



# Polyhydic polymer-functionalized fluorescent probe with enhanced aqueous solubility and specific ion recognition: A test strips-based fluorimetric strategy for the rapid and visual detection of Fe<sup>3+</sup> ions

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## ABSTRACT

A polyhydic polymer-functionalized probe with enhanced aqueous solubility was designed initially by coupling 1-pyrenecarboxyaldehyde (Pyr) onto poly(vinyl alcohol) (PVA) via the one-step condensation reaction. Polyhydic PVA polymer chains could facilitate the Pyr fluorophore with largely improved aqueous solubility and especially strong cyan fluorescence. Importantly, the fluorescence of the PVA-Pyr probes could thereby be quenched specifically by Fe<sup>3+</sup> ions through the strong PVA-Fe<sup>3+</sup> interaction triggering the polymeric probe aggregation. Furthermore, a test strips-based fluorimetric method was developed with the stable and uniform probe distribution by taking advantage of the unique film-forming ability and the depression capacity of “coffee-stain” effects of PVA matrix. The as-developed test strips could allow for the rapid and visual detections of Fe<sup>3+</sup> ions simply by a dipping way, showing a linear concentration range of 5.00–300 μM, with the detection limit of 0.73 μM. Moreover, the proposed method was applied to the evaluation of Fe<sup>3+</sup> ions in natural water samples, showing the analysis performances better or comparable to those of current detection techniques. This test strips-based fluorimetric strategy promises the extensive applications for the rapid on-site monitoring of Fe<sup>3+</sup> ions in environmental water and the outdoor finding of the potential iron mines.

## 1. Introduction

Recent years have witnessed the increasing attentions concentrated on the monitoring of iron levels in environmental water samples for the iron contamination and miner exploration [1]. Although iron element plays a vital role in human life activities, excessive Fe<sup>3+</sup> ions in body, which maybe accumulated from the over uptake of Fe<sup>3+</sup> ions from the environmental water and food, may exert some adverse effects on human physiologic systems [2–4]. Therefore, the quantitative evaluation of Fe<sup>3+</sup> ions in environmental water is highly important for preventing any Fe<sup>3+</sup>-induced public health hazard. Also, the development of a rapid, sensitive, and onsite applicable detection method for exploring Fe<sup>3+</sup> ions may be of significant interest in the outdoor finding of the potential iron mines. Up to date, many analysis methods are available for the determination of Fe<sup>3+</sup> ions, such as inductively

coupled plasma mass spectrometry (ICP-MS), absorption spectrometry, and reflection X-ray fluorimetry [5–7]. However, most of these methods can suffer from rapid detection inability, complex sample pre-treatment, and bulky infrastructure requirement, which can render their ineffectiveness for the applications of in-field iron monitoring. Therefore, a facile, rapid, economical, and portable analysis method is highly desired for the onsite monitoring of Fe<sup>3+</sup> ions in environmental water and especially for the iron miner exploration.

It is well established that the fluorimetric methods with some fluorescent probes are the sensitive analysis strategies [8–15], which are especially applied for the detection of Fe<sup>3+</sup> ions [8–12]. Since the fluorimetric performances may largely depend on the probes, which can translate the recognition information into the fluorescence signals, a number of fluorescent probes have been synthesized for the selective detection of Fe<sup>3+</sup> ions. Nevertheless, most of these reported fluorescent

*Abbreviations:* Pyr, 1-pyrenecarboxyaldehyde; PVA, poly(vinyl alcohol); ICP-MS, inductively coupled plasma mass spectrometry; FTIR, fourier transform infrared; SEM, field emission scanning electron microscope; DMSO, dimethyl sulfoxide; HDS, hexadecyltrimethoxysilane; APS, aminopropyltriethoxysilane; SEM, field emission scanning electron microscope; FTIR, fourier transform infrared

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probes (i.e., organic chromophores and quantum dots) [8,9,11] are poisonous, biologically incompatible, and water-insoluble, which may greatly limit the detection of  $\text{Fe}^{3+}$  ions. Moreover, some probes of organic small molecules can generally encounter with evident drawbacks such as the synthetic difficulty, time-consuming response, and low water solubility for the examination of aqueous samples, which can restrict the practically aqueous applications on a large scale. Therefore, the development of highly selective, sensitive, and water-dispersible fluorescent probes is desired for the detection of  $\text{Fe}^{3+}$  ions. As a result, many efforts have been devoted to the development of polymer-based fluorescent probes due to they can display several important advantages over the common organic fluorescent probes [16–19]. For instance, the fluorescent probes of recognition units-coupled polymers can be easily included in the devices toward the diverse and functional chemoprobes [16,19]. Moreover, it is well recognized that poly(vinyl alcohol) (PVA) as a common polyhydric polymer has concentrated many efforts of applications due to that it is biodegradable, water-soluble, inexpensive, and film forming [20–23]. On the other hand, the pyrene moieties feature the high fluorescence quantum yields, chemical stability, and long fluorescence lifetime, so that they have been widely applied as the fluorophores in the recognitions of a variety of chemical species [24–27]. Considerably low aqueous solubility of pyrene molecules or moieties might limit the wide applications, although they can display the monomer-excimer dual fluorescence [28]. Herein, the introduction of PVA with hydroxyl groups of PVA chains should improve the aqueous solubility of pyrene. Importantly, the combination of PVA and pyrene should enjoy the synergetic advantages of PVA and pyrene for the specific  $\text{Fe}^{3+}$  ions recognition.

In the present work, we have reported a facile and efficient synthesis method to prepare polyhydric polymer-functionalized fluorescent probe for the detection of  $\text{Fe}^{3+}$  ions in environmental water samples. Herein, 1-pyrenecarboxyaldehyde (Pyr) was chosen to be covalently bound onto PVA chains through the acetal reaction yielding the PVA-loaded pyrene (PVA-Pyr) probes, showing dramatically improved aqueous solubility and especially strong cyan fluorescence. More importantly, the fluorescence of the resulted fluorescent probes could be thus selectively quenched by  $\text{Fe}^{3+}$  ions, presumably resulting from the probe aggregation induced by the specific intermolecular hydrogen bonding between  $\text{Fe}^{3+}$  ions and the hydroxyl groups of PVA chains [29–31]. Furthermore, the PVA-Pyr probes were coated onto the test strips by taking advantage of the outstanding film-forming ability of PVA. Interestingly, a stable and uniform distribution of fluorescent probes on test strips could also be expected by introducing the host PVA matrix to depress the formidable “coffee-stain” effects generally occurred in test strips [32]. Subsequently, a test strips-based fluorimetric method was developed for the rapid and visual detection of  $\text{Fe}^{3+}$  ions in the environmental water, showing high detection sensitivity and selectivity.

## 2. Materials and methods

### 2.1. Materials and instrumentation

Poly(vinyl alcohol) (PVA, MW 89,000), dimethyl sulfoxide (DMSO), p-toluenesulfonic acid, 1-pyrenecarboxyaldehyde (Pyr), and Whatman filters used for test strips were purchased from Sigma-Aldrich (Beijing, China). Hexadecyltrimethoxysilane (HDS) and aminopropyltriethoxysilane (APS) were bought from Sinopharm Chemical Reagent Co. (China). All other reagents were of analytical grade. Deionized water ( $> 18 \text{ M}\Omega$ ) was supplied from an Ultra-pure water system (Pall, USA). The environmental water samples (wastewater, river water, seawater, drinking water, and rainwater) were applied to spike  $\text{Fe}^{3+}$  ions of different concentrations.

The fluorescence measurements were conducted using the fluorescence spectrophotometer (F-7000, Hitachi, Japan) operated at an excitation wavelength at 345 nm, with both excitation and emission

slit widths of 5.0 nm. The photographs of different materials and reaction products were recorded under UV light at 365 nm. Fourier transform infrared (FTIR) spectra were obtained by FTIR spectrophotometer (Thermo Nicolet Nexus 470FT, USA). UV-vis spectrophotometer (Shimadzu, UV-3600, Japan) and scanning electronic microscopy (SEM, Hitachi E-1010, Japan) were separately applied for the characterization of different materials or products. The wastewater and river water samples were comparably analyzed in the laboratory with the inductively coupled plasma-mass spectrometry (ICP-MS) of Agilent 7500ce (Agilent Technologies, Waldbronn, Germany).

### 2.2. Synthesis of polyhydric polymer-functionalized fluorescent probes

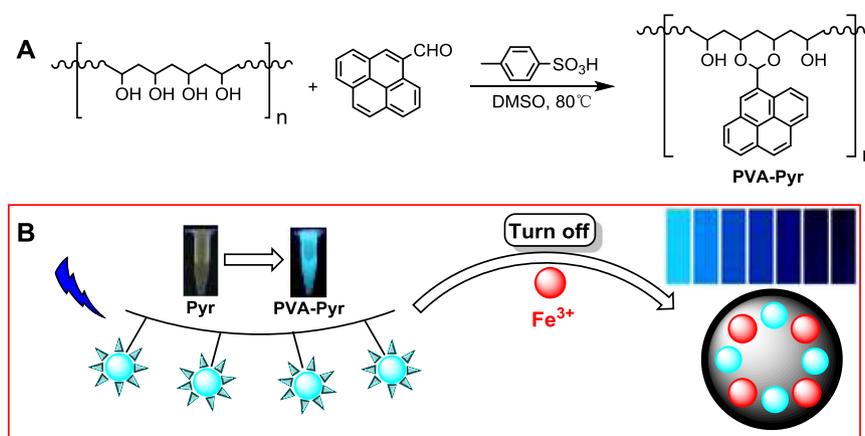
An aliquot of PVA ( $40.0 \text{ mg mL}^{-1}$ ) and Pyr ( $4.34 \mu\text{M}$ ) were mixed in DMSO of 50 mL. Then, p-toluenesulfonic acid ( $5.80 \mu\text{M}$ ) was dropwise added into the mixture to react at  $80 \text{ }^\circ\text{C}$  for 6 h. After being cooled down to room temperature, the mixture was poured into  $\text{CH}_3\text{OH}$  (100 mL) to be precipitated, where the unbound Pyr was separated out. The so purified products of the fluorescent PVA-Pyr probes containing 1.85% Pyr and 98.15% PVA were further washed three times with  $\text{CH}_3\text{OH}$  (50 mL) to be dried under a vacuum (77% yield based on PVA).

### 2.3. Preparation of polyhydric polymer-functionalized fluorescent test strips

The preparation procedure of the polyhydric polymer-functionalized fluorescent test strips for probing  $\text{Fe}^{3+}$  ions were conducted simply by following the procedure reported previously in our group [33]. Typically, the filters papers were first cut into the slices of test strips ( $10 \text{ mm} \times 10 \text{ mm}$ ) and then soaked into the above PVA-Pyr probes ( $5.00 \text{ mg L}^{-1}$ ) for 10 min. After that, the test strips were immediately placed onto the HDS-modified super-hydrophobic patterns to be dried in vacuum for 20 min. Furthermore, the resulted test strips were immersed into APS solutions for 30 s for the hydrophilic treatments. Subsequently, the APS-treated test strips were again placed onto the super-hydrophobic patterns to be dried in vacuum for 10 min to be dried and stored in dark for future usage.

### 2.4. Fluorimetric measurements of $\text{Fe}^{3+}$ ions

The optimization of analysis conditions for the test strips-based fluorimetric detections of  $\text{Fe}^{3+}$  ions were conducted separately using different amounts of PVA-Pyr, pH values, ion strengths, and reaction time. Typically, an aliquot of PVA-Pyr probes was introduced into the  $\text{Fe}^{3+}$  solutions. The  $\text{Fe}^{3+}$ -quenched fluorescence intensities of the probes on test strips were recorded by a fluorescence spectrometer with a holder for the measurements solid-state fluorescence. The quenching efficiencies of PVA-Pyr probes by ions were calculated according to the following equation: quenching efficiencies =  $(F_0 - F) / F_0$ , where  $F_0$  and  $F$  refer to the fluorescence intensities of PVA-Pyr ( $\lambda_{\text{ex}} = 345 \text{ nm}$ ) in the absence and presence of ions. The selective fluorimetric analysis with centrifuge tubes was performed for  $\text{Fe}^{3+}$  ions, together with the possibly interferential ions ( $200 \mu\text{M}$ ) as the control tests, including  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  ions. Under the optimized conditions, the developed test strips-based fluorimetric method with polyhydric polymer-functionalized fluorescent probes were subsequently applied for the detection of  $\text{Fe}^{3+}$  ions of different concentrations spiked in wastewater samples (0, 0.10, 0.50, 1.00, 5.00, 10, 25, 50, 75, 100, 125, 150, 175, 200, 300  $\mu\text{M}$ ). The calibration curves of the fluorimetric detections for  $\text{Fe}^{3+}$  ions were obtained, with the analysis results further compared with those obtained by the classic ICP-MS method.



**Fig. 1.** Schematic illustration of (A) the synthesis reaction for the fluorescent PVA-Pyr probes and (B) the “turn-off” fluorescence of PVA-Pyr caused by the selective PVA-Fe<sup>3+</sup> interaction towards the probe aggregation for the test strips-based fluorimetric analysis of Fe<sup>3+</sup> ions.

### 3. Results and discussion

#### 3.1. Synthesis of polyhydric polymer-functionalized fluorescent probes for the fluorimetric Fe<sup>3+</sup> analysis

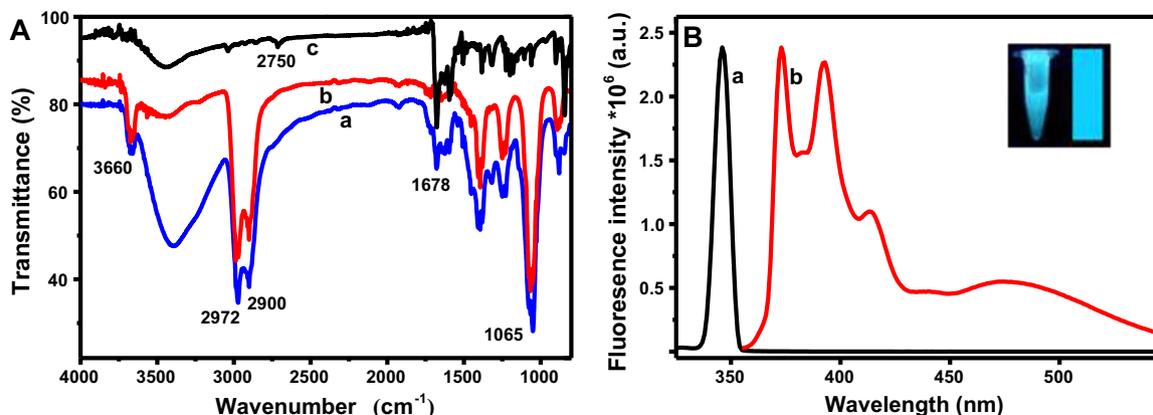
The PVA-loaded pyrene (PVA-Pyr) probes were synthesized by the p-toluenesulfonic acid-catalyzed reaction procedure, as schematically shown in Fig. 1A. A facile one-step condensation reaction between PVA and Pyr occurred to yield the PVA-Pyr probes consisting of 98.15% hosting PVA chains and 1.85% pyrene moieties, showing the bright cyan fluorescence in aqueous system. As can be seen from Fig. 1B, when Fe<sup>3+</sup> ions were introduced, they would specially bind with the hydroxyl groups of PVA chains through the strong intermolecular hydrogen bonds [29–31]. A conformational change in the structure of the PVA host would thus occur to further cause the aggregations of PVA-Pyr probes with the hydrophobic pyrene encapsulated inside the hydrophilic PVA chains. As a result, the pyrene fluorescence of the polymeric probes was quenched. Such a procedure was also described elsewhere for the interactions between amine-derivatized polyethyleneimine polymer and Sr<sup>2+</sup> ions [34]. Subsequently, the developed fluorescent probes were coated onto the test strips by use of the unique film-forming ability PVA, which could additionally serve as a host matrix to achieve the uniform redistribution of fluorescent probes by depressing the formidable “coffee-stain” effects generally occurred in the fabrication of test strips [33]. A test strips-based fluorimetric method was thereby developed for probing Fe<sup>3+</sup> ions in environmental water samples.

The composition of the PVA-Pyr probes was characterized by the FTIR spectroscopy, taking the precursors of Pyr and PVA as the

controls (Fig. 2A). One can find that the spectra of the PVA-Pyr probes (curve a) can include the typical characteristic peaks of native PVA (1065 cm<sup>-1</sup>, 2900 cm<sup>-1</sup>, 2972 cm<sup>-1</sup>, and 3660 cm<sup>-1</sup>) (curve b) and Pyr (1678 cm<sup>-1</sup>) (curve c). Especially the stretching vibration peak at 2750 cm<sup>-1</sup> of aldehyde C-H of Pyr (curve c) would disappear upon the formation of PVA-Pyr probes (curve a), thus confirming the conjugated formation of PVA-Pyr probes. Moreover, it was observed from Fig. 2B that the PVA-Pyr probes give considerably strong cyan photoluminescence both in water and on the test strips under the laser irradiation, as shown in the photographs inserted. When excited at 345 nm (curve a), the PVA-Pyr probes show very strong photoluminescence in the range of 355–550 nm (curve b), with the monomer peaks ranging from 355 to 410 nm and from 450 to 550 nm, respectively.

Moreover, the PVA-Pyr probes were prepared by different batch productions, which robustness and variability were tested with the results shown in Fig. 3. One can note that the obtained PVA-Pyr probes display no significant change in the fluorescent intensities (Fig. 3A). Also, they could be stored in dark with the fluorescence property well sustained over 12 months (Fig. 3B).

Fig. 4A shows the fluorescence spectra of PVA-Pyr probes in the presence and absence of Fe<sup>3+</sup> ions, taking native Pyr and PVA alone as the controls. One can find that the fluorescent probes can display the strong monomer emissions both at 376 and 396 nm (curve a). Notably, Pyr in water could display a strong excimer emission at 472 nm, which would almost disappear after the conjugate formation of PVA-Pyr probes. Furthermore, the PVA-Pyr probes could present the largely improved aqueous solubility, in contrast to Pyr that might be aggregated in water, as illustrated in the corresponding photographs



**Fig. 2.** (A) FT-IR spectra of (a) PVA-Pyr probes, (b) Pyr, and (c) PVA powders; (B) Fluorescence spectra of (a) excitation ( $\lambda_{\text{ex}}=345$  nm) and (b) emission (insert: the photographs of PVA-Pyr probes in water and on the test strips under UV light).

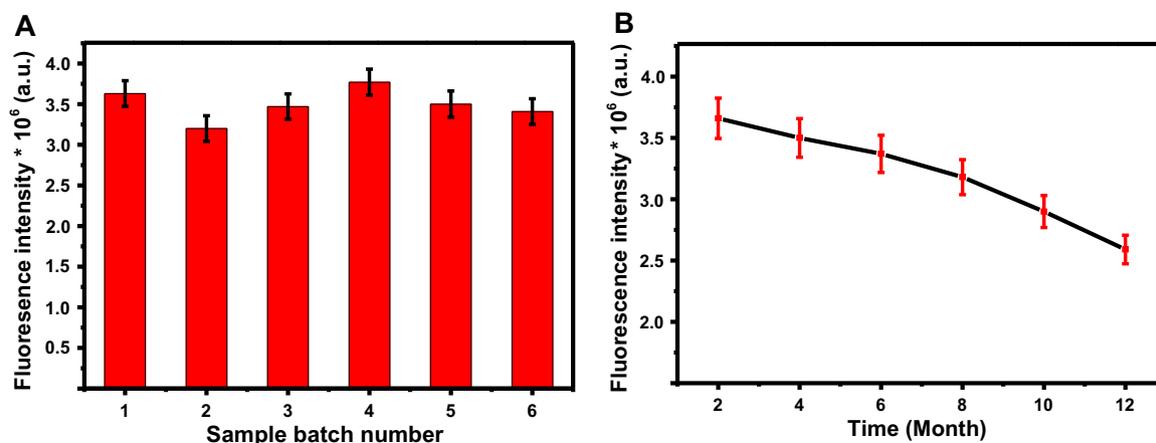


Fig. 3. Fluorescence intensities of the PVA-Pyr probes (A) prepared by different batch productions and (B) stored over different time intervals.

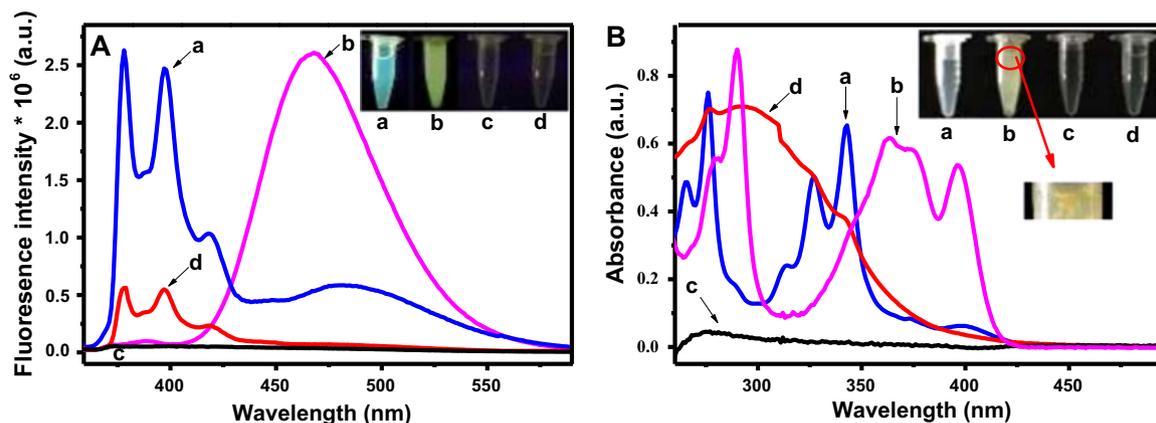


Fig. 4. (A) Fluorescence spectra of (a) PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ), (b) Pyr ( $0.020 \text{ mg L}^{-1}$ ), (c) PVA, (d) PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ) with  $\text{Fe}^{3+}$  ions ( $200 \mu\text{M}$ ) in water; (B) UV-vis spectra of (a) PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ), (b) Pyr ( $0.020 \text{ mg L}^{-1}$ ), (c) PVA, (d) PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ) with  $\text{Fe}^{3+}$  ions ( $200 \mu\text{M}$ ) in water (insert: the corresponding photographs).

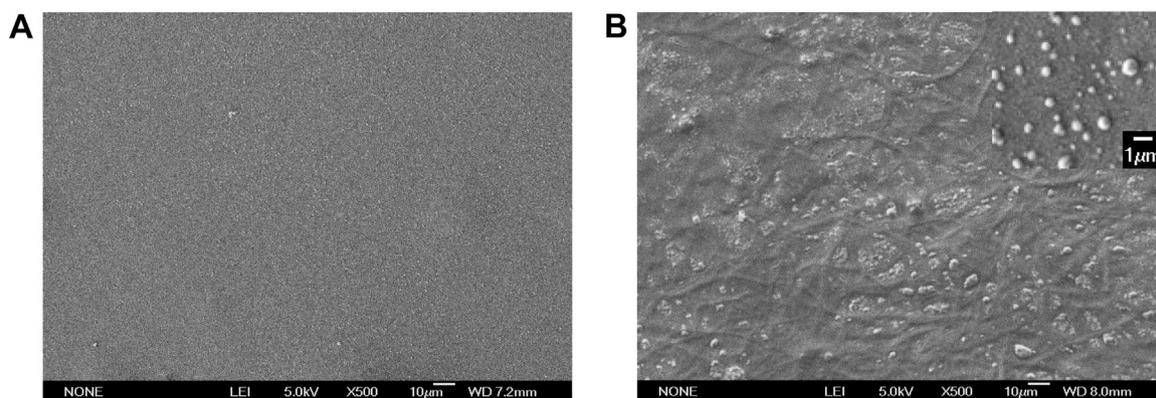
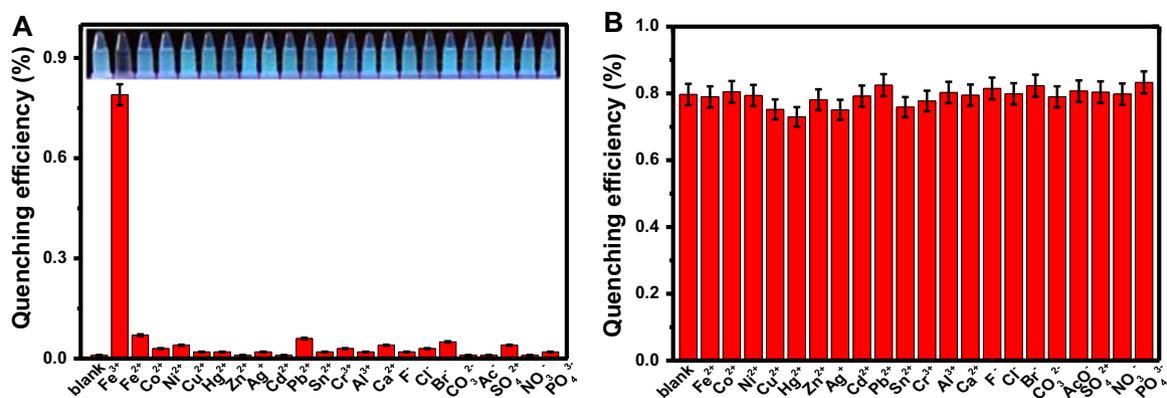


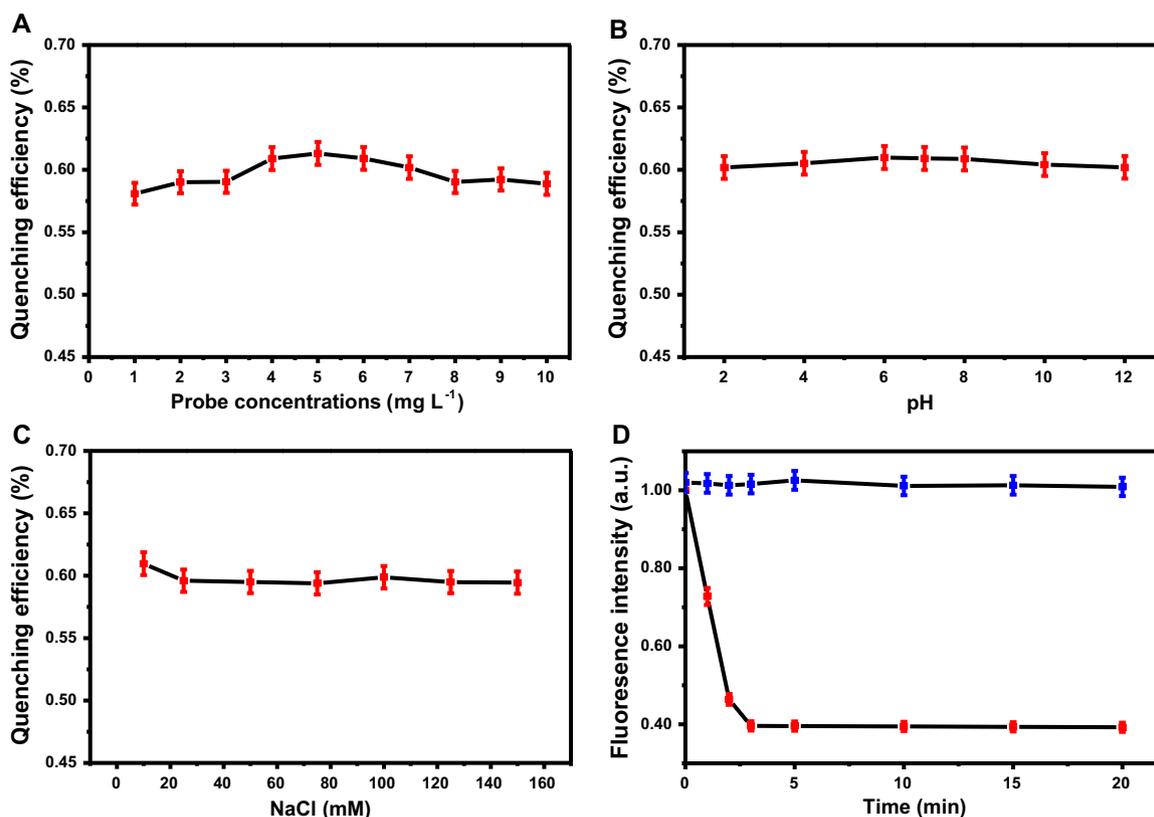
Fig. 5. SEM images of PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ) (A) before and (B) after the addition of  $\text{Fe}^{3+}$  ions ( $0.20 \text{ mM}$ ) (insert: the amplified view).

inserted in Fig. 4. More importantly, the fluorescence intensities of the PVA-Pyr probes could be dramatically quenched upon the addition  $\text{Fe}^{3+}$  ions (curve d). Herein,  $\text{Fe}^{3+}$  ions would specially bind with the hydroxyl groups of PVA chains through the strong intermolecular hydrogen bonds [29–31], thus leading to the aggregation of the PVA-Pyr probes towards the fluorescence quenching as aforementioned. Moreover, UV-vis absorption spectra of PVA-Pyr probes in water were measured with and without the additions of  $\text{Fe}^{3+}$  ions, taking native Pyr and PVA alone as the controls (Fig. 4B). It was discovered that the PVA-Pyr probes could exhibit the absorption peaks in the 232–340 nm region (curve a). Compared to the typical absorption peaks of Pyr alone (curve b), however, they displayed apparently a blue shift of

about 60 nm, indicating the covalent formation of the polyhydric polymer-based fluorescent probes. Remarkably, once the selective interaction between the PVA-Pyr probes and  $\text{Fe}^{3+}$  ions took place, a significant change in the absorption spectra was observed showing a new broad band over the region in which the original pyrene absorption bands were emerged together (curve d). Of note, the Pyr fluorophore could display the poor aqueous solubility, as apparently manifested in the photographs with the amplified view (Fig. 4B, insert). In contrast, greatly improved aqueous solubility was obtained for the PVA-Pyr probes because of the introduction of hydrophilic PVA chains, so that the detection of  $\text{Fe}^{3+}$  ions in water media could be expected.



**Fig. 6.** (A) Fluorescent responses of PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ) to different ions ( $200 \mu\text{M}$ ) alone (inset: the corresponding photographs under UV light); (B) fluorescence quenching efficiencies of PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ) for  $\text{Fe}^{3+}$  ions separately co-existing other ions indicated ( $200 \mu\text{M}$ ). The error bars represent the standard deviations of three replicated measurements.

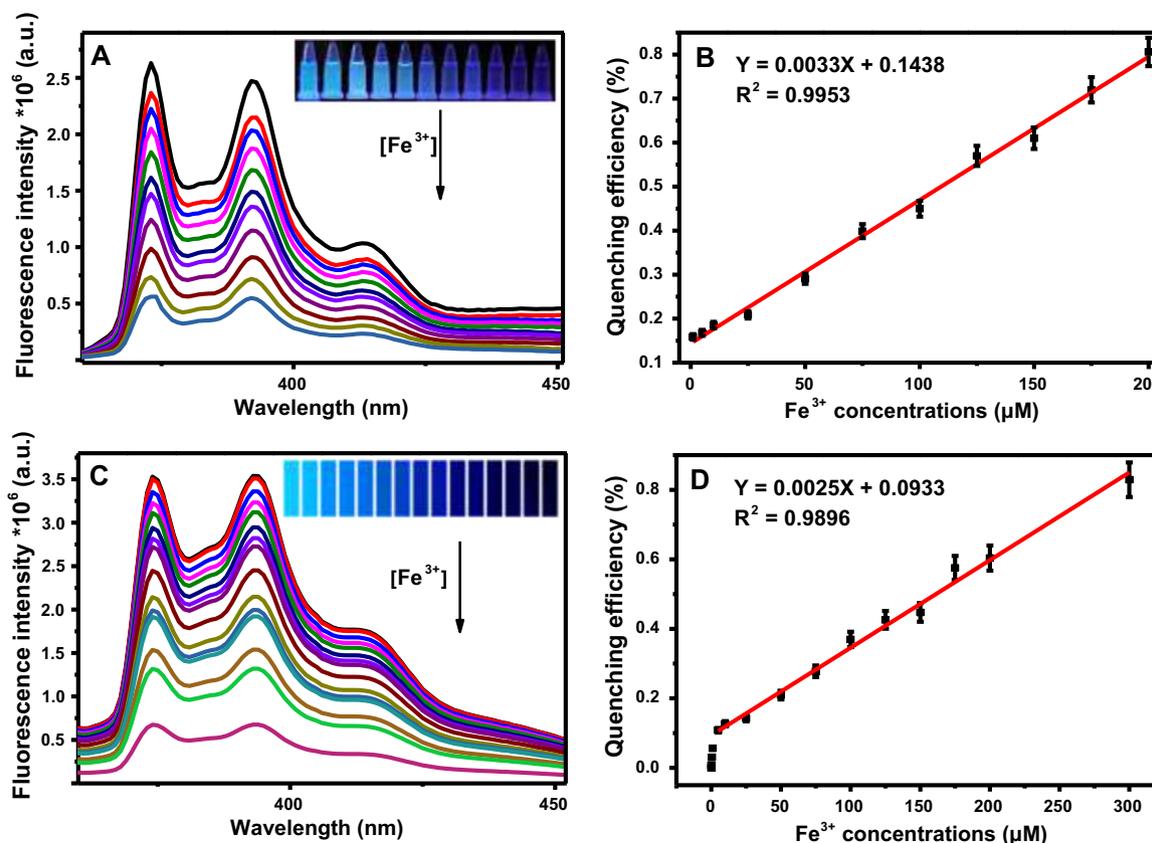


**Fig. 7.** Optimization of the detection conditions for the test strips-based fluorometric method with the fluorescence intensities depending on (A) the PVA-Pyr amounts; (B) pH values; (C) ion strengths of different NaCl concentrations; and (D) reaction time of which the fluorescence intensities of PVA-Pyr probes were recorded in (a) absence and (b) presence of  $\text{Fe}^{3+}$  ions ( $200 \mu\text{M}$ ).

Furthermore, scanning electronic microscopy (SEM) images were performed to comparably investigate the topological structures of the PVA-Pyr probes in the absence and presence of  $\text{Fe}^{3+}$  ions (Fig. 5). Again, it was found that the PVA-Pyr probes could be well monodispersed in the aqueous media (Fig. 5A), resulting from the carriers of hydrophilic PVA chains. Fig. 5B manifests that the addition of  $\text{Fe}^{3+}$  ions could cause the polyhydric polymer-functionalized fluorescent probes to largely aggregate through the PVA- $\text{Fe}^{3+}$  interaction as mentioned in Fig. 1B, which should be responsible for the quenching of their fluorescence intensities.

### 3.2. Selective responses of polyhydric polymer-functionalized fluorescent probes to $\text{Fe}^{3+}$ ions

The selective responses of the PVA-Pyr probes to  $\text{Fe}^{3+}$  ions were assessed with the fluorescence quenching efficiencies, in comparison to those of 22 kinds of common ions that might possibly co-exist (Fig. 6). As shown in Fig. 6A, the fluorescence of PVA-Pyr probes could be obviously quenched by  $\text{Fe}^{3+}$  ions, whereas no significant change in the fluorescence intensity of the probes occurred for other kinds of ions alone tested separately under the same conditions, as more clearly manifested in the corresponding photographs (inset). Furthermore, the polyhydric polymer-functionalized fluorescent probes could present basically the same responses to  $\text{Fe}^{3+}$  ions in the separately competitive co-existence of the tested ions (Fig. 6B). The data imply that the



**Fig. 8.** (A) Fluorescence spectra of PVA-Pyr probes ( $1.00 \text{ mg L}^{-1}$ ) in the presence of different concentrations of  $\text{Fe}^{3+}$  ions spiked in wastewater samples ( $0 - 200 \text{ }\mu\text{M}$ ); (B) the relationship between the fluorescence quenching efficiencies versus the concentrations of  $\text{Fe}^{3+}$  ions; (C) fluorescence spectra of the test strips-based fluorimetric responses to  $\text{Fe}^{3+}$  ions of different concentrations spiked in wastewater samples ( $0 - 300 \text{ }\mu\text{M}$ ) (insert: the corresponding photographs of the developed test strips for  $\text{Fe}^{3+}$  ions under UV light as the standard colorimetric panel); (D) the relationship between the quenching efficiencies versus the concentrations of  $\text{Fe}^{3+}$  ions in wastewater samples, where the solid-state fluorescent intensities of the fluorescent test strips were measured at  $\lambda_{\text{em}} = 392 \text{ nm}$ .

**Table 1**

Comparison of analysis performances of the developed fluorimetric method with polymeric probes with the common analysis methods with other fluorescent probes for the determination of  $\text{Fe}^{3+}$  ions.

| Fluorescent probe       | Detection limit ( $\mu\text{M}$ ) | Linear range ( $\mu\text{M}$ ) | Refs.     |
|-------------------------|-----------------------------------|--------------------------------|-----------|
| Graphene Qdots          | 7.22                              | 0–80                           | [8]       |
| Benzimidazolium probes  | 2.80                              | 350–2700                       | [9]       |
| Au nanoclusters         | 3.50                              | 5.0–1280                       | [10]      |
| Metal-organic framework | 0.90                              | 3.0–200                        | [11]      |
| Polymeric probes        | 0.73                              | 5.0–300                        | This work |

**Table 2**

Comparison of analysis results for  $\text{Fe}^{3+}$  ions in the wastewater and river water samples with ICP-MS analysis methods ( $n=5$ , confidence limit=95%).

| Sample numbers | $\text{Fe}^{3+}$ ions in wastewater |                          | $\text{Fe}^{3+}$ ions in river water |                          |
|----------------|-------------------------------------|--------------------------|--------------------------------------|--------------------------|
|                | This method ( $\mu\text{M}$ )       | ICP-MS ( $\mu\text{M}$ ) | This method ( $\mu\text{M}$ )        | ICP-MS ( $\mu\text{M}$ ) |
| 1              | $73.2 \pm 6.8$                      | $74.7 \pm 4.6$           | $73.4 \pm 6.1$                       | $74.4 \pm 5.8$           |
| 2              | $102.5 \pm 9.7$                     | $101.2 \pm 7.3$          | $102.5 \pm 9.2$                      | $100.8 \pm 7.6$          |
| 3              | $152.8 \pm 11.3$                    | $149.3 \pm 8.9$          | $152.4 \pm 10.1$                     | $150.6 \pm 8.4$          |

**Table 3**

Analysis results of the developed fluorimetric method applied for detecting  $\text{Fe}^{3+}$  ions separately in seawater, drinking water, and rainwater samples ( $n=5$ ).

| Sample         | $\text{Fe}^{3+}$ concentrations |                         | Recoveries (%) |
|----------------|---------------------------------|-------------------------|----------------|
|                | Added ( $\mu\text{M}$ )         | Found ( $\mu\text{M}$ ) |                |
| Seawater       | 20.0                            | $19.1 \pm 1.3$          | 95.5           |
|                | 100.0                           | $103.9 \pm 9.7$         | 103.9          |
| Drinking water | 20.0                            | $21.4 \pm 0.9$          | 107.0          |
|                | 100.0                           | $104.7 \pm 7.2$         | 104.7          |
| Rainwater      | 20.0                            | $20.8 \pm 0.8$          | 104.0          |
|                | 100.0                           | $98.3 \pm 5.3$          | 98.3           |

prepared PVA-Pyr probes could possess the considerably high selectivity in sensing  $\text{Fe}^{3+}$  ions, with no significant interferences from these co-existing ions.

### 3.3. Optimization of the fluorimetric conditions for $\text{Fe}^{3+}$ analysis

The test strips-based fluorimetric method with PVA-Pyr probes was employed to detect  $\text{Fe}^{3+}$  ions, where the test solutions containing  $\text{Fe}^{3+}$  ions would act as the media for the  $\text{Fe}^{3+}$ -probe reactions on the test strips resulting in the fluorescence quenching of the probes. The main conditions of the developed fluorimetric method for  $\text{Fe}^{3+}$  ions were explored (Fig. 7). Fig. 7A shows the quenching efficiencies of fluorimetric test strips depending on the concentrations of probes, indicating that  $5.00 \text{ mg L}^{-1}$  of the probes was the most suitable one to be chosen for the fluorimetric experiments. Moreover, it was surprisingly observed that the developed fluorimetric test strips could allow for the

Fe<sup>3+</sup> detections in the pH range from 2.0 to 12, showing almost invariable.

quenching efficiencies of probe fluorescence (Fig. 7B). Herein, no significant precipitation of Fe(OH)<sub>3</sub> would be formed even at pH 12, presumably due to the concentrations of Fe<sup>3+</sup> ions tested were too low to attain the solubility product of the precipitation. Also, no significant effect on the fluorimetric Fe<sup>3+</sup> analysis was observed for the ionic strengths of NaCl concentrations up to 150 mM (Fig. 7C). In addition, the response time of the test strips-based fluorimetric responses to Fe<sup>3+</sup> ions was evaluated (Fig. 7D). It was noted that the fluorescence intensities of the probes on test strips could tend to be stable within 3 min, so that the probe aggregation could be completed. These data indicate that the developed test strips-based fluorimetric method with the PVA-Pyr probes could facilitate the rapid detection of Fe<sup>3+</sup> ions under the widely applicable conditions.

### 3.4. Calibration curves of fluorimetric analysis for Fe<sup>3+</sup> ions in wastewater samples

Under the optimized conditions, the fluorimetric analysis with PVA-Pyr probes were firstly performed for detecting Fe<sup>3+</sup> ions spiked in wastewater using centrifuge tubes (Fig. 8A). One can observe that the fluorescence intensities of PVA-Pyr probes could rationally decrease as Fe<sup>3+</sup> concentrations increased, as also exhibited in the photographs of the corresponding reaction products in centrifuge tubes. A calibration curve was thus obtained with the fluorescence quenching efficiencies versus different Fe<sup>3+</sup> concentrations (Fig. 8B). Accordingly, Fe<sup>3+</sup> ions in wastewater could be detected over the linear concentrations ranging from 1.00 μM to 200 μM (R<sup>2</sup>=0.9953), with the limit of detection of 0.33 μM, estimated by the 3σ rule. Furthermore, the fluorimetric strategy with test strips was employed for the analysis of Fe<sup>3+</sup> ions spiked in wastewater by the dipping way, with the corresponding fluorescent spectra shown in Fig. 8C. A relationship between the quenching efficiencies and Fe<sup>3+</sup> concentrations was attained showing the linear Fe<sup>3+</sup> concentrations ranging from 5.00 to 300 μM (R<sup>2</sup>=0.9896), with a limit of detection of about 0.73 μM (Fig. 8D). Accordingly, the analysis results of the test strips-based fluorimetric method are comparable to those of the one using centrifuges tubes in term of detection sensitivity. Of note, the fluorimetric test strips could additionally enable the visual determination of Fe<sup>3+</sup> ions simply by the comparison of the tested strips with the standard colorimetric panel under UV light (Fig. 8C, insert).

Furthermore, the analysis performances of the developed test strips-based fluorimetric method were compared with those of some fluorimetric methods with other fluorescent probes (Table 1). It could be seen that the present fluorimetric strategy could exhibit better or comparable performances for the Fe<sup>3+</sup> detection in terms of linear concentration range and detection limit.

### 3.5. Evaluation of practical applications of the test strips-based fluorimetric method

To explore the feasibility of practical applications, the test strips-based fluorimetric method was employed to probe Fe<sup>3+</sup> ions separately in wastewater and river water samples (Table 2). The results were compared with those of ICP-MS using a *t*-test at 95% confidence limits, showing no significant difference (*P* > 0.05).

Moreover, the test strips-based fluorimetric method was employed to probe Fe<sup>3+</sup> ions separately in seawater, drinking water, and rain-water samples, with the results summarized in Table 3. After the additions of a known quantity of Fe<sup>3+</sup> ions into the testing solutions, the measured concentrations of Fe<sup>3+</sup> ions are in well consistent with the added ones. The recoveries so calculated are ranged from about 95.5–107.0%, indicating that the developed test strips-based fluorimetric method is feasible for detecting Fe<sup>3+</sup> ions in various environmental media, including for the finding of the potential iron mines.

## 4. Conclusions

In summary, a polyhydric polymer-functionalized fluorescent probe was successfully synthesized by covalently loading Pyr fluorophore onto the PVA chains using a facile one-step acetal reaction. The resulted PVA-Pyr probes were further coated onto the test strips towards a rapid and visual fluorimetric analysis method for Fe<sup>3+</sup> ions by taking advantage of the unique film-forming ability of PVA. The polyhydric PVA polymer chains can facilitate the Pyr fluorophore with dramatically improved aqueous solubility and strong cyan fluorescence, which could be specifically quenched by Fe<sup>3+</sup> ions through the PVA-Fe<sup>3+</sup> interaction by triggering the probe aggregation. Moreover, the test strips-based fluorimetric method can enjoy the stable and uniform distribution of the polymeric probes on test strips. Particularly, it may promise the in-field applications for the onsite monitoring of Fe<sup>3+</sup> ions in environmental water samples including the outdoor finding of potential iron mines. Such a facile and effective probe fabrication route with polyhydric polymers may open a new door toward the design of a variety of organic fluorescent probes with the improved aqueous solubility and selective recognition for targeting ions.

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