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Phosphodiesters quaternary ammonium nanoparticles as label-free light scattering probe for turn-off detection of tyrosine

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ABSTRACT

In this contribution, a new highly sensitive and selective sensor of the determination of tyrosine has been proposed based on the downturn effect of light scattering (LS) using phosphodiesters quaternary ammonium nanoparticles (PQANPs). Phosphodiesters quaternary ammonium (PQA), one of Gemini zwitterionic surfactants, self-aggregated into the micelle named as PQANPs, which generated strong LS signal in aqueous solution under the optimum condition. Interestingly, the powerful LS intensity of PQANPs with the maximum peak located at 391 nm significantly decreased after introducing trace amount of tyrosine. The decreased value of the LS intensity of the PQA–tyrosine system (ΔI_{LS}) was in proportion to tyrosine concentration in the ranges from 5.5 $\times 10^{-8}$ mol/L to 4.68 $\times 10^{-6}$ mol/L, with a detection limit of 1.38 $\times 10^{-8}$ mol/L. Based on this decreased LS situation, the novel approach of the determination of tyrosine was first developed. The reaction mechanism for the interaction between PQANPs and tyrosine was also investigated. Moreover, the proposed LS assay was applied to the detection of tyrosine concentration in human serum and urine samples with satisfactory results.

1. Introduction

L-Tyrosine (Tyr), as a non-essential aromatic acid, is one of the important precursors of several neurotransmitters such as dopamine, norepinephrine and epinephrine [1]. The absence of L-tyrosine cause albinism [2], meanwhile high concentration of L-tyrosine induces Parkinson's disease, depression and mood disorders [3,4]. Several methods including spectroscopy [5], fluorescence [6,7], chemiluminescence [8,9], enzyme analysis [10], and electrochemical method [11,12], and high-performance liquid chromatography (HPLC) [13] have been employed to determine the tyrosine concentration. However, the methods suffer from unavoidable drawbacks. For example, fluorescence methods are always limited by cumbersome labeling process. Enzyme analysis requires harsh experimental conditions. The HPLC assays suffer from the complex operation and expensive apparatus. In addition, other methods undergo lower sensitivity or selectivity. Thus, developing a rapid, sensitive and selective determination approach of L-tyrosine is of great significance.

Light scattering (LS) is a highly sensitive and selective technique for monitoring molecular aggregation processes. Since Pasternack and coworkers first established LS technique to study biological macromolecules with a common fluorescence spectrometer [14,15], LS studies have attracted great interests among researchers. In the decade years, LS technique has been used to determine various analytes including nucleic acid [16], protein [17], polysaccharide [18], metal ions [19,20] and small molecules [21–23]. However, there are only few papers about the detection of amid acids such as histidine [24] and cysteine [25] by LS technique. To the best of our knowledge, the determination of tyrosine by LS technique has not yet been reported.

In this contribution, the new approach of detecting tyrosine has been proposed based on downturn effect of LS (Scheme 1). In this experimental assay, phosphodiesters quaternary ammonium (PQA), one of zwitterionic Gemini surfactants, was selected for constructing LS sensor. The proposed declined LS strategy effectively improved the sensitivity. PQA molecules tended to self-aggregate and formed the structure named PQANPs, which induced quite strong LS signal. Interestingly, upon the addition of the analyte tyrosine, the competitive combination between tyrosine and PQA molecule led to disaggregation, which produced remarkably decreased LS signal. Based on these situations, a novel LS-based sensor for tyrosine detection was developed. Compared with traditional methods, our present approach exhibited good performances such as label-free, facile fabrication, high sensitivity and selectivity.

2. Experimental

2.1. Materials and Apparatus

Tyrosine was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All other reagents used were of analytical grade without further

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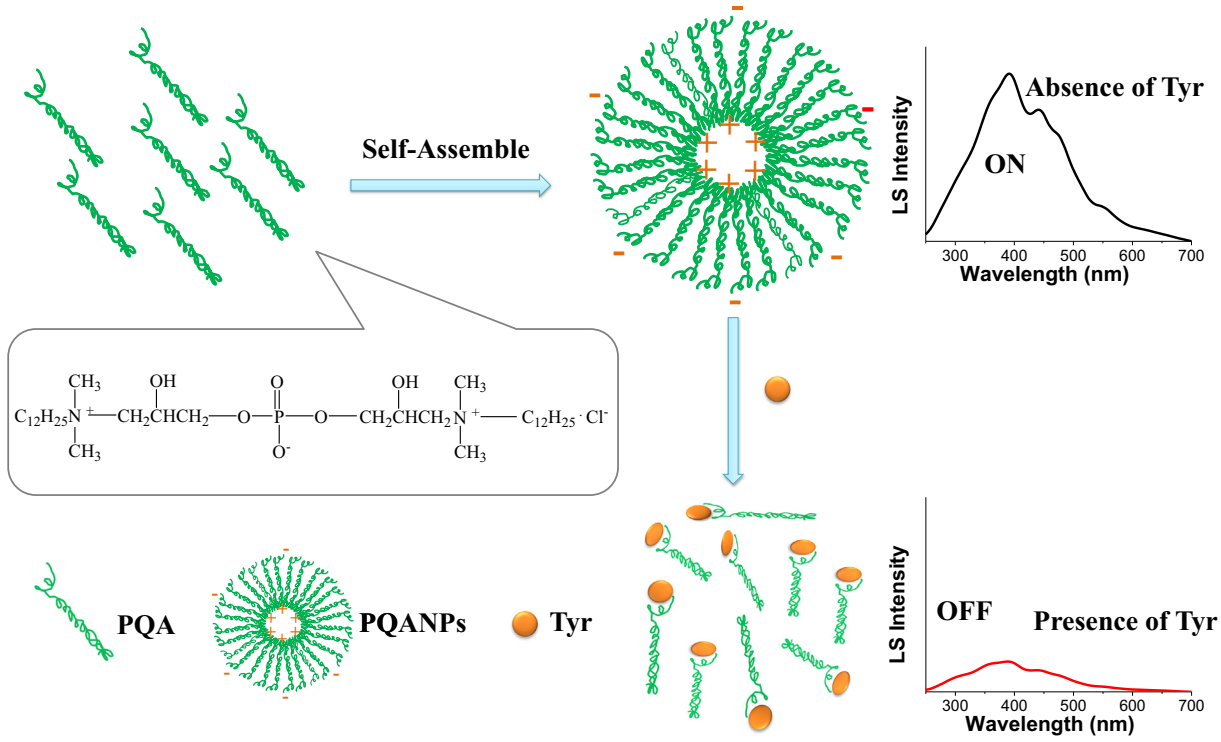

Scheme 1. Schematic illustration of the detection of tyrosine by decreased LS intensity of PQANPs.

purification or the best grade commercially available. Millipore Milli-Q ultrapure water (18.2 MΩ·cm) was used in all experiments.

The Britton-Robinson (BR) buffer solution (pH 8–12) was used to control the acidity of the solution, which was made up of 0.04 mol/L phosphoric acid, 0.04 mol/L acetic acid, 0.04 mol/L boric acid, and 0.2 mol/L sodium hydroxide.

The LS spectra and fluorescence spectra were measured with an LS-55 spectrofluorometer (Perkin-Elmer, USA) using a quartz cuvette (1.0 cm × 1.0 cm). The absorption spectra were determined by 8453 UV–visible Spectrophotometer (Agilent Technologies, USA). All pH measurements were made with a DELTA 320-Sacidity meter (Mettler-Toledo Instruments Co. Ltd., Shanghai, China).

2.2. Synthesis of PQA

Phosphodiesters quaternary ammonium (PQA) was synthesized and characterized by the infrared (IR) spectrum according to the literature [26]. The structure of prepared PQA was illustrated in Scheme 1. The 4.0×10^{-3} mol/L working solution was prepared by directly dissolving 0.262 g precisely weighed PQA product in 100 mL freshly obtained doubly distilled water.

2.3. Sample Preparation

One milliliter Britton-Robinson buffer, 1.50 mL PQA solution and appropriate standard tyrosine or sample solution were successively added to a 10 mL calibrated flask, and then the mixture was diluted to the mark with doubly distilled water and stirred thoroughly. The sample was removed from the calibrated flask and placed in a cuvette for LS spectra and fluorescence spectra measurements.

2.4. LS Spectra Determination Assay

Light scattering (LS) spectrum was obtained by scanning simultaneously the excitation and emission monochromators ($\Delta\lambda = 0.0$ nm) from 250 to 700 nm [27,28]. The extent of light scattering was measured at the maximum wavelength with slit width at 5.0 nm for the excitation and emission. Based on the spectrum, the LS intensity was measured at 391.0 nm. The change value of LS intensity of PQANPs decreased by the addition of tyrosine was represented as $\Delta I_{LS} = I^0_{LS} - I_{LS}$, where I^0_{LS} and I_{LS} were LS intensities of PQANPs in the absence and presence of the tyrosine.

3. Results and Discussion

3.1. Detection of Tyrosine Based on Decreased LS Spectra

The working principle of our study is displayed in Scheme 1. In the typical assay, phosphodiesters quaternary ammonium (PQA) was chosen for constructed LS sensor. As possessing two long hydrophobic hydrocarbon chains and two polar headgroups covalently attached through a spacer group as bionic phosphate ester structures, PQA molecules self-aggregated into the micelle called PQANPs, which produced intense LS signal, named as "ON" state. Upon the introduction of the analyte, tyrosine combined with PQA molecule and disturbed the aggregation process, forming smaller size particles, which induced significantly decreased LS signal, called as "OFF" state. Therefore, based on the down-turn effect, a new LS sensor was developed using PQANPs.

The LS spectra of tyrosine (tyr), PQANPs and the PQANPs-tyr system were displayed. As shown in Fig. 1, PQANPs solution exhibited intense LS signal in aqueous solution over the scanning wavelength range of 250–700 nm. The maximum peak located at 391 nm with a shoulder peak at 443 nm was observed. Interestingly, after the addition of trace amount of tyrosine solution, LS signal of PQANPs remarkably declined. With increasing concentrations of tyrosine, LS intensity of the PQANPs-tyr system continuously decreased. The change value of LS intensity (ΔI_{LS}) was in proportion to the concentration of tyrosine. A good linearity was obtained from 5.5×10^{-8} mol/L to 4.68×10^{-6} mol/L. The limit of detection is 1.38×10^{-8} mol/L. The decreased LS phenomenon indicated that the interaction between PQA and tyrosine occurred which disaggregated PQA assembly process, resulting in the remarkable decrease of intense LS intensity of PQANPs. According to the Rayleigh