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Design of a novel naked-eye and turn-on fluorescence sensor based on the 5,10,15,20-(4-sulphonatophenyl) porphyrin ($TPPS_4$)-Hg^{2+} system: Monitoring of glutathione (GSH) in real samples and DFT calculation

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ABSTRACT

In the present work, we proposed a novel naked-eye and turn-on fluorescence sensor based on the 5,10,15,20-(4-sulphonatophenyl) porphyrin ($TPPS_4$)-Hg^{2+} system with short assay time and high sensitivity to detect glutathione (GSH) in real samples. The $TPPS_4$ was the first time to detect GSH because of its high fluorescence quantum yield. The initial fluorescence from $TPPS_4$ was quenched by Hg^{2+} with an electron transfer process. However, when put a certain concentration of GSH into this system, the fluorescence sensor was turned to the "on" state, which was related to a competitive affinity of Hg^{2+} to GSH and the N atoms of porphyrin ring. Under the optimal conditions, the naked-eye detection limit was 0.43 nM and the limit of detection (LOD) was arrived to 16 fM (S/N = 3) for GSH. The linear regions are obtained by two ranges varying from 0 to 28.5 μM and from 38.15 to 61.87 μM. Furthermore, it was confirmed that the $TPPS_4$-Hg^{2+} fluorescence probe has excellent selectivity, high sensitivity and quick fluorescence response for GSH.

1. Introduction

Tripeptide reduced glutathione (GSH), which is made of glutamic acid, cysteine and glycine, is a kind of important tripeptide compound that simultaneously containing γ-glutamyl and thiol, and which also is the most abundant low molecular weight nonprotein thiol species in most mammalian tissues [1–4]. This important biothiol has a pivotal role in regulating redox homeostasis, signal transduction and antioxidation [5–7]. Biomedical researchers have proved that appropriate levels of glutathione are closely related to multifarious diseases, such as AIDS, cancer, aging, Parkinson·s and liver damage [8]. Once the level of GSH decreases, people are more likely to disease and in pressing need of exogenous antioxidant to maintain their antioxidant ability. Hagen et al. said that dietary GSH can be absorbed absolutely and result in an apparently increase in blood plasma GSH [9], which process can enhance tissue availability of GSH. So it is important to search a method of detection GSH in real samples, such as food and biosome, which can play an important role in maintaining GSH balance and avoiding many diseases. In the past few years, various analytical methods have been utilized to detect GSH, including fluorescence techniques [4,10], high-performance liquid chromatography (HPLC) [11,12], electrochemical assays [13,14], surface-enhanced Raman scattering (SERS) [15] and UV–vis sensor [16,17]. Among them, the fluorescence techniques draw attention to more and more researchers with the advantages of nondestructive, high sensitivity, simple, real-time and low cost [18,19]. Nowdays, a lot of efforts have been poured into detecting GSH. For instance, the Graphitic Carbon Nitride quantum dot (g-CNQD)-Hg^{2+} chemosensor [4], BINOL-bsaed [20], a gold-nanocluster (AuNCs) [21], Rhodamine 6G conjugated-quantum dots [10] and MnO_2-nanosheet-modified g-C_3N_4 probes [7] were found efficient to recognize GSH. However, these methods also have some disadvantages, such as higher limit of detection, time cost, and so forth. Therefore, it is still highly acclaimed to develop a simple, efficient, low cost and high sensitivity probe for the fluorescence detection of GSH.

Porphyrins are a class of naturally occurring macrocyclic compounds and play an important role in the metabolism of living organisms [22]. Due to the special photoelectric properties [23–28], such as taking strong light absorption, high emission, and rich coordination chemistry, porphyrins have been widely utilized in the UV–vis sensor [29], photoelectrochemical sensor (PEC) [30,31], and electrochemiluminescence (ECL) [32–34], etc.

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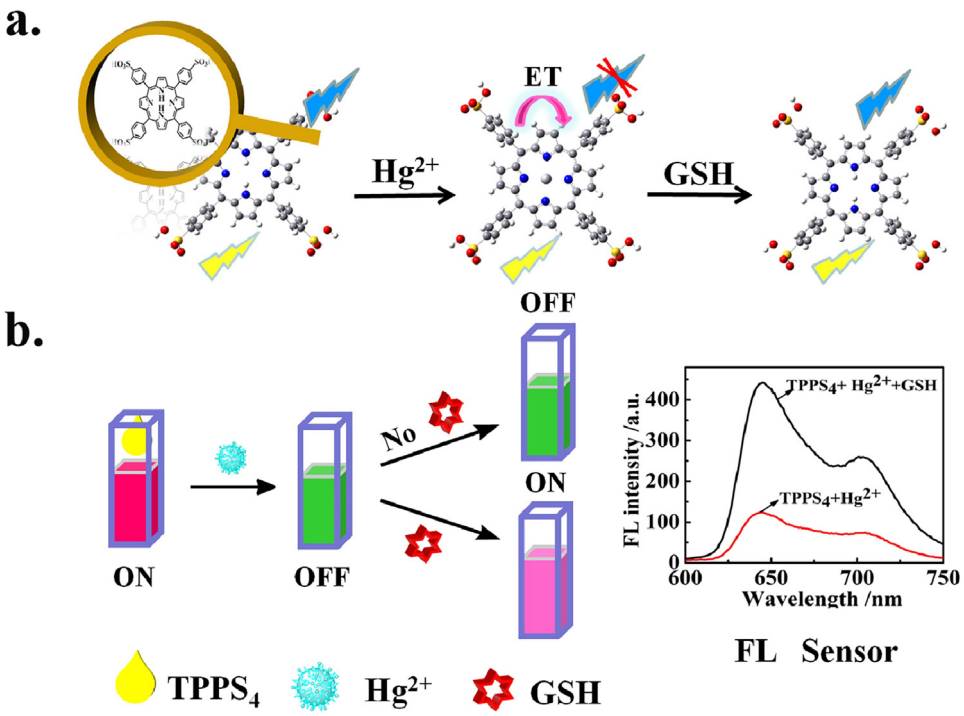

Scheme 1. Schematic Illustration of the Principle of the "OFF-ON" Fluorescence Sensor for GSH Based on the $TPPS_4$-Hg^{2+} system.

In this work, we firstly fabricated a novel fluorescence probe $TPPS_4$-Hg^{2+} via the "OFF-ON" process for detecting GSH with high efficiency and sensitivity. The "OFF-ON" process of the $TPPS_4$-Hg^{2+} system for the GSH detection is illustrated with Scheme 1. Based on the electrons transfer (ET) from $TPPS_4$ to Hg^{2+} and the coordination between Hg^{2+} and GSH, we designed a colorimetric and fluorescence sensor for GSH. In addition, we further demonstrated that such $TPPS_4$-Hg^{2+} fluorescence probe could detect GSH with high efficiency and sensitivity rather than other interfering biomolecules.

2. Experimental section

2.1. Materials

The 5,10,15,20-tetraphenylporphyrin (TPP) and 5,10,15,20-(4-sulphonatophenyl)zinc porphyrin ($ZnTPPS_4$) were synthesised according to the previously reported synthetic method [35,36]. Glutathione (GSH) was purchased from Aladdin Chemical Reagent Co. (Shanghai, China). The fetal calf serum got from the local hospital. Concentrated sulfuric acid (H_2SO_4, 98%), Mercury (II) chloride ($HgCl_2$) and other metal salts were obtained from Baishi Chemical Co. Ltd. (Tianjin, China). All organic solvents were purchased from Guangfu Chemical Co. Ltd. (Tianjin, China). All chemicals were analytical reagent grade and used without further purification. The aqueous solution used throughout all experiments was purified through the doubly distilled water by a Milli-Q system (Milli-Q, Millipore Corp, >18.25 MΩ cm).

2.2. Apparatus and characterization

A TU-1901 double-beam UV–vis spectrophotometer (Purkine General Instrument Co. Ltd., Beijing, China) was used to record absorption spectra and measure absorbance. Fluorescent emission spectra were recorded on the Cary Eclipse Fluorometer (Agilent Technologies Co., Palo Alto, USA). FT-IR spectra were performed on a Nicolet Nexus 670 Fourier transform infrared spectrometer (Nicolet Instrument Co. Madison, WI, USA) using KBr pellets, scanning from 4000 to 400 cm^{-1} at room temperature.

2.3. Synthesis of 5,10,15,20-(4-sulphonatophenyl)porphyrin ($TPPS_4$)

5,10,15, 20-(4-sulphonatophenyl)porphyrin ($TPPS_4$) was prepared according to the method [37,38] with a little modification, which sulfonated TPP at room temperature (for experimental details, see the Supporting Information).

2.4. Fluorescence sensing of GSH

The fluorescence sensor for GSH detection was proceeded at room temperature in a PBS (25 mM, pH = 7) buffer solution. In a typical procedure, 50 μL of the $TPPS_4$ solution (1 mM) was added into 1000 μL of PBS (25 mM, pH = 7) buffer solution followed by the addition of a calculated amount of Hg^{2+} ions, and added a certain amount of GSH standard solution after 6 min at room temperature. The excitation wavelength was 515 nm. The scanning range of emission wavelength was 600–800 nm. The emission and excitation slits were 10 × 10 nm, respectively. The fluorescence emission intensity was measured at 645 nm.

2.5. The food samples preparation and sensor

The food samples were prepared according to the previously reported work with a little modification [39]. All of the food samples were shopped in the BHG market place in Lanzhou, China. To begin with, all the food samples were washed through tap water and deionized water more than three times. Until the samples were naturally dried in the air and precise weighed, they were triturated. After centrifuging in a refrigerated centrifuge at 5000 rpm for 6 min, the supernatant was moved and diluted to appropriate concentration on the detection range with deionized water, and all food samples were stored in a refrigerator at 4 °C.