenching of Fe<sup>3+</sup> were synthesized using 7-amino-4-methylcoumarin (AMC), and dicarboxylic cellulose nanocrystals (DCN) prepared by sequential periodate–chlorite oxidation. The sensing characteristics and detection mechanism of FDCN for Fe<sup>3+</sup> were studied by fluorescence spectrophotometry, Fourier-transform infrared spectroscopy (FTIR), the Stern–Volmer equation, Job's plot method, and the Benesi–Hildebrand equation. The results showed that FDCN was highly selective for Fe<sup>3+</sup>, and other metal ions did not reduce the selectivity. High sensitivity with a detection limit of 0.26 μM and a Stern–Volmer quenching constant of 0.1229 were also achieved. The coordination between Fe<sup>3+</sup> and the carboxylic, hydroxyl, and amide groups on the surface of FDCN and the carbonyl of coumarin lactones to form FDCN/Fe<sup>3+</sup> complexes prevented the intramolecular charge transfer (ICT) process and led to the fluorescence quenching of FDCN. EDTA restored the fluorescence emission of quenched FDCN. The complexation stoichiometry of Fe<sup>3+</sup> to FDCN was 1 : 1, and the association constant was 3.23 × 10<sup>4</sup> M<sup>-1</sup>. The high hydrophilicity, sensitivity, and selectivity of FDCN for Fe<sup>3+</sup> make the chemosensor suitable for Fe<sup>3+</sup> trace detection in drinking water and biology.

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## Introduction

Iron ions are widely distributed in nature and are a vital nutrient for animal and plant growth and human health.<sup>1</sup> However, excessive consumption of Fe<sup>3+</sup> damages human tissues, leading to functional impairment of organs such as the kidneys, liver, and heart. Studies also show that excessive Fe<sup>3+</sup> intake can easily cause cancer and neurological diseases, such as Alzheimer's disease and Parkinson's disease.<sup>2–4</sup> Meanwhile, Fe<sup>3+</sup> deficiency can easily cause tissue or cell hypoxia, leading to serious health problems.<sup>5,6</sup> Therefore, it is crucial to develop a method that can selectively identify trace Fe<sup>3+</sup> in the most consumed substances – especially water. Fe<sup>3+</sup> detection methods mainly include atomic absorption spectrometry (AAS),<sup>7,8</sup> inductive coupling, plasma mass spectrometry (ICP-MS),<sup>9</sup> and electrochemical methods.<sup>10</sup> However, these methods have drawbacks such as complicated detection processes and expensive instrumentation. Fluorescence detection has become the preferred method for detecting Fe<sup>3+</sup> in water because of its

high sensitivity, selectivity, and ease of detection.<sup>11</sup> Many fluorescent probes or chemosensors for detecting Fe<sup>3+</sup> have been developed.<sup>12–15</sup> However, some fluorescent probes still have limitations such as toxicity, poor hydrophilicity, and low biocompatibility. Hence, there is still a need for further research to develop Fe<sup>3+</sup> fluorescent probes.

Among numerous materials, nanocellulose is an attractive material for synthesizing fluorescent probes due to its carbon neutrality,<sup>16</sup> low cytotoxicity,<sup>17</sup> good biocompatibility, and availability in a vast source of raw materials.<sup>18</sup> Various studies have proven nanocellulose as a suitable matrix material for the synthesis of fluorescent probes.<sup>19–22</sup> For instance, the immobilization of fluorescent dyes on nanocellulose has been demonstrated to improve the performance of fluorescent probes.<sup>23,24</sup> Elsewhere, citrate-based fluorophore-modified cellulose nanocrystals (CF-CNC) were prepared with sulfuric acid hydrolysis of citric acid/cysteine-treated microcrystalline celluloses. The CF-CNC exhibited typical fluorescence characteristics, including a high quantum yield of 83%, good photostability, and a selective quenching effect toward Fe<sup>3+</sup> ions.<sup>25</sup> Xue *et al.* mixed citric acid, ethylenediamine, and cellulose nanofibrils prepared by 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (TEMPO)-mediated oxidation and processed them with a one-step hydrothermal treatment. Fluorescent cellulose nanofibrils were obtained

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through amide bonds from the grafted carbon quantum dots. The fluorescent cellulose nanofibrils demonstrated significant selectivity toward  $\text{Fe}^{3+}$  ions.<sup>26</sup> Py-CNC were prepared by grafting pyrene onto cellulose nanocrystals (CNC) prepared by sulfuric acid hydrolysis. The Py-CNC had excellent selectivity for  $\text{Fe}^{3+}$  over a wide linear concentration range, and the fluorescent emission was stronger than that of pyrene alone.<sup>24</sup>

The process of periodate oxidation is safer and simpler than sulfuric acid hydrolysis. Also, the content of carboxyl groups on dicarboxylic cellulose nanocrystals (DCN) prepared by sequential periodate–chlorite oxidation is higher than that of cellulose nanofibrils prepared by TEMPO-mediated oxidation.<sup>18</sup> Furthermore, the high carboxyl group content results in better dispersibility in water and easy chemical modification. Fluorescent dicarboxylic cellulose nanocrystals (FDCN) were prepared by attaching 7-amino-4-methylcoumarin (AMC) to DCN prepared by sequential periodate–chlorite oxidation under 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) catalysis. Many studies have shown that coumarin derivatives containing amide bonds exhibit selective fluorescence quenching of  $\text{Fe}^{3+}$ .<sup>27–29</sup> Although the fluorescent CNC prepared by grafting AMC onto CNC derived from sulfuric acid hydrolysis also contained amide bonds, and they exhibited a selective fluorescence quenching effect on  $\text{Cu}^{2+}$ .<sup>30</sup> To the best of our knowledge, there is no relevant report on detecting metal ions by FDCN, and the metal ion binding properties of FDCN are still unclear.

Hence, the objective of this study was to determine the fluorescence properties of FDCN and its detection mechanism for metal ions in water. The experimental results showed that FDCN exhibited a selective fluorescence quenching effect on  $\text{Fe}^{3+}$  ions. The sensing characteristics and detection mechanism of FDCN for  $\text{Fe}^{3+}$  were studied by fluorescence spectrophotometry, Fourier-transform infrared spectroscopy (FTIR), the Stern–Volmer equation, Job's plot method, and the Benesi–Hildebrand equation.

## Experimental

### Materials and characterizations

**Materials.** All reagent-grade chemicals were used as received and without further purification. All chemical stock solutions were prepared with deionized water in all experiments. FDCN was prepared with the synthesis method of FCNC-5 as previously described.<sup>22</sup> The chemicals that were used in the experiments include the following: cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ), lithium sulfate ( $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ), zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), copper(II) sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), iron(II) sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), silver sulfite ( $\text{Ag}_2\text{SO}_3$ ), manganese(II) sulfate ( $\text{MnSO}_4$ ), cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6(\text{H}_2\text{O})$ ), nickel(II) chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ), lead(II) nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and iron(III) chloride ( $\text{FeCl}_3$ ).

**Characterisations.** The infrared spectrum of absorption or emission of the samples was recorded and analyzed using the Fourier-transform infrared (FTIR) spectrometer (mod. Nicolet iS50 FTIR, Thermo Fisher Scientific (Pty) Ltd, China). The

fluorescence of the samples was recorded on a fluorescence spectrophotometer (mod. F-7100, Hitachi (Pty) Ltd, Japan) with the slit set to 5 nm/5 nm. The excitation wavelengths of AMC and FDCN were 350 nm and 335 nm, respectively.

### Selectivity experiment of FDCN toward metal ions

Thirteen common metal ions were selected to explore the fluorescence response of FDCN. Ten mg of FDCN powder were placed in 10 mL of 1 mM  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^+$ , and  $\text{Ba}^{2+}$  ion solutions, respectively. The mixture was then uniformly dispersed using sonication (mod. KQ-200KDE, Kunshan Ultrasonic Instruments (Pty) Ltd, China) for 5 min. 2 mL of the dispersion solution was pipetted into a quartz cuvette, and its fluorescence spectrum was measured at room temperature. All experiments were performed in triplicates.

### Competition experiments of metal ions

For the practical application of probes, most samples contain a variety of metal ions, and it is necessary to study the change in the selective quenching ability of FDCN to specific metal ions in the presence of other metal ions. Ten mg of FDCN powder were placed in 10 mL of 1 mM  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ba}^{2+}$  ions and 1 mM  $\text{Fe}^{3+}$  ions coexistence solutions, respectively. Ultrasonic dispersion was performed for 5 min to ensure even dispersion. 2 mL of the dispersion solution was removed using a pipette and placed in a quartz cuvette, and the fluorescence spectra were recorded at room temperature. Experiments were performed in triplicates.

### Fluorescent titration experiments

Fluorescent titration experiments were performed at various concentrations of  $\text{Fe}^{3+}$  to obtain insight into the binding properties of FDCN to  $\text{Fe}^{3+}$  ions. The effect of  $\text{Fe}^{3+}$  concentration on the fluorescence intensity of FDCN was studied in the 1–500  $\mu\text{M}$  range. The  $\text{Fe}^{3+}$  concentration was in the range of 1–5  $\mu\text{M}$  in the Stern–Volmer fluorescence quenching experiments. The Stern–Volmer eqn (1) was used to explore the nature of the quenching process in the complexation of metal ions.<sup>31</sup>

$$\frac{F_0}{F} = 1 + K_{\text{SV}}[Q] \quad (1)$$

where  $F$  and  $F_0$  are the fluorescence intensities of FDCN in the presence and absence  $\text{Fe}^{3+}$  ions.  $K_{\text{SV}}$  is the Stern–Volmer fluorescence quenching constant, and  $Q$  is the  $\text{Fe}^{3+}$  concentration ( $\mu\text{M}$ ).

The association stoichiometry between FDCN and  $\text{Fe}^{3+}$  was determined using the Job's plot method.<sup>12</sup> The addition ratio of  $\text{Fe}^{3+}$  and FDCN was maintained at 0–1. The total concentration was kept at 10  $\mu\text{M}$  while the molar ratio of FDCN to  $\text{Fe}^{3+}$  was gradually changed. The fluorescence intensities of the mixture with different addition ratios were recorded, and the Job's plot was made by taking eqn (2) as the ordinate eqn (3) as the abscissas.<sup>32</sup>

$$XF_0 - F \quad (2)$$



$$[\text{Fe}^{3+}]/([\text{FDCN}] + [\text{Fe}^{3+}]) \quad (3)$$

Benesi-Hildebrand eqn (4) calculated the association constant ( $K_{ac}$ ).<sup>33</sup>

$$\frac{1}{F_0 - F} = \frac{1}{K_{ac}(F_0 - F_{\min})[\text{Fe}^{3+}]^n} + \frac{1}{F_0 - F_{\min}} \quad (4)$$

where  $F$  and  $F_0$  are the fluorescence intensities of FDCN at a wavelength of 440 nm in the presence and absence of  $\text{Fe}^{3+}$  ions,  $F_{\min}$  is the minimum fluorescence intensity in the titration experiment of FDCN and  $\text{Fe}^{3+}$ , and  $n$  is the binding stoichiometry of FDCN and  $\text{Fe}^{3+}$  ions.

## Results and discussion

### Selectivity experiments of FDCN for metal ions

Thirteen common metal ions were selected to explore the fluorescence response of FDCN. Fig. 1 shows the relative fluorescence intensity of FDCN at an excitation wavelength of 335 nm and an emission wavelength of 440 nm in different metal ion solutions. In  $F/F_0$ ,  $F$ , and  $F_0$  are the fluorescence intensities of FDCN in the presence and absence of metal ions, respectively. Different metal ions caused different degrees of change in the fluorescence intensity of FDCN. The addition of  $\text{Ag}^+$ ,  $\text{Li}^+$ ,  $\text{Ba}^{2+}$ , and  $\text{Fe}^{2+}$  slightly increased the fluorescence intensity of FDCN. The fluorescence intensity of FDCN did not change significantly in the presence of  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$ . The addition of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ , or  $\text{Ba}^{2+}$  slightly attenuated the fluorescence intensity of FDCN. The fluorescence intensity was significantly reduced in the presence of  $\text{Fe}^{3+}$ , and fluorescence quenching occurred. These results show that only  $\text{Fe}^{3+}$  had a substantial fluorescence quenching effect on FDCN.

### Competition of metal ions

Most actual samples contain a variety of metal ions; therefore, it is necessary to explore the change in the selective quenching effect of FDCN on  $\text{Fe}^{3+}$  in the presence of other metal ions. Fig. 2 shows the effects of different metal ions on  $\text{Fe}^{3+}$  detection by FDCN. After adding other metal ions, the response of FDCN to  $\text{Fe}^{3+}$  did not change significantly. Also, the quenching effect was not greatly affected, and the fluorescence intensity remained

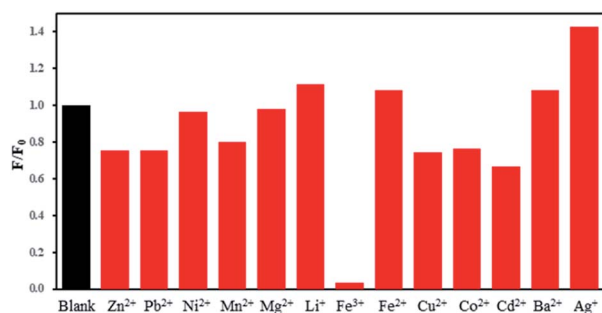


Fig. 1 Effects of different metal ions on the fluorescence intensity of FDCN.

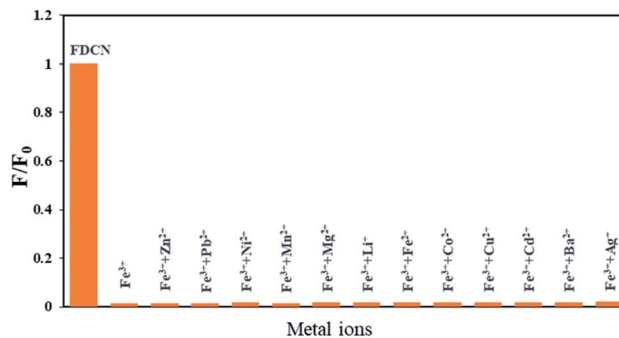


Fig. 2 Effects of different metal ions on the  $\text{Fe}^{3+}$  detection of FDCN.

unchanged. This result shows that other metal ions have little effect on the quenching of FDCN to  $\text{Fe}^{3+}$ , and their potential interference can be ignored. Most importantly, this outcome shows that FDCN had a highly selective quenching effect on the  $\text{Fe}^{3+}$  ions.

Five electrons occupy five orbitals in a spin-parallel manner in the free ionic state because the outer electron orbital of the  $\text{Fe}^{3+}$  ion has a  $3d^5$  structure, and there are five under-filled electron orbitals. When  $\text{Fe}^{3+}$  encounters FDCN, the electrons are rearranged to three d orbitals, forming six  $d^2sp^3$  hybrid orbitals by vacating two d orbitals and the outer 4s and 4p orbitals. This hybrid orbital accepts six pairs of ligand electrons. Among the ions in this experiment, only  $\text{Fe}^{3+}$  can form  $d^2sp^3$  hybrid orbitals, and the bonding affinity of  $d^2sp^3$  hybrid orbitals is the strongest in s-p hybridization. Therefore, FDCN has a high selectivity for  $\text{Fe}^{3+}$  ions.

### Fluorescence titration

Fig. 3 shows the fluorescence spectrum of FDCN with  $\text{Fe}^{3+}$  concentrations in the range of 1–500  $\mu\text{M}$ . An increase in  $\text{Fe}^{3+}$  concentration decreased the fluorescence intensity of FDCN; however, the emission wavelength did not shift. Fig. 4a shows the relationship between the fluorescence intensity change ratio ( $F/F_0$ ) of FDCN and  $\text{Fe}^{3+}$  concentration.  $F/F_0$  gradually decreased with increasing  $\text{Fe}^{3+}$  concentration. When the  $\text{Fe}^{3+}$

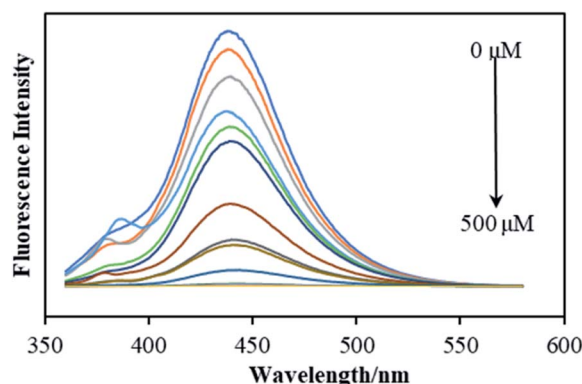


Fig. 3 Effect of  $\text{Fe}^{3+}$  concentration on the fluorescence intensity of FDCN.



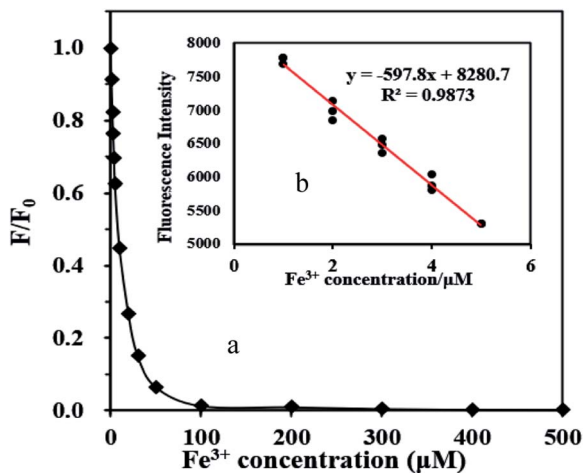


Fig. 4 Relationship between  $F/F_0$  and  $\text{Fe}^{3+}$  concentration in the range of 1–500  $\mu\text{M}$  (a), and the relationship between the fluorescence intensity and  $\text{Fe}^{3+}$  concentration (b).

concentration was 1–5  $\mu\text{M}$ , there was a good linear relationship between the fluorescence intensity and  $\text{Fe}^{3+}$  concentration as shown in Fig. 4b. When the  $\text{Fe}^{3+}$  concentration was above 50  $\mu\text{M}$ , the value of  $F/F_0$  tended to be stable as the  $\text{Fe}^{3+}$  concentration was increased further. When the  $\text{Fe}^{3+}$  concentration was above 100  $\mu\text{M}$ ,  $F/F_0$  approached 0 with increasing  $\text{Fe}^{3+}$  concentration.

### Sensitivity studies

As shown in Fig. 5, the fluorescence quenching of FDCN by  $\text{Fe}^{3+}$  conformed to the Stern–Volmer eqn (1), indicating that it was a dynamic quenching process. There was a good linear relationship between  $F_0/F$  and  $\text{Fe}^{3+}$  concentrations in the range of 1–5  $\mu\text{M}$ , and the fitted linear equation was as in eqn (5) as follows:

$$F_0/F = 0.1229x + 0.9596 \quad (R^2 = 0.9832) \quad (5)$$

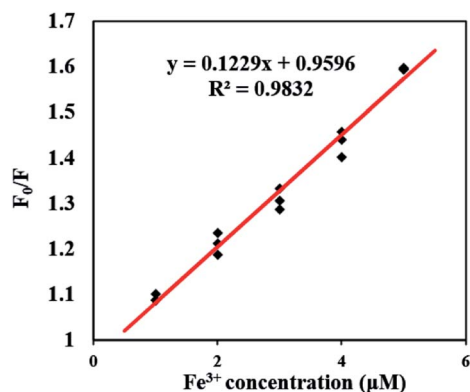


Fig. 5 Change fluorescence intensity of FDCN with the increasing  $\text{Fe}^{3+}$  concentration (1 to 5  $\mu\text{M}$ ).

The Stern–Volmer fluorescence quenching constant was 0.1229, larger than those reported by Chen *et al.* (0.0379)<sup>25</sup> and Zhang *et al.* (0.0336).<sup>24</sup> The result shows that the probe in this study has a higher sensing sensitivity to  $\text{Fe}^{3+}$  ions. The detection limit of  $\text{Fe}^{3+}$  was determined to be 0.26  $\mu\text{M}$  using the  $3s/k$  equation. The determination limit of  $\text{Fe}^{3+}$  was 0.77  $\mu\text{M}$  using the  $6s/k$  equation. The symbol  $s$  is the standard deviation of the blank samples for 10 times,  $k$  is the slope of the line mentioned in Fig. 4b.<sup>12,34</sup> As shown in Table 1, the detection limit of this study reached a low level, far below the limit of  $\text{Fe}^{3+}$  concentration in drinking water of 5.357  $\mu\text{M}$  compared with other research results.<sup>32</sup> Therefore, the fluorescence sensor can detect  $\text{Fe}^{3+}$  in drinking water rapidly.

Bozkurt *et al.* showed that when the  $\text{Fe}^{3+}$  concentration reached 20 mM, the AMC fluorescence intensity decreased by approximately 40%.<sup>12</sup> In this study, the fluorescence quenching effect of FDCN exceeded 90% when the  $\text{Fe}^{3+}$  concentration reached 100  $\mu\text{M}$ . It was proven that the detection response-ability of FDCN to  $\text{Fe}^{3+}$  was higher than that of AMC. The Stern–Volmer quenching constant of AMC to  $\text{Fe}^{3+}$  was 0.0596,<sup>12</sup> while the quenching constant of FDCN was 0.1229. This outcome also indicates that the sensitivity of FDCN to detect  $\text{Fe}^{3+}$  was higher than that of AMC. The unreacted carboxyl groups of DCN may have influenced this result, and newly formed amide bonds in FDCN greatly enhance the selective quenching effect of FDCN on  $\text{Fe}^{3+}$  ions.

### Stoichiometry determination

A Job's plot analysis was conducted to determine the association stoichiometry between FDCN and  $\text{Fe}^{3+}$ .<sup>12</sup> Eqn (2) showed a maximum value when the molar fraction based on eqn (3) was approximately 0.5, and the molar ratio between FDCN and  $\text{Fe}^{3+}$  ions was close to 1 : 1, indicating that the complexation stoichiometry of FDCN to  $\text{Fe}^{3+}$  ions was 1 : 1 (Fig. 6).

### Association constant determination with Benesi–Hildebrand equation

The Benesi–Hildebrand equation was used to calculate the association constant ( $K_{ac}$ ) when the binding stoichiometry for FDCN and  $\text{Fe}^{3+}$  was 1. Linear fitting was performed with  $1/[\text{Fe}^{3+}]$  as the abscissa and  $1/(F_0 - F)$  as the ordinate (Fig. 7). The fitting equation was found to be eqn (6) as follows:

$$y = 1.3462 \times 10^{-9}x + 4.3519 \times 10^{-5} \quad (R^2 = 0.9856) \quad (6)$$

Table 1 Comparison of detection performance of nanocellulose-based fluorescence sensor for  $\text{Fe}^{3+}$

Fluorescent sensor	$K_{sv} (\text{M}^{-1})$	$K_{ac} (\text{M}^{-1})$	LOD ( $\mu\text{M}$ )	Ref.
Py-CNC	$3.36 \times 10^4$	$3.68 \times 10^4$	1.0	24
CNF-DA	—	—	0.5	35
N-CDs	$6.68 \times 10^3$	—	1.14	36
FDCN	$1.229 \times 10^5$	$3.23 \times 10^4$	0.26	This study



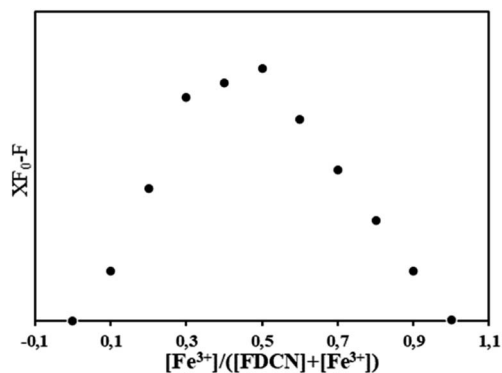


Fig. 6 Job's plot of FDCN with  $\text{Fe}^{3+}$  in water.

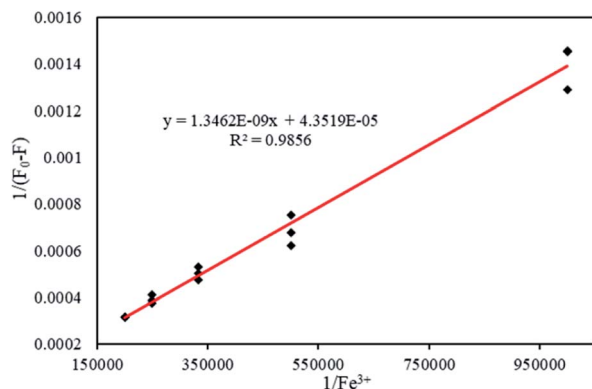


Fig. 7 Benesi-Hildebrand plot based on a 1 : 1 association stoichiometry between FDCN and  $\text{Fe}^{3+}$ .

The association constant was  $3.23 \times 10^4 \text{ M}^{-1}$  calculated from the slope and intercept of the line. This result was higher than those reported by Zhang *et al.* ( $1.6 \times 10^4 \text{ M}^{-1}$ )<sup>32</sup> and Chen *et al.* ( $2.2 \times 10^4 \text{ M}^{-1}$ ),<sup>27</sup> indicating that FDCN could better recognize  $\text{Fe}^{3+}$  ions.

### The mechanism of complexation between the FDCN and $\text{Fe}^{3+}$ ions

The mechanism of complexation between FDCN and  $\text{Fe}^{3+}$  was determined using FTIR spectroscopy.  $\text{Fe}^{3+}$  was added to the FDCN dispersion and stirred for 5 min. After centrifugation, the FDCN/ $\text{Fe}^{3+}$  complex was obtained from the precipitate by freeze-drying and measured using a Fourier transform infrared spectrometer. Fig. 8 shows the FTIR spectra of AMC, DCN, FDCN, and FDCN/ $\text{Fe}^{3+}$  complexes. The analysis of FTIR spectra was referred mainly the Sadtler Handbook of Infrared Spectra.<sup>37</sup> After AMC was grafted onto DCN, the grafted product FDCN showed a characteristic peak of  $\text{C}=\text{C}$  at  $1618 \text{ cm}^{-1}$ , corresponding to the carbon-carbon double bond between position 3 and 4 of coumarin lactone.<sup>38</sup> An apparent characteristic peak was detected at  $1529 \text{ cm}^{-1}$ , corresponding to the combination of N-H deformation and C-N stretching vibration of the newly formed amido groups between the carboxyl groups of DCN and the amino groups of AMC.<sup>37</sup> In addition, a broad band appeared

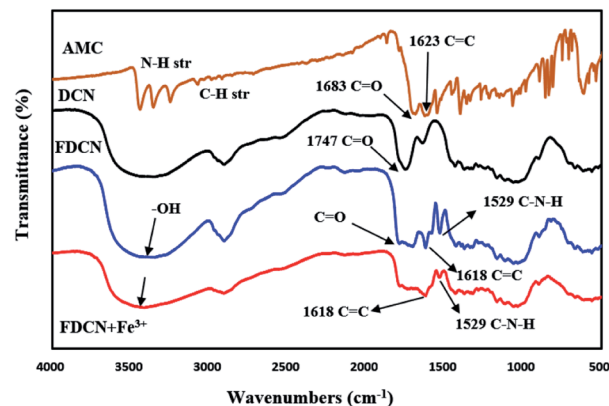


Fig. 8 FTIR spectrum of AMC, DCN, FDCN, and FDCN +  $\text{Fe}^{3+}$ .

between  $1700$  and  $1786 \text{ cm}^{-1}$  of FDCN FTIR, corresponding to the overlapping peaks formed by the carbonyl groups of DCN, amide, and AMC.<sup>37</sup> Thus, it can be deduced that AMC was grafted onto DCN through an amide bond. Owing to the amidation reaction of the amino group, the electron-pushing ability of the amino group at the position 7 was weakened, and the fluorescence emission of FDCN was blue-shifted and weakened relative to AMC (Fig. 9).

After adding  $\text{Fe}^{3+}$  ions, the stretching vibration of the hydroxyl groups ( $-\text{OH}$ ) at  $3420 \text{ cm}^{-1}$  changed from a strong and sharp absorption band to a mild and broad band. This result shows that the hydroxyl groups were involved in the complexation with  $\text{Fe}^{3+}$  ions.<sup>24</sup> The characteristic peak of the amide bonds at  $1529 \text{ cm}^{-1}$  was also weakened from a strong and sharp absorption peak to a weak peak, indicating that the amide bonds were also involved in the complexation with  $\text{Fe}^{3+}$  ions (N-Fe bonds).<sup>35</sup> The characteristic broad band of carbonyl at  $1700$ – $1786 \text{ cm}^{-1}$  also changed significantly, indicating that carbonyl groups are also important functional groups for complexation with  $\text{Fe}^{3+}$  ions.<sup>35</sup> According to the results, the fluorescence quenching mechanism of  $\text{Fe}^{3+}$  on FDCN was determined (Fig. 10).

The fluorescence emission mechanism of AMC involves intramolecular charge transfer (ICT).<sup>39,40</sup> After  $\text{Fe}^{3+}$  was added to

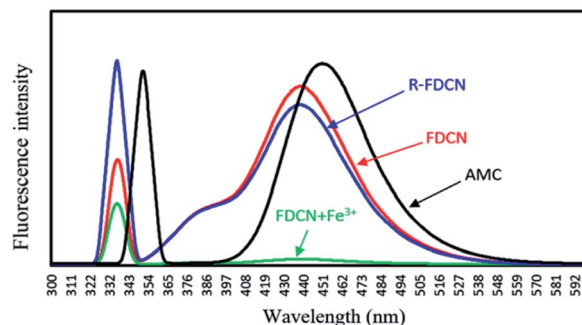


Fig. 9 Fluorescence spectra of AMC, FDCN, FDCN +  $\text{Fe}^{3+}$  and R-FDCN (FDCN +  $\text{Fe}^{3+}$  + EDTA) (AMC concentration was  $2 \times 10^{-4} \text{ M}$ , corresponding to the grafting concentration of AMC on FDCN).



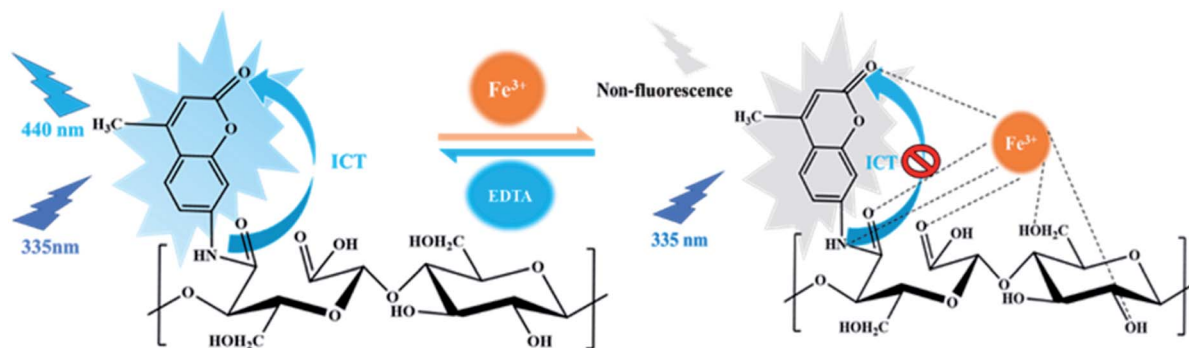


Fig. 10 The mechanism of complexation between the FDCN and  $\text{Fe}^{3+}$  ions.

the FDCN dispersion solution, the  $\text{Fe}^{3+}$  ions complexed with the amide groups and coumarin lactone carbonyl of FDCN and carbonyl and hydroxyl groups of DCN to form a coordination compound, which prevented the ICT process and led to fluorescence quenching of FDCN. After adding EDTA to the mixture, because the binding affinity of EDTA was greater than that of FDCN, the  $\text{Fe}^{3+}$  ions were removed by EDTA to form a coordination compound, and the ICT process of FDCN was restored. The fluorescence emission capability of the chemosensor was also restored (Fig. 9 R-FDCN).

## Conclusions

A highly selective and sensitive fluorescent chemosensor was synthesized for  $\text{Fe}^{3+}$  based on dicarboxylic cellulose nanocrystals and 7-amino-4-methylcoumarin. The detection mechanism of the chemosensor for  $\text{Fe}^{3+}$  was evaluated using FTIR spectroscopy. The coordination between  $\text{Fe}^{3+}$  and the amide groups, the carboxyl and hydroxyl groups on the surface of FDCN, and the carbonyl of coumarin lactones to form FDCN/ $\text{Fe}^{3+}$  complexes prevented the ICT process and led to the fluorescence quenching of FDCN. The detection limit of FDCN for  $\text{Fe}^{3+}$  was  $0.26 \mu\text{M}$ , and the selectivity and sensitivity to  $\text{Fe}^{3+}$  were not affected by the metal ions  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Li}^{+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ag}^{+}$  and  $\text{Fe}^{2+}$ . Job's plot analysis showed the association stoichiometry between FDCN and  $\text{Fe}^{3+}$  to be 1 : 1 and an association constant of  $3.23 \times 10^4 \text{ M}^{-1}$  calculated by the Benesi-Hilderbrand equation. The high hydrophilicity, low cytotoxicity, high sensitivity, and selectivity of FDCN for  $\text{Fe}^{3+}$  qualified the chemosensor for  $\text{Fe}^{3+}$  trace detection in drinking water and biology.

## Conflicts of interest

There are no conflicts to declare.

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