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Novel highly selective fluorescent sensor based on electrosynthesized poly(9-fluorenecarboxylic 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-fluorenecarboxylic 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.

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

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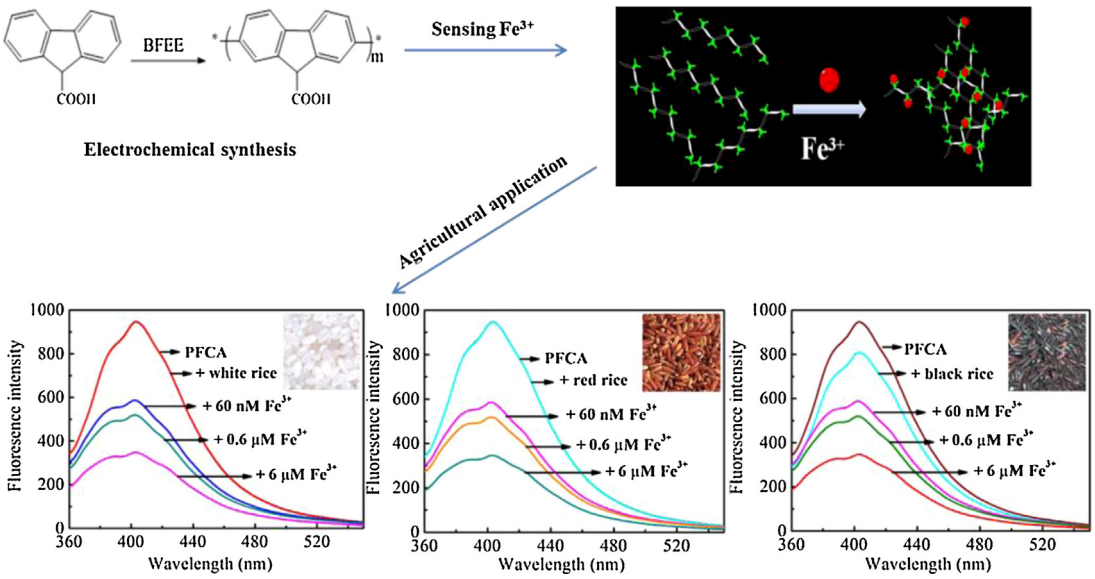
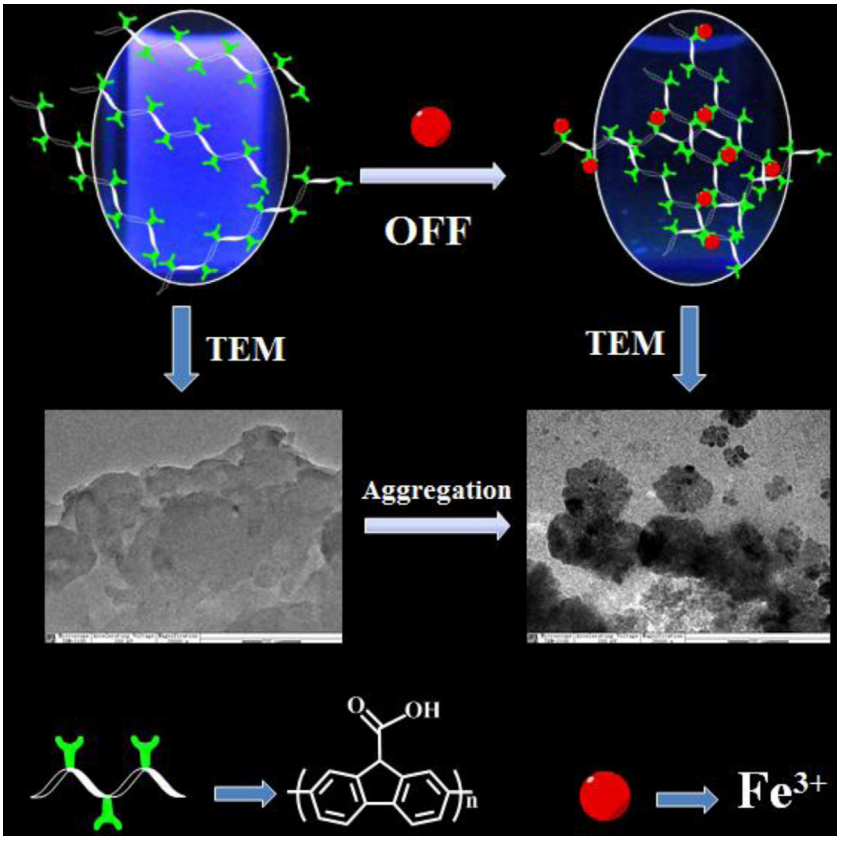


Scheme 1. The fabrication of Fe^{3+} sensor based on fluorescent PFCA and its application to white rice (Wufengyou T025), red rice (Jinggang Red), and black rice (black glutinous). (For interpretation of the references to color in this scheme legend, the reader is referred to the web version of this article.)



Scheme 2. The fluorescence quenching mechanism of PFCA, and TEM of PFCA and PFCA–Fe^{3+}.

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