



Copper nanocluster coupling europium as an off-to-on fluorescence probe for the determination of phosphate ion in water samples

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ABSTRACT

This paper reports an “off-to-on” fluorescence (FL) probe for sensitively and selectively detecting phosphate ions (Pi's). Fabrication of the probe was based on the competition between Pi's and tannic acid-stabilized copper nanoclusters (TA-Cu NCs) for Eu³⁺ binding. The addition of Eu³⁺ ions to TA-Cu NCs triggered the aggregation of TA-Cu NCs, which quenched the FL of TA-Cu NCs. After Pi addition, the aggregated TA-Cu NCs solubilized into the aqueous solution to facilitate the Pi-triggered dispersion of TA-Cu NCs. This phenomenon was due to the stronger binding ability between Pi's and Eu³⁺ than that between TA and Eu³⁺, leading to FL recovery of Cu NCs. The degree of redispersion of TA-Cu NCs was directly related to Pi concentration. Thus, Pi concentration can be quantitatively determined by the change in FL of the TA-Cu NCs dispersion. Under the optimized conditions, the change in FL presented a linear relationship with Pi concentration from 0.07 μmol L⁻¹ to 80 μmol L⁻¹. The limit of detection for Pi was 9.6 × 10⁻³ μmol L⁻¹ at a signal-to-noise ratio of 3. For Pi determination in real samples, only 1 mL water sample was needed. The proposed probe was highly sensitive, free from the interference of other common species in aqueous media, and particularly useful for the fast and simple diagnosis of water-eutrophication extent.

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1. Introduction

Excess phosphate ions (Pi's) in water can lead to increased algal growth, eutrophication, and reduced water quality. Thus, the development of sensitive, selective, and reliable analytical techniques for Pi determination is important [1,2]. Various methods, such as colorimetric [3], electrochemical [4,5] and fluorescence (FL) methods [6–9], have been proposed. Sensors based on changes induced by Pi's in FL are attractive because of their simplicity and low detection limit (LOD) [10,11]. For example, several FL approaches were reported for the detection of Pi's. Bai et al. proposed a photoluminescent sensor for Pi detection by using GQDs as an effective sensing platform with a detection limit of 1.0 × 10⁻¹ μmol L⁻¹ [6]. Wang et al. found that cysteine capped CdS quantum dots and Ag NPs could be used as FL probes for the detection of phosphate with a detection limit of 1.0 × 10⁻² μmol L⁻¹ [9]. Ganjali et al. reported a bis(8-hydroxy quinoline-5-solphonate) cerium(III) chloride as a fluorescent sensor for phosphate recognition with a detection limit of 2.5 × 10⁻² μmol L⁻¹

[12]. Mitra et al. proposed a FL quenching method for Pi using a glucose-based naphthylimino conjugate(L)-Zn²⁺ complex with a detection limit of 2.2 μmol L⁻¹ [13]. Hatai et al. reported that *N,N*-(ethoxy carbonyl methyl)-ethylenediamine-Cu²⁺ complex could be used as a FL chemosensor for inorganic phosphates with a detection limit of 1.0 × 10⁻¹ μmol L⁻¹ [14]. Zhao et al. proposed carbon dots-based FL probe for the detection of phosphate with a detection limit of 5.0 × 10⁻² μmol L⁻¹ [15]. However, fabricating an effective FL probe for Pi's is challenging because of the inherent tetrahedral structure of Pi's [16,17].

Recently, metal nanoclusters (MNCs) have drawn considerable interest because of their unique electrical, physical, and optical properties for catalysis, biological imaging, and chemical sensors [18–20]. MNCs are generally composed of a few atoms, with a subnanometer-sized core, which provide the missing link between atomic and nanoparticle behavior in metals [21]. With sizes comparable to the Fermi wavelength of electrons, MNCs display molecule-like properties, including discrete electronic states and size-dependent FL [22,23]. Compared with quantum dots and organic dyes, MNCs possess excellent photostability, large Stokes shift, and low environmental hazard [24].

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The FL of Au and Ag nanoclusters (NCs) have been extensively investigated because of their chemical stability and facile synthesis [19,24–26]. Compared with Au and Ag NCs, copper NCs (Cu NCs) are significantly cheaper and widely used in industries [27]. However, to date, only a few studies have applied Cu NCs as FL probes in biological and chemical sensing [28–31]. For example, Vilar-Vidal et al. proposed a selective and sensitive method for the detection of lead ions by using copper clusters as FL probes, which were electrochemically prepared. Interestingly, the as-prepared copper clusters exhibit efficient photocatalytic activity and can be used for the photocatalytic elimination of lead ions [32]. The observed effects can be explained in terms of an efficient electron transfer due to the Lowest Unoccupied Molecular Orbital (LUMO) energy of the cluster overlapping with the ion redox potential, and a possible size dependence of the selectivity was also reported. Ling et al. synthesized stable and highly fluorescent polyethyleneimine capped Cu NCs for the label-free FL detection of Sudan dyes in food samples [33]. Gao et al. prepared bovine serum albumin-capped Cu NCs for the selective, sensitive and label-free FL detection of kojic acid in food stuff [34]. It is noted that in the previous works, macromolecular surface protecting ligands, such as DNA, proteins, and polymers, have been employed to synthesize Cu NCs. These templates have resulted in the formation of Cu NCs with large hydrodynamic radius, which limit the potential applications of Cu NCs. To overcome this limitation, by using small-molecule tannic acid as a stabilizing reagent, we have recently proposed a simple and facile strategy for the synthesis of FL Cu NCs for sensitive and selective sensing of ferric ions [35]. This method is based on the selective coordination of Fe^{3+} with tannic acid on the surface of TA-Cu NCs, leading to a strong FL quenching of the TA-Cu NCs via an electron transfer mechanism [35]. Here, we interestingly find that the lanthanide ions, including Eu^{3+} , Yb^{3+} , Tb^{3+} and Ce^{3+} , also cause FL quenching of the TA-Cu NCs by acting as a bridge for the induction of Cu NC aggregation. With Eu^{3+} as an example, Scheme 1 shows that adding Eu^{3+} into the TA-Cu NCs triggers the aggregation of TA-Cu NCs, leading to the quenching of the FL of TA-Cu NCs. After adding Pi's, the aggregated TA-Cu NCs tend to solubilize into an aqueous solution to facilitate a dispersion of TA-Cu NCs triggered by Pi's (Scheme 1). This phenomenon is due to the stronger binding ability between Pi's and Eu^{3+} than that between TA and Eu^{3+} [6,15,36], thereby triggering the FL. Thus, the lanthanide ions cause TA-Cu NCs to aggregate, while addition of Pi's causes the lanthanide ion-triggered aggregated TA-Cu NCs to remain dispersed. The degree of redispersion of TA-Cu NCs is directly related to the concentration of Pi's. Hence, this principle could be used for sensing Pi's through the change in

FL of the dispersed TA-Cu NCs. To the authors' knowledge, this study is the first to report on sensing Pi's with small molecule-stabilized Cu NCs as FL probes.

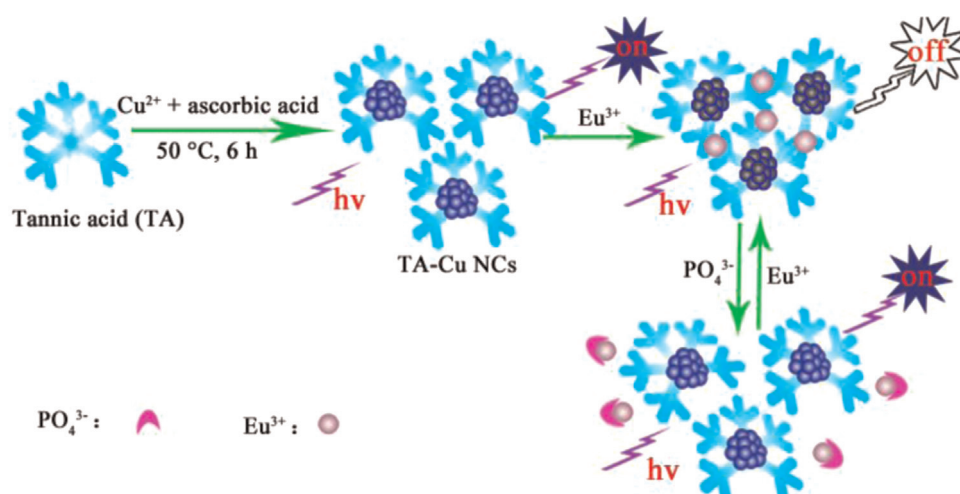
2. Materials and method

2.1. Reagents and solutions

Tannic acid was purchased from Qiangshun Chemical Reagent Co., Ltd. (Shanghai, China). Na_3PO_4 and L-ascorbic acid were purchased from Chengdu Kelong Chemistry Reagent Factory (Sichuan, China). $\text{Yb}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$, and $\text{Ce}(\text{NO}_3)_3$ were from Signopharm Chemical Reagent Co., Ltd. (Shanghai, China). CuSO_4 , NaOH, HCl, NaF, and citrate acid were obtained from Chongqing Chemical Reagent Company (Chongqing, China). Eu_2O_3 (99.99%) was purchased from Signopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used to prepare $\text{Eu}(\text{NO}_3)_3$. $\text{Eu}(\text{NO}_3)_3$ was prepared by dissolving a proper amount of Eu_2O_3 in 5 mL concentrated nitric acid, and then it was recrystallized from the solution containing nitric acid. Finally, $\text{Eu}(\text{NO}_3)_3$ was dissolved in 50 mL of ultrapure water. Mercaptosuccinic acid (MSA) was purchased from Aladdin Chem. Co. Ltd. (Shanghai, China). Ultrapure water was prepared in the laboratory using a water treatment device. All chemicals and reagents were of analytical grade and used as received without further purification, and ultrapure water was used throughout the work. TA-Cu NCs with a diameter of approximately 2.0 nm were synthesized as previously reported [35]. In a typical procedure, to prepare fluorescent Cu NCs, 0.2 mL CuSO_4 (0.1 M) aqueous solution was mixed with 0.1 mL tannic acid (1 mmol L^{-1}) in 20 mL distilled water, the resulting mixture was stirred for 5 min at room temperature. Then, 0.5 mL L-ascorbic acid (0.4 mol L^{-1}) was added to the mixture and stirred for 6 h at 50°C to obtain yellowish Cu NCs. The as-synthesized Cu NCs were stored at 4°C in a refrigerator for further use. The re-prepared Cu NCs was very stable and no obvious change in fluorescence intensity could be found even after two months of storage [35].

2.2. Instrumentation

The FL spectrum and intensity were recorded on a Hitachi F-7000 FL spectrophotometer (Kyoto, Japan). The FL lifetimes were measured with a time-resolved FL spectrometer model FLS 900 (Edinburgh, England). Zeta potential determination was performed on a Malvern Zetasizer Nano-ZS instrument (Malvern, UK). The morphology of the nanoparticles was observed using transmission electron microscopy



Scheme 1. Schematic of fluorescent TA-Cu NCs for sensing Pi.

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