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Dual lanthanide-doped complexes: the development of a time-resolved ratiometric fluorescent probe for anthrax biomarker and a paper-based visual sensor

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ABSTRACT

In this work, a novel time-resolved ratiometric fluorescent probe based on dual lanthanide (Tb: terbium, and Eu: europium)-doped complexes (Tb/DPA@SiO_2-Eu/GMP) has been designed for detecting anthrax biomarker (dipicolinic acid, DPA), a unique and major component of anthrax spores. In such complexes-based probe, Tb/DPA@SiO_2 can serve as a stable reference signal with green fluorescence and Eu/GMP act as a sensitive response signal with red fluorescence for ratiometric fluorescent sensing DPA. Additionally, the probe exhibits long fluorescence lifetime, which can significantly reduce the autofluorescence interferences from biological samples by using time-resolved fluorescence measurement. More significantly, a paper-based visual sensor for DPA has been devised by using filter paper embedded with Tb/DPA@SiO_2-Eu/GMP, and we have proved its utility for fluorescent detection of DPA, in which only a handheld UV lamp is used. In the presence of DPA, the paper-based visual sensor, illuminated by a handheld UV lamp, would result in an obvious fluorescence color change from green to red, which can be easily observed with naked eyes. The paper-based visual sensor is stable, portable, disposable, cost-effective and easy-to-use. The feasibility of using a smartphone with easy-to-access color-scanning APP as the detection platform for quantitative scanometric assays has been also demonstrated by coupled with our proposed paper-based visual sensor. This work unveils an effective method for accurate, sensitive and selective monitoring anthrax biomarker with backgroud-free and self-calibrating properties.

1. Introduction

Bacillus anthracis (anthrax) is a potential biological warfare agent and inhalation of more than 10^4 its spores can result in death (Cable et al., 2007; Rosen et al., 1997). Its spores have been wrongly employed as biological weapons in bioterrorism attack, causing huge threat to animals and human beings (Rosen et al., 1997). Dipicolinic acid (DPA, 2,6-pyridinedicarboxylic acid) is a unique and major component of anthrax spores (5–15% of dry mass), which cannot be found in other common bacteria (Goodacre et al., 2000). Therefore, DPA can serve as a useful biomarker for anthrax and it is important to detect the concentration of DPA in anthrax assays. During the past decades, various methods have been reported for the detection of DPA, including surface enhanced Raman spectroscopy (SERS) (Zhang et al., 2005), electrochemical assay (Zhou et al., 2005), mass spectrometry (Beverly et al., 2000), opto-electrochemical assay (Tan et al., 2011), and so on. However, most of these methods generally require long time-consuming, sophisticated equipment and expensive reagents. Accordingly, a simple, sensitive, cost-effective and accurate method for DPA detection is highly significant to prevent the attack of biological diseases.

Recently, fluorescent detection is especially attractive due to its advantages like good selectivity, high sensitivity and rapid response time. Many fluorescent probes for DPA detection have been reported (Pellegrino et al., 1998; Ai et al., 2009; Xu et al., 2012), however, most of these fluorescent probes cannot eliminate the interferences from background signal, which may inevitably influence the accuracy of detection results. An ideal tool to efficiently avoid the background fluorescence interferences is time-resolved fluorescence detection technique, which utilizes temporal domain to distinguish short-lifetime

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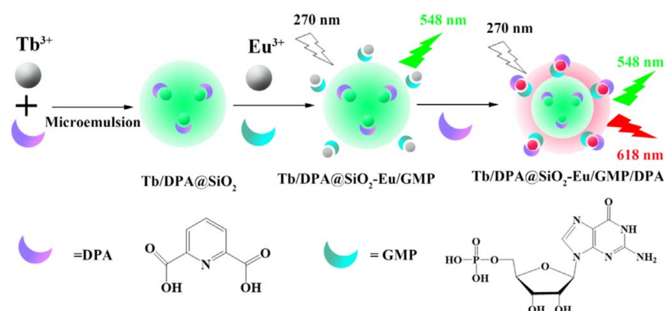
autofluorescence from long-lifetime fluorescence-labeled targets (Zhu et al., 2011; Zhang et al., 2013; Xue et al., 2016). To date, lanthanide-based fluorescent probes have obtained considerable attention owing to their special spectroscopic properties, including sharp emission bands, large Stoke shift, and long fluorescence lifetime (Massue et al., 2008; Zhang et al., 2014a, 2014b). These characteristics help to efficiently eliminate the interferences from background signal and make them suitable for time-resolved fluorescence detection. As a newly fascinating probe, lanthanide/nucleotide complexes, self-assembled by lanthanide and nucleotide via coordination bonds, have attracted wide attention due to their adaptive capability of guest encapsulation and structural tailorability. For instance, Kimizuka group (Nishiyabu et al., 2009) reported that majority complexes composed of lanthanide and guanosine monophosphate (GMP) exhibit weak fluorescence (except Tb/GMP) due to enhanced nonradiative quenching effect, which results from the vibronic coupling of the lanthanide excited states with OH oscillators in H_2O. However, upon displacing H_2O using other molecules, the fluorescence of lanthanide complexes will switch to a fluorescence enhancement state. Therefore, the fluorescence of lanthanide-GMP can be suited as a signal response for the development of time-resolved probes.

Nevertheless, most fluorescent assays only switch fluorescence signal indicator to a single “turn-on” state (fluorescence enhancement) or a “turn-off” state (fluorescence quenching), which can be easily influenced by environment factors including pH, temperature or ionic strength, leading to poor repeatability and weak anti-jamming properties. Therefore, facile ratiometric fluorescent probes are desirable for reducing the negative background influence (Wang et al., 2014; Li et al., 2015; Qi et al., 2015). Based on determining the change of fluorescence intensity ratio at two different wavelengths, ratiometric fluorescent probes can get rid of fluorescence intensity fluctuations from instrumental or environmental factors, thus providing a more accurate method for practical applications. For example, a ratiometric fluorescent method was developed for the detection of DPA with carbon dots chelated Eu-based nanomaterials (Song et al., 2015). However, there are few reports about DPA assay in a time-resolved ratiometric fluorescent format.

Enlightened by the above facts, herein, we have proposed a novel strategy to construct a dual lanthanide-doped time-resolved ratiometric fluorescent probe for the detection of DPA, as illustrated in Scheme 1. Firstly, Tb/DPA@SiO_2 was synthesized by a reverse micro-emulsion method and then modified with amino group. Tb/DPA@SiO_2 can emit strong green fluorescence owning to the antenna effect of DPA. Secondly, Tb/DPA@SiO_2 was then encapsulated into the network structure of self-assembled Eu/GMP coordination polymers (CPs) to form Tb/DPA@SiO_2-Eu/GMP complexes. Upon exposure to DPA, Tb/DPA@SiO_2-Eu/GMP/DPA was constructed through the exclusion of H_2O from Eu/GMP CPs, which significantly enhanced the red fluorescence of Eu by the sensitization effect from DPA. Therefore, Tb/DPA@SiO_2-Eu/GMP can represent a novel dual-emission ratiometric fluorescent probe for DPA detection, in which Tb/DPA@SiO_2 serves as a stable reference signal and Eu/GMP CPs acts as a sensitive response signal. In consideration that ratiometric fluorescent probe possess two fluorescence channel, our work provides a novel method for internal correction of the external environment interference, thus reducing the measurement error in the whole determination process compared with single channel approaches. Moreover, the probe shows long fluorescence lifetime, which can help to reduce the autofluorescence interferences from biological samples by using time-resolved fluorescence measurement.



Scheme 1. Schematic representation of our proposed fluorescent probe for DPA detection based on Tb/DPA@SiO_2-Eu/GMP complexes.

2. Materials and methods

2.1. Materials and instruments

$Tb(NO_3)_3$ and $Eu(NO_3)_3$ were purchased from Diyang Chemical (Shanghai) Co. Ltd. Guanosine 5′-monophosphate disodium salt (GMP) was purchased from Sangon Biotech (Shanghai) Co. Ltd. Dipicolinic acid (DPA, 2,6-pyridinedicarboxylic acid), 2,3-pyridinedicarboxylic acid (2,3-PA), 2,4-pyridinedicarboxylic acid (2,4-PA), 3,5-pyridinedicarboxylic acid (3,5-PA) were purchased from TCI (Shanghai) Co. Ltd., Aladdin (Shanghai) Co. Ltd, J & K scientific Ltd, Tansoole Co. Ltd, respectively. Tetraethylorthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), N-Hydroxysuccinimide (NHS) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma-Aldrich (St. Louis, MO). Phenoxyacetic acid (POA), p-phthalic acid (*p*-PA), benzoic acid (BA), cysteine (Cys), glutamic acid (Glu), *n*-hexanol, cyclohexane, Triton X-100 were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All the solutions were prepared in ultrapure water purified by a Milli-Q purification system (18.2 M cm^{-1} , Millipore Corp., Bedford, MA). Tris-HCl buffer (50 mM, pH=7.4) was prepared by adding certain amounts of Tris in Milli-Q system then adjusted pH=7.4 with HCl. All reagents are analytical purity grade and used directly without further purification.

Fluorescence spectra were recorded in a microplate reader system (infinite M200 pro, TECAN, Switzerland) using a black 384-well microplate (Corning, U.S.A.). The excitation wavelength used was 272 nm for the emission spectra. A delay time of 50 μs and a gate time of 2 ms were used for the time-resolved fluorescence spectra recording. Transmission electron microscopy (TEM) images were obtained by a JEOL-2100F electron microscope (JEOL, Tokyo, Japan). The FT-IR spectra were obtained with a Nexus 670 optical bench (Nicolet, USA).

2.2. Preparation of Tb/DPA@SiO_2

Tb/DPA@SiO_2 were prepared according to previous report with minor modification (Tan et al., 2015). Firstly, 500 μL anhydrous ethanol containing 9.0 mg of EDC and 2.8 mg of NHS was added to 600 μL of 20 mM DPA solution and then stirred for 40 min. Next, 100 μL APTES was added for reacting 100 min. And then, 200 μL of 20 mM $Tb(NO_3)_3$ solution was added into the mixture. The obtained mixture was employed as precursor. Then, a reverse microemulsion method was used for the preparation of Tb/DPA@SiO_2. The microemulsion containing 1 mL of *n*-hexanol, 1 mL of Triton X-100 and 4 mL of cyclohexane were added into 300 μL as-prepared Tb/DPA solution after 40 min continuous stirring, 25 μL of ammonia solution (28%) and 85 μL of TEOS were added. The stirring reaction was continued for 24 h. Equal volume of acetone were used to isolate the nanoparticles from the micromusion then centrifuge and wash with ethanol and water for 3 times. To prepare amino-modified Tb/DPA@SiO_2 (NH_2-Tb/DPA@SiO_2), Tb/DPA@SiO_2 was resuspended in the microemulsion solution mentioned above. Then, 20 μL of APTES was added into the solution for 2 h stirring reaction. Finally, the nanoparticles were collected using the same procedure as above. The obtained NH_2-Tb/DPA@SiO_2 was dried in oven at 40 °C.

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