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Near-infrared fluorescent turn-on detection of paraquat using an assembly of squaraine and surfactants

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ABSTRACT

Paraquat (PQ) is one of an effective herbicides but it has extremely toxic effects on animals and humans. It is of great importance to selectively detect PQ with fluorescence response. The first "off–on" fluorescent method based on mechanism of surfactant-controlled aggregate–deaggregate of squaraines (SQ) for paraquat (PQ) recognition in near infrared region was constructed. In this approach, remote-controlled regulation endows unique advantages to fulfill the turn-on response to electron-deficient featured PQ which prefers to quench all reported fluorophores through electron transfer. The assembled system can selectively recognize PQ over other herbicides. The detection limit was calculated to be 95.7 $\mu g\,L^{-1}$ (3.72×10^{-7} M), which is lower than that of value (200 $\mu g\,L^{-1}$) recommended by the US Environmental Protection Agency (EPA). In addition, the system can be used for PQ detection in real sample.

1. Introduction

Paraquat (1,1′-dimethyl-4,4′-dipyridinium ion, PQ) is one of the most widely used herbicides in many countries [1]. It can kill green plant with non-selectivity, rapid action, effectiveness, and more importantly, without activation on soil, thereby making it be widely used in presowing and inter-row weed control of ploughed land, and application for stubble cleaning and pasture renovation [2]. However, PQ is resistant to microbial degradation and decomposition by sunlight, it can exist in soil from 10 months to nearly 13 years and more possibly be transferred from foliage to foodstuffs [3,4]. Correspondingly, PQ has extremely toxic effects on animals and humans after acute exposure. It is easily absorbed into the digestive tract, respiratory tract, and skin, resulting in organ damage or even death. Usually the main target organ is the lung as a consequence of PQ accumulation, followed by rapid distribution to the kidneys, livers, muscle and thyroid [5,6]. Although many treatments have been proposed, none are supported by convincing clinical efficacy. That is, there are no specific antidotes at present. The detailed biochemical mechanism of PQ toxicity has been discovered, which involves the improvement of intracellular levels of superoxide ($O_2^{\bullet-}$) by redox cycling. Consequent cascade radical chain reactions are involved in deleterious cellular effects by oxidizing lipids, proteins, and nucleic acids [7]. PQ is included on a list of compounds to be monitored in pollution control by several governmental organizations, including WHO, US EPA, and ECB [8]. Thus, it is desirable to develop reliable approaches for rapid detection PQ with high selectivity and sensitivity.

Considerable efforts have been devoted to detect PQ, including spectroscopy [9], liquid chromatography [10], HPLC [11], immunoassay [12] and capillary electrophoresis [13]. However, these methods are time-consuming and require expensive experimental equipment. Accordingly, it is impossible to rapidly detect PQ using these methods. In contrast, fluorescent probe-based assay for PQ sensing would provide efficient tools because of its simplicity, high sensitivity, selectivity and spatiotemporal resolution [14]. In general, the fluorescence turn-on response induced by targets is preferable to the case of fluorescence quenching because the former is less interfered with the background [15,16]. Unfortunately, PQ quenches all fluorophores without exception as PQ, also named methyl viologen (MV^{2+}), has electron-defect quenching nature. As a well-known electron transfer agent, the quenching efficient of PQ is very larger and beyond others, the quenching constant was obtained as high as nearly $10^7\ M^{-1}$ (K_{sv}) from Stern-Volmer relationship plot [17]. Therefore, it is a great challenge to achieve PQ sensing with turn-on fluorescence response.

In order to prevent fluorescence quenching, and meanwhile preserve the capacity of fluorescence enhancement by PQ, smart design is needed. As far as we know there are only two strategies that have been reported [18,19]. One approach is to replace and release the fluorescent dyes from host–guest complexes by PQ. For example, Peng's group utilized a cucurbit[8]uril host to block

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PQ as a consequence of releasing fluorescent methylene blue dye [18]. The second approach is to tune dye aggregates through intermolecular interaction with PQ, which is developed by Huang et al. Through this strategy they switch the monomer–excimer transformation of pyrene, producing ratiometric fluorescent response to PQ [19]. These two strategies are all confined to specific fluorescent dyes, and more the latter is needed to perform in organic solvents, which seriously limit widely application for fluorescence turn-on detection of PQ. In addition, there is no near-infrared (NIR) fluorescence probe for PQ sensing. NIR fluorescence is much more favorable due to its minimum photodamage to biological samples, good tissue penetration, and weak autofluorescence interference from the complicated living systems [20]. Thus, it is desirable to develop NIR detection for PQ.

Squaraines (SQ) are an interesting class of dyes possessing sharp and intense absorption and fluorescence in the red to near infrared region. In aqueous solution, squaraine dyes tend to assemble with aggregates. The aggregates spontaneously array in different fashions (paralleled-oriented or head-to-tail arrangement) and degree, which depend on the variation of the solvents or ionic species added, leading to the observation of interesting spectroscopic response. The spectroscopic change derived from the transform between different types of aggregates and/or monomers could provide an effective means of relevant targets detection. With these properties, squaraines have been used as NIR sensors for sensing ions and biomolecules [21,22]. Surfactant, an amphiphilic molecule, tends to form micelles in aqueous solution with higher concentration (more than its critical micelle concentration). The surfactant micelle can encapsulate poorly water-soluble guests in its hydrophobic cavity [23].

Herein, we present a SQ self-assembly for NIR fluorescence turn-on detection of PQ in the presence of cationic surfactants sodium dodecyl sulfate (SDS). The design rationale for detection is illustrated in Scheme 1. In this system, PQ cannot absolutely quench the fluorescence of SQ due to the presence of block of aggregates that efficiently restricts electron transfer. Additionally, the surfactants prevent PQ from accessing to SQ. It is presumed to separate distance between PQ and SQ, thereby reducing the possibility of electron transfer from SQ to PQ and blocking the quenching way. The new "surfactants" derived from the added PQ and SDS through ion–π interaction would disperse SQ aggregates, leading to NIR fluorescence turn-on response [24].

2. Experimental

2.1. Materials and equipments

All chemicals were purchased from Aladdin, Shanghai Mayer chem. Reagents Co. (Shang, China), Xiaan Wolsen Bio. Reagents Co. (Xiaan, China), and were used as received. **SQ** was synthesized and purified as reported previously [21]. Absorption and emission spectra were collected by using a Shimadzu 1750 UV–visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively. Water surface tension was recorded with BZY-3B surface tension measurer (China).

2.2. Sample Preparation and Titration

Stock solutions of pesticides, metal ions and 4,4′-bipyridine were prepared in distilled water. Stock solutions of SDS (1.0×10^{-2} M) were prepared in distilled water for titration experiments. Stock solution of SQ (5.0×10^{-4} M) was prepared in ethanol and diluted to 5.0×10^{-6} M for titration experiments. Analytes were added to the solution of SQ, UV and fluorescence spectra were monitored after 1 min.

2.3. Calculation of detecting limit

Detecting limit $DL = K \times S_{b1}/S$, where $K = 3$, Sb1 is the standard derivation of the blank solution and S is the slope of the calibration curve [25].

2.4. Preparation of Chinese cabbage samples

1.0 g Chinese cabbage samples purchased from supermarket were mashed and dissolved in 1 mL water. After ultrasonic extraction, the mixture was centrifuged and then filtered through an ultrafiltration membrane (0.23 μm). To avoid the influence of low pH values and some metal ions in certain vegetables, the filtrate was diluted by 2 mM phosphate buffer (pH 7.4) containing 2.0 mM EDTA. These samples were spiked with varying levels of paraquat (PQ), followed by measurement of the detailed concentration with fluorescence method.

3. Results and discussion

3.1. Spectra response of SQ upon addition of SDS

The absorption and fluorescence changes of SQ in aqueous solution with addition of surfactant SDS were investigated (Fig. S1). The absorption spectra of SQ revealed three bands (λ_{max} = 625, 567 and 540 nm), which were assigned to the monomer, hypsochromic dimer, and oligomer absorption, respectively [22]. The monomer and dimer absorption gradually decreased with increasing concentrations of SDS. Observation of a new band at about 520 nm indicated that SQ molecules were transformed to H-aggregates. However, when the concentrations of SDS added are more than 0.3 mM, the process was reversed. The aggregates absorption decreased and the monomer absorption peak was clearly observed with 12 nm red-shift. These results suggest that SQ experienced monomer–aggregate–monomer transformation. The inflection concentration (0.3 mM) is referred to the critical micelle concentration (CMC) of surfactant SDS [26]. The CMC (0.22 mM) of SDS obtained by another method, the water surface tension, is also consistent with the data (Fig. S2). Correspondingly, with increasing concentration of SDS, the fluorescence of SQ underwent on–off–on changes with 20 nm red-shift from 640 to 660 nm upon excitation at 600 nm. Due to the aggregation-caused quenching (ACQ) property of SQ, low concentration of surfactants causes SQ to aggregate and fluorescent quenching, but high one increases solubility of SQ and could activate SQ to deaggregate, which results in fluorescence enhancement. The successive process could provide a method for turn-on detection of PQ.

3.2. Spectra response of SQ upon addition of PQ in the absence and presence of SDS

In aqueous solution, the fluorescence of SQ was quenched upon addition of PQ (Fig. S3). As an electron-deficient agent, PQ easily quenches most of fluorophores via electron transfer [17]. The quenching process was probed by Stern–Volmer analysis [27]. The relative fluorescence intensity (I_0/I) of SQ is plotted versus the concentration of PQ, where the slope of the line is equivalent to K_{sv}. As shown in Fig. S4, a linear line is observed and the K_{sv} constant is calculated to be 1.8×10^3 M^{-1}, which is far lower than that reported [17]. It is presumed that the block of aggregates reduce the electron transfer from inner SQ to PQ. Interestingly, in the solution with low concentration of SDS, fluorescence turn-on rather than quenching was demonstrated upon addition of PQ. The more concentration of SDS added (more than 0.3 mM), the higher turn-on fluorescence was obtained (Fig. 1). Considered the linear response range and fluorescence intensity change for PQ detection, the 0.6 mM of SDS was