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Monitoring of photoluminescence decay by alkali and alkaline earth metal cations using a photoluminescent bolaamphiphile self-assembly as an optical probe

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ABSTRACT

Photoluminescence (PL) decay induced by the displacement of an ionic fluorescence component, Tb^{3+}, with alkali and alkaline earth metal cations was investigated using photoluminescent spherical self-assemblies as optical probes. The photoluminescent spherical self-assembly was prepared by the self-organization of a tyrosine-containing bolaamphiphile molecule with a photosensitizer and Tb^{3+} ion. The lanthanide ion, Tb^{3+}, electrically bound to the carboxyl group of the bolaamphiphile molecule, was displaced by alkali and alkaline earth metal cations that had stronger electrophilicity. The PL of the self-assembly decayed remarkably due to the substitution of lanthanide ions with alkali and alkaline earth metal cations. The PL decay showed a positive correlation with cation concentration and was sensitive to the cation valency. Generally, the PL decay was enhanced by the electrophilicity of the cations. However, Ca^{2+} showed greater PL decay than Mg^{2+} because Ca^{2+} could create various complexes with the carboxyl groups of the bolaamphiphile molecule. Microscopic and spectroscopic investigations were conducted to study the photon energy transfer and displacement of Tb^{3+} by the cation exchange. This study demonstrated that the PL decay by the displacement of the ionic fluorescent compound was applied to the detection of various cations in aqueous media and is applicable to the development of future optical sensors.

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1. Introduction

Optical detection and quantitative analysis of alkali and alkaline earth metal cations, such as sodium and magnesium in an aqueous solution, are required for many practical uses such as water purification and ion chromatography [1,2]. Generally, the optical quantitative analysis of the concentrations of such cations is conducted using fluorescent photo-induced electron transfer (PET), in which the fluorescence from the fluorophore is controlled by the association of the cation with a cation receptor [3–5]. Fluorophores with various receptors have been developed to enhance the receptor sensitivity since the interaction of the cation with the fluorophore is the key factor in fluorescent PET [6,3]. In contrast to the enhanced fluorescence of the PET system, quenching (or decay) of the fluorescence by a cation is also exploited for optical sensing. For example, the fluorescence quenching of an anionic fluorescent polymer by a noble metal cation was applied for the quantitative analysis of the cation concentration, where electrical attraction of the cation was the key factor in reducing the fluorescence from the anionic polymer [7]. In a similar way, the complexation of a crown ether compound which led fluorescence quenching was also exploited for quantitative analysis of the alkali metal cation [8]. Though these approaches offered fluorescent molecular probes for selective cation detection, development of a novel optical probe to easily detect alkali and alkaline earth metal cations with visual observation is still needed.

Self-assembly of amphiphilic molecules is a facile way to prepare optical probes at a submicron scale. Generally, self-organization of bolaamphiphilic molecules associated with specific functional molecules has been exploited to prepare a solid platform with diverse physical, chemical and optical functions [9,10]. These bolamphiphile self-assemblies have been applied as templates to produce diverse hybrid materials such as inorganic-organic nanospheres and microtubes [11–13]. Besides the use of template, association of fluorescent molecules with bolaamphipile was used to prepare optical materials [14,15]. We recently reported a photoluminescent nanospherical self-assembly made of tyrosine-containing bolaamphiphile molecules with fluorescent Tb^{3+} ions

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[14]. The self-assembly of the bolaamphiphile molecule functioned as a host matrix enhancing the photon energy transfer from the photosensitizer to the lanthanide ions through an antenna effect of the tyrosine moiety. Whereas, the lanthanide ions were electrically bound to the carboxyl group of the bolaamphiphile molecule such that exchange of the lanthanide ion with another ion would reduce the photoluminescence (PL) emission. Based on these principles, the photoluminescent bolaamphiphile self-assembly may be applicable as an optical probe for cation sensing.

In this study, we examined PL decay by substitution of lanthanide ion with alkali metal and alkaline earth metal cations using the photoluminescent bolaamphiphile self-assembly as an optical probe. When a cation with higher electrophilicity than Tb^{3+} was added to the suspension of the photoluminescent self-assemblies, PL from the self-assembly was reduced by the displacement of the lanthanide ion with cations. Schematics of the PL and the chemical structure of the tyrosine-containing bolaamphiphile (Tyr-C7) are shown in Scheme 1. The correlations between cation concentration, PL decay, and excitation energy changes were investigated. The degree of PL reduction was positively proportional to the concentration, valency, and electrophilicity of the cation. These positive correlations demonstrated that optical detection of the cation concentration could be achieved using the photoluminescent bolaamphiphile self-assembly, where the displacement of the Tb^{3+} ion functioned as the origin of PL decay.

2. Experimental

2.1. Materials

The self-assembling molecule bis(N-alpha-amido-tyrosine)-1,7-heptane dicarboxylate (Tyr-C7) was synthesized according to a previously reported protocol [11]. Terbium(III) chloride hexahydrate ($TbCl_3·6H_2O$, 99.9%, Sigma–Aldrich) and salicylic acid (SA, ACS grade, Sigma–Aldrich) were chosen as photosensitizing chemicals because they associated well with the Tyr-C7 assembly and demonstrated PL enhancement in a previous study [14]. Alkali and alkaline earth metal chloride salts were used as cation sources. Sodium chloride (NaCl, 99%, Sigma–Aldrich), lithium chloride (LiCl, extra pure, Junsei), potassium chloride (KCl, 99.5%, Kanto chemical), magnesium chloride ($MgCl_2$, H_2O content <5%, Sigma–Aldrich), calcium chloride ($CaCl_2$, 96%, Sigma–Aldrich), and strontium chloride hexahydrate ($SrCl_2·6H_2O$, 99% Sigma–Aldrich) were the compounds of cation sources. All the chemicals were used as received.

2.2. Synthesis of the photoluminescent Tyr-C7 self-assemblies

For the preparation of the photoluminescent optical probes by Tyr-C7 self-assembly, the synthesized Tyr-C7 powder was dissolved in an aqueous solution containing SA and $TbCl_3$ (10 mM each) at a concentration of 2 mg/ml. Due to the polarity of Tyr-C7, photoluminescent probes of the spherical self-assembly were instantaneously produced. To prevent effects from other salts, such as buffer salts, the optical probe preparation was performed in dd-water with a pH of 6.4 ± 0.3.

2.3. Monitoring PL changes

For monitoring of PL decay by alkali (Li^+, Na^+, and K^+) and alkaline earth metal cation (Mg^{2+}, Ca^{2+}, and Sr^{2+}) exchange, 0.1 ml of the cation solutions in a variety of concentrations (0.5–2.0 M) was added to 1.9 ml of the optical probe suspension. The concentration range of cations in the mixture was 25–100 mM. After vortexing the mixture for 5 min to exchange Tb^{3+} ion fully with the cations, the emission and excitation spectra of each sample were monitored. The emission spectra were scanned at 500–650 nm under an excitation beam at 330 nm. The excitation spectra were obtained at 220–500 nm under 545 nm emission. The reduction of PL by the cation was calculated by comparing the PL emission intensity at 545 nm using the intensity from the intact optical probes suspension as a reference.

2.4. Instruments

The PL emission and excitation were examined using a spectrophotofluorometer (RF-5301PC, Shimadzu Co.). A monochromated Xe lamp and a quartz cuvette with a1-cm beam path length were used for the PL measurements. The sample PL was visualized using a fluorescence microscope (Eclipse Ti-S, Nikon) under UV light (λ_{ex} = 330 nm), where the suspension of the photoluminescent samples was prepared in a 24-well microplate in a volume of 0.2 ml. Inductively coupled plasma optical emission spectrometry (ICP-OES, ICP-730ES, Varian) was used to examine the amount of Tb ions released by cation substitution. For the ICP-OES tests, 0.5 ml of the NaCl and $CaCl_2$ solutions (1 M) were added to 9.5 ml of the photoluminescent self-assembly suspension. After 5 min of shaking, the solid substance in the suspension was isolated by centrifugation, and the supernatant solution was acquired for the determination of Tb concentration.

3. Results and discussion

The optical probe of the spherical photoluminescent Tyr-C7 self-assembly emitted blue light under the UV excitation of λ = 330 nm. The fluorescent component emitting PL was the Tb^{3+} ion, while the bolaamphiphile self-assembly worked as the host matrix offering binding sites for the Tb^{3+} ion and photosensitizer [14]. When alkali or alkaline earth metal cations were added to the photoluminescent Tyr-C7 self-assembly, the Tb^{3+} ion was released such that the PL from the self-assembly decayed remarkably. Fig. 1 shows the morphology of the photoluminescent nanospherical assembly and the fluorescence microscopy images demonstrating decay of the blue PL light with an increase in the Na^+ concentration. These fluorescence microscopy images imply that the photoluminescent self-assembly is a reliable optical probe in which the PL decay has positive correlation with cation concentration. The fluorescence microscopy study also indicated that PL would not be influenced by the aggregation of the optical probes. As shown in Fig. 1(b), all of the spherical photoluminescent self-assemblies were coagulated to form random aggregates; however, the PL is dependent only on the ion concentration. Considering that the fluorescence of some proteins is quenched by aggregation [16], this photoluminescent bolaamphiphile self-assembly is free from such aggregation-driven quenching.

Detailed studies on the PL decay were performed to investigate the effects of alkali and alkaline earth metal cations. First, the effects of cation concentration on the PL decay were observed. In agreement with the fluorescence microscopy, the intensity of the PL decreased with an increase of the cation concentration. Fig. 2(a) shows the emission spectra where the characteristic PL emission at 545 nm decayed with Li^+ ion concentration. Similar PL decay was observed for other alkali metal ions of Na^+ and K^+. The degree of PL decay of every alkali metal cation was plotted against cation concentration (Fig. 2b). The PL decay plot showed positive correlation between ion concentration and PL decay; particularly at concentrations greater than 25 mM, with nearly linear dependency. This linearity supports that the photoluminescent Tyr-C7 self-assembly is applicable as an optical probe to reliably detect the alkali metal ion in a high concentration range. Decay of PL was sensitive to the kind of alkali metal cation, where a higher degree of PL decay was observed with a decrease in the atomic number. Considering the

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