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Luminescent polystyrene latex nanoparticles doped with β-diketone europium chelate and methacrylic acid

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ABSTRACT

Luminescent polystyrene latex NPs with a diameter of 83 nm are prepared by stepwise process of chelation of β -diketonate europium complexes followed by conjugation on poly(St-*co*-DVB-*co*-NaSS-*co*-MAA) [St = styrene; DVB = divinylbenzene; Nass; 4-styrenesulfonic acid sodium salt hydrate; MAA = methacrylic acid] NPs. The europium complexes composed of mixed-ligands of β -diketone [1-(2-Naphthoyl)-3,3,3-trifluoroacetone (NTA)], phosphorous-containing neutral ancillary ligand [triphenylphosphine (TPP)] and carboxylic acid are studied by the luminescent spectroscopy. The PL spectra of the EuNPs composed of typical Eu³⁺ show red emission, assigned to the transition between the first excited state and the multiplet. The integrated intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ of EuNPs is significantly enhanced due to the hypersensitive effects because of strong PS-Eu³⁺ interaction. The MAA retains the constant polarization of Eu³⁺ ions against photobleaching because carboxylic group in MAA protects the distortion of the symmetry around the Eu³⁺ ions due to influence from pH or strong chelating with Eu³⁺. The cytotoxic effects of EN₂T doped PSDNMA latex NPs are evaluated on PC12 cell lines by Annexin V assay.

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1. Introduction

The optical aspects of lanthanide complexes lie in their furthermost striking luminescence that gives sharp, intense emission lines upon irradiation with ultraviolet light due to effective intramolecular energy transfer from suitable coordinated ligands (those whose triplet states match well with the emitting level of the lanthanides) to the luminescent lanthanide ions, which, in turn, undergo a corresponding radiative process [1,2]. Thus, lanthanides with chelating ligands have sufficient requests, e.g. in immunoassays [3], and more recently in the progress of novel constituents based on sol-gel glasses [4], liquid crystals [5], polymers [6] and LED [7]. It is a challenge of manipulative of appropriate expanded π -conjugated system molecules to sensitize the europium ion to emit red emission under excitation of visible light.

The β -diketone is one of the most studied ligands due to their chemical stability, highly molar extinction efficiency and high energy transfer efficiency from the ligand to the Ln(III) ions [8]. 1,3-Diketones are reported as very promising antennaligands for Ln(III)-centered emission [9], where the rigidity of the complex structure is a reason for lesser radiationless decay [10]. Europium complexes are emit highly monochromatic red light at around 615 nm with a narrow band width and a large

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Stokes shift (~270–290 nm), which can spectrally distinguish their luminescence from that emitted from coexisting molecules in biological samples. A general method to synthesize such complexes is developed by Melby et al. [11] Basically, three equivalents of the diketone in water–ethanol solution are treated with 3 equiv of NaOH or KOH followed by the addition of one equivalent of the lanthanide salt, usually a chloride or nitrate [12]. Pikramenou et al. [13] report a dinuclear samarium complex based on a bis- β -diketone ligand 1,3-bis(3-phenyl-3-oxopropanoyl)benzene which is used as a derivative of dibenzoylmethane (DBM). The photoluminescent studies show that luminescence signal is more intense (about 11 times) than the corresponding DBM complex, although the two ligands possess the similar triplet state levels [14].

The design and synthesis of organic ligands with larger absorption coefficient are very important to improve the europium complexes luminescent properties [10]. Especially, the luminescence lifetime of the europium complexes is generally up to several hundreds of microseconds, which is significantly longer than that of typical organic fluorescent molecules [15]. Nevertheless, europium complexes are composed of hydrophobic molecules which can't be directly used in hydrophilic environments. Consequently, one effective method for protecting the europium complexes from exposure to the aqueous environments and retaining their intact luminescence properties is to incorporate the europium complexes in hydrophobic polymer matrices [16,17]. Several methods are reported to incorporate the europium complexes in polymeric matrix by directly encapsulation inside of polymeric particles or covalently bounding the luminescent molecules on outer surface of particles [18]. Aikawa et al. reports preparation of luminescent polystyrene latex particles by miniemulsion polymerization of styrene with dissolved europium complexes in the presence of bovine serum albumin (BSA) and poly(ethylene glycol) monomethoxy methacrylate as surfactants [17]. Also, methacrylic acid (MAA) is more strongly chelating with Eu^{3+} than other compositional molecules of europium complexes such as 1-(2-Naphthoyl)-3,3,3-trifluoroacetone (NTA) and thenoyltrifluoroacetonate (TTA). When UV light is irradiated onto the europium complexes without carboxyl group, it could be easily dissociated. In this case, carboxylic group from MAA protect the dissociation due to influence from pH or chemical cleavage by UV light. Moreover, previously reported work where the europium complexes are formed by electrostatic interaction, MMA interact with europium complex via coordination bond of Eu(TTA)₃(TOP)₃ [TOP = Trioctylphosphine], which is much stronger than the electrostatic interaction [19]. Based on several attempt to produce stable europium complexes, triphenylphosphine (TPP) was selected because phosphine will be form more strong coordination bond like a TOP. Also, other publications are just used electrostatic interaction between hydrophobic surface of polystyrene and europium complexes. In this case, it can be easily dissociated in certain environments such as changing the pH values or intact with hydrophobic conditions, i.e. blood vessel or cell membrane, etc. In the case of direct in cooperation of europium complexes during the formation of polystyrene, Eu³⁺ chelates with unwanted chemicals resulting in lower luminescent properties $(QY \le 10\%)$ [17]. Another reported work is loading the europium complexes after swelling the polystyrene nanoparticles in acetone/mixture of chloroform and 1-butanol [20]. To resolve the dissolution of europium complexed from polymeric matrix, carboxylic acid is directly activated inside/outside of polystyrene nanoparticles to link europium complexes by covalent bond resulting in antileaking constituents.

In this study, luminescent polystyrene latex NPs with a diameter of 83 nm are prepared by stepwise process of chelation of β -diketonate europium complexes followed by conjugation on PSDNMA [poly(St-*co*-DVB-*co*-NaSS-*co*-MAA), St = styrene; DVB = divinylbenzene; Nass; 4-styrenesulfonic acid sodium salt hydrate] NPs. Especially, MAA is used for the activation of carboxylic group for covalent conjugation with europium complexes. Also, thermodynamic equilibrium calculations are used to predict for proper synthesis conditions of europium complex in Eu³⁺—H⁺—Cl⁻ system at a wide pH range between 1 and 12. The chemical structure of the europium complexes and overall schematic structure of the europium complex and polystyrene latex NPs are illustrated in Scheme 1. Europium complexes are prepared by chelating Eu³⁺ with 1-(2-Naphthoyl)-3,3-trifluoroacetone (NTA) and triphenylphosphine (TPP). PSDNMA with a diameter of 76 nm are modified with EN₂T [Eu(NTA)₂(TPP)]. The concentration of NTA is varied in order to establish the optimal compositions by evaluating the PL intensity. The cytotoxic effects of EN₂T doped PSDNMA latex NPs are evaluated on PC12 cell lines by Annexin V assay.

2. Experiment details

2.1. Materials

Europium (III) chloride hexahydrate (EuCl₃·6H₂O) and 4-styrenesulfonic acid sodium salt hydrate (H₂C=CHC₆H₄SO₃ Na·xH₂O, NaSS) is purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Triphenylphosphine (TPP, 99.0%), sodium bicarbonate (SBC) and ammonia solution (28.0–30.0%) are purchased from Samchun Chemicals (Kyunggido, South Korea).

1-(2-Naphthoyl)-3,3,3-trifluoroacetone (NTA) is supplied by Maybridge (Cornwall, U.K.). Divinylbenzene (DVB, 80%), potassium persulfate (PPS), methacrylic acid (MAA), tetrahydrofuran (THF, anhydrous, 99.9%, inhibitor-free) and 3-[4,5-dime thylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) are purchased from Sigma-Aldrich Chemical Co. (St. Louis, U.S.A. Ethyl Alcohol (EtOH, 99.9%) is purchased from Duksan Reagents. Polyvinylpyrrolidone (PVP) is supplied by Biosesang Inc. (Seoul, South Korea). Styrene (St) is supplied by Junsei Chemicals (Chuo-Ku, Tokyo). The PC12 cell line was purchased from the American Tissue Culture Collection (ATCC; Rockville, MD, USA). All the chemicals are used without further purification unless otherwise noted. Monomer styrene is passing through a short column of basic alumina prior to use to remove the inhibitor mono methyl ether hydroquinone (MEHQ). Triple distilled and deionized water is used throughout. Ultrapure water (type I, 18.2 M Ω cm⁻¹) is obtained from Millipore water purification system.

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