The electrosynthesized PFCA displayed **high** selectivity towards Fe^{3+} and was successfully employed for **sensing** Fe^{3+} in color rice samples with satisfactory results.

Novel **highly selective fluorescent sensor based on electrosynthesized poly(9-fluorenicarboxylic acid) for efficient and practical detection of iron(III) and its agricultural application**

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ABSTRACT

An efficient and practical conjugated polymer-based fluorescent sensor for the nanomolar detection of iron(III) in color rice samples has been successfully fabricated using an alcohol-soluble poly(9-fluorene-carboxylic acid) (PFCA), which was facilely electrosynthesized in boron trifluoride diethyl etherate. PFCA displayed high selectivity toward Fe^{3+} over different substances existing in agricultural crops and their products, such as common metal ions, anions, natural amino acids, carbohydrates, and organic acids, even organs of crops. Fluorescent intensities of PFCA showed a linear response to Fe^{3+} in the concentration range of 1 nM-0.782 mM with a detection limit of 0.611 nM. Fe^{3+} was tested by PFCA in real samples with satisfactory results, suggesting that the PFCA-based fluorescent sensor will provide a good model for constructing an advanced and promising fluorescent sensing platform for the determination of Fe^{3+} in agricultural samples. The sensing mechanism that Fe^{3+} induced the significant aggregation of PFCA chains and led to a significant fluorescent quenching of PFCA was proposed.

Keywords: Fluorescent sensor, Conjugated polymer, Iron(III), High selectivity, Agricultural application

1. Introduction

Iron as one of the most important trace elements is indispensable for all living organisms [1,2]. But both its deficiency and excess from the normal permissible limit can induce serious disorders [3,4]. This has led to burgeoning interest in the development of selective techniques for both qualitative and quantitative determination of iron ions in clinical, medical, biological, and environmental samples in recent years. Fluorescent sensors have been proven to be essential and powerful tools to monitor biological and environmental iron ions mainly due to their advantages over other analytical methods in terms of high sensitivity, superior selectivity, shorter response time, non-complicated sampling, non-destructive and non-invasive properties, and aptitude for real-time monitoring of the processes occurring at different time scales [5-7]. Thus, the design of highly selective and sensitive fluorescent sensors for iron ions remains as an emerging frontier.

Recently, fluorescent conjugated polymers (FCPs) have been playing an increasingly important role in the improvement of fluorescence sensing performance for important analytes. Firstly, the delocalizable π -electronic conjugated “molecular wire” polymer can greatly amplify the fluorescent response signal compared with the corresponding monomer units [7]. Secondly, the cooperative interaction with the side chain recognition moieties can realize a completely novel sensing mode, which is never observed for the monomer units [8]. Finally, the use of soluble polymers enables the inexpensive solution-processible or layer-by-layer formation of films and microcapsules, which will lead to the ready integration of sensor functions in practical

devices [9]. Thus, FCPs have been successfully used as optical sensing platforms for highly selective and sensitive detection of important substances in innocuous and environmentally friendly water or alcohol systems [7-11]. Moreover, FCPs-based sensors for the fluorescent detection of iron ions, especially Fe^{3+} have been widely reported [10-20]. From Table 1, these Fe^{3+} sensors based on FCPs display the outstanding performance in different solvents and some ones have been successfully used in actual samples, such as cerebrospinal fluid, fresh saliva, actual water and blood serum. However, quantitative detection of Fe^{3+} often has limitation such as interference from other metal ions, especially Fe^{2+} . Thus, most previous work mainly focused on excluding the interference of common metal ions. Also in practical samples, other anions, neutral substances, even compounds containing iron could inevitably bring noises. But these substances have not been noticed fully, which leads to the lack of suitable highly selective fluorescent Fe^{3+} sensors in practical application. Therefore, highly selective sensing of Fe^{3+} without the interference of other mixed ions and neutral substances through fluorescence quenching is still a challenge nowadays [21, 22]. To our best knowledge, the highly selective Fe^{3+} fluorescent sensors based on FCPs have not been reported, especially in agricultural samples.

In our previous work, polyfluorene (PF) derivatives with hydroxyl and carboxyl substitution were electrosynthesized and characterized, and its electrochemical properties, spectroscopic properties, thermal stability, morphology, and electrical conductivity, etc. were studied in detail [23]. In addition, the water-soluble poly(9-aminofluorene) (P9AF) as a turn-on fluorescent chemosensor for the detection

of Fe^{3+} was reported[17], but different carboxylates could also be detected at different levels by P9AF [24], PF functionalized with amino group ($-\text{NH}_2$) in C-9 position (P9AF) was substituted with that functionalized with carboxyl group ($-\text{COOH}$) in C-9 position (poly(9-fluorene-carboxylic acid), PFCA), which could avoid the interference of carboxylates and further improve the selectivity to Fe^{3+} . Moreover, one-step electropolymerization was favored by many researchers due to its flexibility, relatively low cost, and the ease with which the morphology, structure, and orientation of the final products can be controlled [25-27]. In this work, a series of experimental results showed that PFCA exhibited a higher selectivity toward Fe^{3+} than other metal ions, anions, natural amino acids, carbohydrates, organic acids, and organs of crops. Then PFCA was employed for the fluorescent determination of Fe^{3+} in color rice samples with satisfactory results.

2. Materials and Methods

2.1 Materials

The 9-fluorene-carboxylic acid (FCA) was bought from Acros Organics and was used directly. Boron trifluoride diethyl etherate (BFEE, Beijing Changyang Chemical Plant, China) was purified by distillation before use. Aqueous solutions of Hg^{2+} , Ba^{2+} , Sn^{2+} , Mn^{2+} , Pd^{2+} , and K^{+} were prepared from their chloride salts; aqueous solutions of Pb^{2+} , Ca^{2+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Co^{2+} , Cr^{3+} , Sr^{2+} , Zn^{2+} , Cu^{2+} , Mg^{2+} , and Cd^{2+} were prepared from their nitrate salts. Aqueous solutions of SO_4^{2-} , Cl^- , CH_3COO^- , PO_4^{3-} , and $\text{S}_2\text{O}_8^{2-}$ were prepared from their sodium salts; F^- , Br^- , I^- , SCN^- , NO_3^- , and $\text{Cr}_2\text{O}_7^{2-}$ were prepared from their potassium salts. Agricultural crops were obtained from the

experimental field in Jiangxi Agricultural University. Organic acids, carbohydrates, starch, and natural amino acids were obtained from Beijing Biodee Biotechnology Co., Ltd.

2.2 Instruments

Electrochemical polymerization was performed in a one-compartment cell with the use of Model 263A potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. Absorption spectra were measured using an Agilent 8453 UV-vis spectrophotometer. All fluorescence experiments were carried out using a Hitachi F-4500 **spectrofluorometer** with excitation slit set at 5 nm and emission slit at 5 nm. Gel permeation chromatography (GPC) measurements of the PFCA were performed in THF with a Waters Breeze GPC system. Different concentrations of Fe^{3+} were added using a pipette. Transmission electron microscopy (TEM) was performed with a JEM-2100 transmission electron microscope. **The fluorescence lifetime measurements were carried out on Hamamatsu compact fluorescence lifetime spectrometer C11367 (λ_{ex} , 340 nm; λ_{em} , 395-405 nm).**

2.3 Electrochemical synthesis of PFCA films

The working and counter electrodes were platinum (Pt) wire with a diameter of 0.5 mm. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode. Prior to each experiment, these electrodes mentioned above were carefully polished with abrasive paper (1500 mesh), cleaned successively with water and acetone, and then dried in air. PFCA was obtained by the electrosynthesis in distilled BFEE containing 0.02 mol L^{-1} monomer FCA. To obtain a sufficient amount of the

polymer films, a Pt electrode and a stainless steel sheet with surface areas of 4 and 6 cm² each were employed as the working and counter electrodes, respectively. The amount of the polymer film deposited on the electrode was controlled by the integrated current passed through the cell. In order to remove the electrolyte, oligomers, and monomer, the polymer film was rinsed with anhydrous diethyl ether. The molecular weight of polymers which dissolved in ethanol was measured by GPC (Mn = 4832, Mw = 5579). For spectral analyses, they were dedoped with dilute HCl solution for 3 days and then washed repeatedly with pure water. Finally, they were dried at 60 °C under vacuum for 24 h.

2.4 Detection of Fe³⁺

Fluorescent emission quenching experiments were carried out by sequentially adding the Fe³⁺ solution with different concentrations to a PFCA solution. The concentration of PFCA in cuvette was adjusted to be 5.0×10^{-6} M.

2.5 Preparation of practical sample solutions

White rice (Wufengyou T025), red rice (Jinggang Red), and black rice (black glutinous) were obtained from key laboratory in Jiangxi Agricultural University. Other organs of crops were obtained from the experimental field in Jiangxi Agricultural University. Double-distilled deionized water was added into above samples, respectively, and homogenized for 10 min using a blender. Then homogenates were filtered to remove residues. The prepared sample solutions were kept at 4 °C when not using. The as-fabricated PFCA was employed to detect all sample solutions with Fe³⁺ or without Fe³⁺. All color rice sample solutions were obtained by adding different content of Fe³⁺.

3. Results and discussion

3.1 Electrosynthesis of PFCA

PFCA was readily electrosynthesized by cyclic voltammetry (CVs) at a potential scan rate of 100 mV s^{-1} in BFEE containing 0.02 mol L^{-1} commercially available monomer FCA. The electrochemical synthesis of PFCA was shown in Fig. 1. As the first cycle of CVs exhibited, current densities on the reverse scan were higher than that on the forward scan. The formation of this loop was the characteristic of nucleation process, which could be found only in the first cycle. Increased redox current densities with the increasing cycle number of potential scans implied that the polymer film was gradually formed, and the amount of the polymer onto the surface of the working electrode increased with each cycle. Broad redox waves of the as-formed PFCA film may be ascribable to the wide distribution of the polymer chain length. In addition, visual inspection also indicated that a brown polymer film was formed on the surface of the working electrode.

3.2 High sensitivity to Fe^{3+}

In this work, ethanol, an innocuous and environmentally friendly solvent, was selected for dissolving PFCA. The recognition ability of PFCA toward Fe^{3+} was studied experimentally by fluorescence method. As shown in Fig. 2, the addition of Fe^{3+} immediately induced large quenching in the fluorescence of PFCA, which could be observed under UV light, and a >99% reduction in intensity at 405 nm occurred. In addition, the relationship between fluorescent intensities (I) and the concentration of Fe^{3+} ($[\text{Fe}^{3+}]$) was presented in Fig. 2 inset. Obviously, I linearly decreased with

increasing the Napierian logarithm of $[\text{Fe}^{3+}]$ ($\ln[\text{Fe}^{3+}]$), revealing that this method was suitable for detecting the unknown content of Fe^{3+} . The I vs. $\ln[\text{Fe}^{3+}]$ graph in Fig. 2 inset revealed that there was a good linear range from 1 nM to 0.782 mM. The limit of detection (LOD) and limit of quantification (LOQ) were calculated by $\text{LOD} = 3 \text{ s/m}$ and $\text{LOQ} = 10 \text{ s/m}$ [28, 29], where s was the standard deviation of peak intensities (three runs) of the lowest concentration of the linearity range and m was the slope of linear equation in Fig. 2 inset. The calculated LOD and LOQ were 0.611 nM and 2.04 nM, respectively.

3.3 *High selectivity to Fe^{3+}*

The selective and competitive experiments of PFCA were monitored by luminescent spectra. Fig. 3 showed the fluorescent quenching efficiencies of PFCA in the presence of various metal ions. Almost no emission quenching was observed upon addition of Cu^{2+} , Hg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Ba^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , K^+ , Cr^{3+} , Cd^{2+} , Al^{3+} , Sr^{2+} , Pb^{2+} , Sn^{2+} , Pd^{2+} and Fe^{2+} , while the addition of Fe^{3+} had a dramatic enhanced effect on quenching fluorescent emission, indicating that PFCA was highly sensitivity and selectivity towards Fe^{3+} than other common metal ions. This is due to the stronger electron-withdrawing ability of Fe^{3+} that could be attributed to its relatively high charge density that partially fills all the d orbitals (Scheme S1), and higher standard electrode potential (SEP, Table S1) compared with the other metal ions examined [30]. The higher charge density/SEP of a cation possesses, the stronger electronic affinity it provides [11]. From Table S1 and Scheme S1, we know that the Fe^{3+} possesses the strongest electrophilicity ability among the cations mentioned above. So the strong

coordinate interaction between Fe^{3+} and the large π electron conjugated system of PFCA could dramatically quench the fluorescence of PFCA due to the strong electrophilicity ability of Fe^{3+} . It is known that achieving a high selectivity for the analyte of interest over a complex background of potentially competing species is a challenging task in sensor development. Fig. 4 and Fig. S1 illustrated fluorescent responses of PFCA in the presence of various competing ions. The effect of PFCA in the presence of these competing ions was negligible, but obvious fluorescence quenching could be observed by adding Fe^{3+} into PFCA solution containing other ions or their mixtures, indicating that fluorescence quenching of PFCA in the presence of Fe^{3+} was hardly affected by these commonly coexistent ions.

Considering solvent effects, the water with different volumes, equivalent to the volumes of Fe^{3+} solution detected, was successively added into PFCA solution. In Fig. S2, only small fluorescent changes of PFCA were observed after adding different volumes of water, indicating that the solvent of Fe^{3+} solution had a negligible effect on the fluorescent intensities of PFCA. In the case of PFCA- Fe^{3+} , absorption spectroscopy can yield important information. From UV-vis spectra, PFCA exhibited a broad absorption band at 330 nm, which was attributed to the conjugated backbone of PFCA (Fig. S3). After adding Fe^{3+} , its absorption band was blue-shift caused by aggregation that had forbidden radiative decay from the excited stated. But additions of other metal ions and anions led to no obvious absorbance enhancements under the same conditions (Fig. S4 and S5). Although adding $\text{Cr}_2\text{O}_7^{2-}$ into PFCA solution also caused obvious change of UV-vis spectra, from Fig. S5 inset we know it was the

characteristic absorption of $\text{Cr}_2\text{O}_7^{2-}$.

More importantly, different substances existing in agro-products such as organic acids, carbohydrates, and natural amino acids were tested to exclude interferences in practical application. As shown in Fig. 5, the addition of these substances gave rise to almost no obvious fluorescence quenching. But an obvious fluorescent change was observed by adding Fe^{3+} to afore-mentioned mixtures, indicating the sensing of Fe^{3+} by PFCA was hardly affected by these coexistent substances. All these are very beneficial for quantitatively testing Fe^{3+} in practical samples of agriculture.

To illustrate specific recognition of PFCA towards Fe^{3+} , different derivatives containing iron was selected to test the selectivity of as-fabricated fluorescent sensor. The addition of different derivatives did not cause an obvious change in fluorescent intensities (Fig. S6). Crops and their products possess inorganic iron ions and iron chelates, such as roots, stems, leaves, flowers, fruits, and seeds. Organs of different crops were also used to evaluate anti-interference ability of sensing Fe^{3+} using PFCA. Although there are some other ions, micromolecules, and biomacromolecules coexisted in organs of different crops, PFCA did not display an obvious fluorescent response to these organs, indicating that PFCA could not interact with these substances, and there might not be Fe^{3+} in these organs of crops (Fig. S6).

3.4 Fe^{3+} sensor for agricultural application

To evaluate the feasibility and practicability of the as-prepared sensor, PFCA was used for the determination of Fe^{3+} in agro-product samples. Herein, the different color rice sample solutions with or without Fe^{3+} were prepared, respectively. As shown in

Fig. S7-9, white and red rice samples induced no observable fluorescence quenching, but the black rice sample brought about the significant fluorescence quenching, indicating the black rice might contain Fe^{3+} . Then PFCA was used for the detection of Fe^{3+} in color rice samples solutions by the standard addition method. From Table 2, the Fe^{3+} content in white and red rice sample could be determined using PFCA, and the determined concentrations of Fe^{3+} were accordance with the standard ones. Moreover, the recovery ranges were from 105.5% to 102.0% in white rice samples and 99.0% to 96.3% in red rice samples, and the RSD ranges were from 1.3% to 0.4% in white rice samples and 1.1% to 0.5% in red rice samples. Recoveries and RSD values of the sensor within an acceptable range indicated that PFCA could be feasible for practical application without sample purification step and other complex process, even though the target was in complex matrices. Moreover, satisfactory results also revealed that the proposed method was suitable, efficient and accurate for the trace level detection of Fe^{3+} in real sample analysis in agricultural fields. Delightfully, PFCA could detect Fe^{3+} in black rice and its concentration is about 5.47 nM. It is well known that Fe^{3+} was easily generated by the oxidization of Fe^{2+} in the presence of oxidants that was produced by biochemical reactions, which can be easily realized by a series of biochemical reactions with the help of different biochemical reaction chains in organisms. So Fe^{2+} could also be indirectly detected by the oxidation of Fe^{2+} in presence of oxidants like hydrogen peroxide which will provide a new way for bio/chemo-sensing application.

3.5 Sensing mechanism of PFCA

In this work, we think both carboxy-group (-COOH) and polymer backbone of PFCA could interact with Fe^{3+} . Firstly, we prepared PF via electrosynthesis and studied its sensing ability toward Fe^{3+} under the same conditions. As shown in Fig. S10, the addition of Fe^{3+} immediately induced fluorescent quenching of PF, suggesting that the fluorene backbone could bind with Fe^{3+} . Interestingly, PFCA was more sensitive than the PF for Fe^{3+} (LOD of the PF-based sensor for Fe^{3+} was approximately 10^3 -fold that of the PFCA-based sensor for Fe^{3+}), implying that carboxy-groups (-COOH) of PFCA could also bind with Fe^{3+} , which enhanced recognition capability of PFCA and sensing ability toward Fe^{3+} .

The usual quenching mechanism of FCPs-based fluorescent sensors was analyte-induced aggregation of polymer chains in solution [5, 7, 9]. The quenching mechanism of PF derivatives-based fluorescent sensors also revealed that polymer chains of PF derivatives were well separated and took on a random distribution of conformations along the whole polymer backbone before addition of metal ions. Metal ions could readily interact with functional group and the backbone of monomer units of PF derivatives when metal ions were added into soluble PF derivatives. As shown in TEM of Scheme 2, polymer chains of PFCA were well separated and took on a random distribution of conformations along the whole polymer backbone before addition of Fe^{3+} . Fe^{3+} might coordinate with one or two even more carboxy-groups (-COOH) and fluorene rings of PFCA in different intra/inter PFCA chains, which led to a significant quenching of PFCA emission. Thus the sensing mechanism of PFCA for Fe^{3+} was that Fe^{3+} induced the significant aggregation of PFCA chains and led to a

significant fluorescent quenching of PFCA, which was demonstrated in Scheme 2. In addition, the sensing mechanism of PFCA for Fe^{3+} was also indirectly confirmed by UV-vis spectra of PFCA and PF. The energy state of PFCA and PF had an obvious difference in the presence and absence of Fe^{3+} , and the successive addition of Fe^{3+} resulted in a blue shift and clear increase of intensities, indicating that PFCA and PF interact with Fe^{3+} (Fig. S3 and S11). Namely, the aggregation of PFCA chains in solution took place after adding Fe^{3+} . Fluorescence decay analysis (Fig. S12) of PFCA in the presence of Fe^{3+} showed decrease in lifetime which suggested the dynamic nature of the quenching process [31,32].

4. Conclusions

To summarize, an alcohol-soluble fluorescent conjugated polymer PFCA was facilely electrosynthesized in BFEE and employed for the highly sensitive detection of Fe^{3+} with a detection limit of 0.611 nM. Delightfully, PFCA showed high selectivity toward Fe^{3+} over common metal ions, anions, natural amino acids, carbohydrates, organic acids, and organs of crops. PFCA was then used to practically detect Fe^{3+} in color rice samples and satisfactory results suggested that PFCA was an efficient and practical fluorescent sensing platform for the determination of Fe^{3+} in real sample analysis of agricultural fields. The sensing mechanism of PFCA that Fe^{3+} induced aggregation of polymer chains and resulted in a significant fluorescent quenching of PFCA was proposed. Its further agricultural application in agro-ecosystem, crops, agro-products, and food for the detection of important substance via a designing model of biochemical reaction chain is also in progress.

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Table 1 Parameters and performance of different Fe³⁺ sensors based on FCPs in previous reports

Sensors	Solvents	Sensor concentration (μM)	Working concentration range (M)	LOD (nM)	Interference exclusion	Applications
P-1;	DMSO;	10;	$(0-26.7) \times 10^{-6}$;	77;	Metal ions;	ND;
P-2 [12]	MeOH	10	$(0-21.7) \times 10^{-6}$	79	Metal ions	ND
PHQ [13]	THF-H ₂ O (4:1)	6.6	ND	ND	Metal ions	In cerebrospinal fluid samples
PBP [14]	THF-H ₂ O (4:1)	1.6	ND	ND	Metal ions	In fresh saliva samples
MEH-PPV [15]	H ₂ O	ND	$(0.25-50) \times 10^{-3}$	ND	Metal ions	In cell imaging
PFPNa [16]	Tris-HCl buffer	1	ND	ND	Metal ions	ND
P1 [10]	H ₂ O	0.4	ND	ND	Metal ions	In blood serum samples
P9AF [17]	HEPES buffer	0.12	$(0.005-7660) \times 10^{-9}$	0.0037	Metal ions	In actual water samples and cell imaging
M1 [18]	THF	1	$(5-200) \times 10^{-6}$	ND	Metal ions	ND
PACA [11]	DMF-H ₂ O (9:1)	23.6	$(0.001-1000) \times 10^{-7}$	0.02	Metal ions	In actual water samples
P5CI (film) [19]	H ₂ O	ND	$(0.02-50) \times 10^{-4}$	16.1	Metal ions; anions	ND
Film-P1 (film) [20]	H ₂ O	ND	$(2.5-20) \times 10^{-6}$	2500	Metal ions	ND
PFCA (this work)	EtOH	5	$(0.001-782) \times 10^{-6}$	0.611	Metal ions; anions; acids; carbohydrates	In agricultural samples

ND: not discussed. LOD: the limit of detection.

Table 2 Determination of Fe³⁺ in color rice sample solutions using PFCA.

Samples	Fe ³⁺ spiked (M)	Fe ³⁺ found ($\bar{x} \pm \text{SD}$) (M) ^a	Recovery (%)	RSD (%)
	–	–	–	–
White rice	6.0×10^{-8}	$(6.33 \pm 0.079) \times 10^{-8}$	105.5	1.3
	6.0×10^{-7}	$(6.27 \pm 0.042) \times 10^{-7}$	104.5	0.7
	6.0×10^{-6}	$(6.12 \pm 0.025) \times 10^{-6}$	102.0	0.4
	–	–	–	–
Red rice	6.0×10^{-8}	$(5.78 \pm 0.062) \times 10^{-8}$	96.3	1.1
	6.0×10^{-7}	$(5.86 \pm 0.046) \times 10^{-7}$	97.6	0.8
	6.0×10^{-6}	$(5.94 \pm 0.027) \times 10^{-6}$	99.0	0.5
	–	$(5.47 \pm 0.100) \times 10^{-9}$	–	1.8
Black rice	6.0×10^{-8}	$(6.83 \pm 0.093) \times 10^{-8}$	105.0	1.4
	6.0×10^{-7}	$(6.23 \pm 0.04) \times 10^{-7}$	103.0	0.6
	6.0×10^{-6}	$(6.08 \pm 0.031) \times 10^{-6}$	101.0	0.5

^a Average of five determinations $\pm$ SD, SD is standard deviation.

Scheme 1 The fabrication of Fe³⁺ sensor based on fluorescent PFCA and its application to white rice (Wufengyou T025), red rice (Jinggang Red), and black rice (black glutinous).

Scheme 2 The fluorescence quenching mechanism of PFCA, and TEM of PFCA and PFCA-Fe³⁺.

Fig. 1 Electropolymerization of FCA at a potential scan rate of 100 mV s^{-1} in BFEE using cyclic voltammetry. Inset: the mechanism for the electrosynthesis of PFCA.

Fig. 2 The fluorescence emission spectra of PFCA (5.0×10^{-6} M in repeat units) in ethanol with successive addition of Fe^{3+} containing (1) blank; (2) 1.00×10^{-9} M; (3) 2.49×10^{-9} M; (4) 4.98×10^{-9} M; (5) 1.49×10^{-8} M; (6) 2.98×10^{-8} M; (7) 5.44×10^{-8} M; (8) 3.01×10^{-7} M; (9) 5.47×10^{-7} M; (10) 3.00×10^{-6} M; (11) 5.45×10^{-6} M; (12) 2.99×10^{-5} M; (13) 5.42×10^{-5} M; (14) 1.52×10^{-4} M; (15) 2.49×10^{-4} M; (16) 3.46×10^{-4} M; (17) 5.39×10^{-4} M; (18) 7.82×10^{-4} M. Inset: The I of PFCA vs. $\ln([\text{Fe}^{3+}])$.

Fig. 3 Fluorescence quenching efficiencies of PFCA (5.0×10^{-6} M) in the presence of various metal ions (each 8.0×10^{-4} M) in ethanol. I_0 corresponds to the fluorescence emission of solution without ions and I to the fluorescence emission of solution with ions.

Fig. 4 Ions selectivity of PFCA (5.0×10^{-6} M) in ethanol. The green bars represent the fluorescence emission that PFCA and competing ions (8.0×10^{-4} M). The red bars represent the fluorescence changes that occur upon addition of Fe³⁺ to the solution containing PFCA and competing ions. 1: only PFCA; 2: PFCA + Fe³⁺; 3: Pb²⁺; 4: Cu²⁺; 5: Hg²⁺; 6: Ni²⁺; 7: Co²⁺; 8: Zn²⁺; 9: Ba²⁺; 10: Ca²⁺; 11: Mg²⁺; 12: Sn²⁺; 13: Mn²⁺; 14: K⁺; 15: Cr³⁺; 16: Cd²⁺; 17: Al³⁺; 18: Sr²⁺; 19: Fe²⁺; 20: Pd²⁺; 21: F⁻; 22: Cl⁻; 23: Br⁻; 24: I⁻; 25: SO₄²⁻; 26: PO₄³⁻; 27: CH₃COO⁻; 28: NO₃⁻; 29: SCN⁻; 30: S₂O₈²⁻; 31: Cr₂O₇²⁻; 32: all the metal ions and anions.

Fig. 5 The fluorescence emission spectra of PFCA (5.0×10^{-6} M) in ethanol with twenty natural amino acids (a), organic acids, and carbohydrates (b) (each 8.0×10^{-4} M).

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