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The preparation and performance of visible-light-sensitized luminescent nanoparticles based on europium complex

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ABSTRACT

Long-wavelength-sensitized luminescent materials are desired for bio-detection. In this paper, we prepared a new kind of luminescent europium nanoparticles by a co-precipitation-condensation method. The luminescent europium complex $Eu(tta)_3{\cdot}bpt$ (tta = thenoyltrifluoroacetonate; bpt = 2-(*N,N*-di-ethylanilin-4-yl)-4,6-bis(pyrazol-1-yl)-1,3,5-triazine) was used as the active material, being encapsulated in the nanoparticles formed from 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyltrimethoxysilane (PFOTS) and poly(styrene-co-methyl methacrylate) [P(ST-co-MMA)]. The prepared nanoparticles not only can be well dispersed in water but also were of high photostability. Importantly, the nanoparticles displayed maximal excitation wavelength at 425 nm as well as an extended excitation wavelength up to 480 nm and a quantum yield for Eu^{3+} luminescence of 0.22 (λ_{ex} = 425 nm, room temperature).

1. Introduction

Luminescent substances have been intensively applied in the field of bio-detection in fluorescence immunoassays [1–5], DNA detection [6–11] and bio-imaging [12–20]. Luminescent lanthanide complexes are promising for bio-detection because of their long luminescence lifetimes, large Stokes shifts, and narrow-line emission [21–24]. More importantly, when luminescent lanthanide complexes are used as bio-probes, the interference of short-lived background fluorescence from the biological tissue and light scattering from the instrument on the luminescence imaging is so little that an enhanced signal-to-noise ratio is obtained. Unfortunately, most luminescent lanthanide complexes are excited by ultraviolet (UV) light [25,26], which damages biological samples and has a short penetration depth. To overcome these problems, it is necessary to develop luminescent lanthanide complexes that respond to longer wavelengths of light, such as visible light [27–34]. Furthermore, to realize the application of luminescent lanthanide complexes in bio-detection, bio-probes based on luminescent lanthanide complexes with long excitation wavelength need to be developed.

A few europium complexes excited by visible light have been reported [27–34], typical examples including $Eu(tta)_3{\cdot}dpbt$ [27] (tta = thenoyltrifluoroacetonate; dpbt = 2-(*N,N*-diethylanilin-4-yl)-4,6-bis(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine) (Scheme 1a), $Eu(tta)_3{\cdot}dmbpt$ [29] (dmbpt = 2-(*N,N*-diethyl-2,6-dimethylanilin-4-yl)-4,6-bis(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine) (Scheme 1b), $Eu(tta)_3{\cdot}bpt$(bpt = 2-(*N,N*-di-ethylanilin-4-yl)-4,6-bis(pyrazol-1-yl)-1,3,5-triazine) (Scheme 1c), and $Eu(tta)_3{\cdot}mpbt$ [30] (mpbt = 2-(*N,N*-diethylanilin-4-yl)-4,6-bis(3-methylpyrazol-1-yl)-1,3,5-triazine) (Scheme 1d). Their photophysical data is summarized in Table 1. $Eu(tta)_3{\cdot}bpt$, with the longest wavelength and highest quantum efficiency, became the best choice for luminescence imaging among these europium complexes. Moreover, the way of energy transfer for $Eu(tta)_3{\cdot}bpt$ being probably dominated by a singlet energy-transfer pathway breaks the restriction of excitated-triplet-state energy level and contributes to the excellent visible-light-sensitized luminescence efficiency. However, because of its bad solubility in water and instability in polar solvents, such as DMF, THF and alcohols, it is difficult to directly apply $Eu(tta)_3{\cdot}bpt$ as a bio-probe in bioassay applications. Therefore, to meet the demand of applying $Eu(tta)_3{\cdot}bpt$ as a bio-probe, treatment of $Eu(tta)_3{\cdot}bpt$ to solve these problems must be pursued.

One viable way to prepare colloidal nanoparticles based on the complex $Eu(tta)_3{\cdot}dpbt$ has been tried. The two-photon-excitation imaging of $Eu(tta)_3{\cdot}dpbt$ nanoparticles in live cancer cells was

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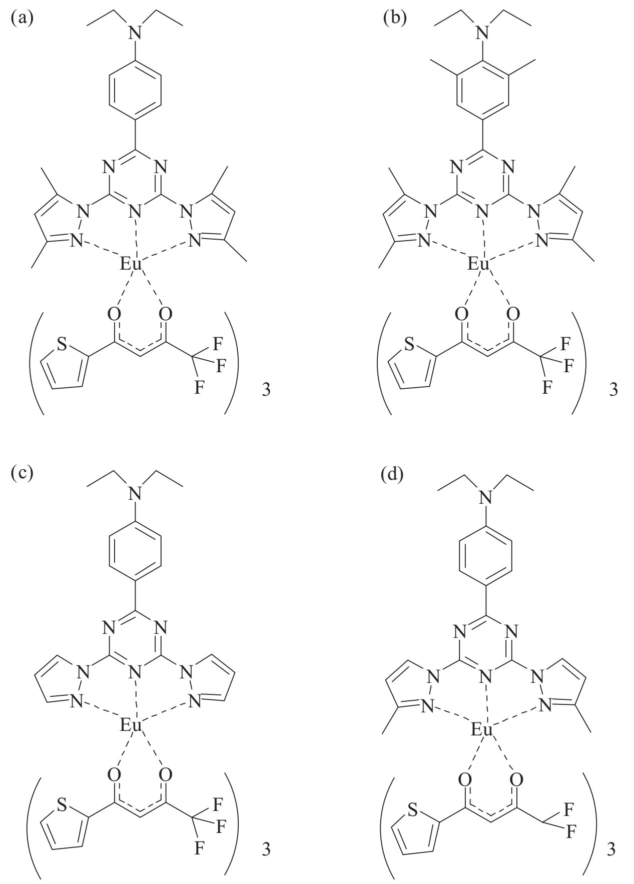

Scheme 1. Molecularstructures of Eu(tta)$_3$·dpbt (a), Eu(tta)$_3$·dmbpt (b), Eu(tta)$_3$·bpt (c) and Eu(tta)$_3$·mpbt (d).

reported by Wang *et al.*. [35–37]. The nanoparticles were prepared by encapsulating Eu(tta)$_3$·dpbt in hydrophobic cores of water-dispersible biocompatible nanoparticles of poly(methyl methacrylate-co-methacrylic acid), showing good luminescence properties, dispersion stability, and photostability in water solution. However, the visible-light-sensitized luminescence properties of the complex Eu(tta)$_3$·dpbt in nanoparticles were still to be improved. Another way is preparing europium nanoparticles with the ligand dpbt, as presented by Yuan *et al.* [38–41]. Their preparation processes are mainly composed of two steps: first, the tetradentate β-diketonate-Eu^{3+}-dpbt complexes were covalently bound to silane derivatives to form functionalized precursors; second, the nanoparticles were obtained by the copolymerization of the above conjugates and silane reagents in a water-in-oil reverse microemulsion. However, some problems appeared in these nanoparticles, such as strong scattering to visible light ($\lambda > 450$ nm) and the weak absorption peak of europium complex in the UV–visible absorption spectrum.

Table 1
Photophysical data for Eu(tta)$_3$·dpbt, Eu(tta)$_3$·dmbpt, Eu(tta)$_3$·bpt and Eu(tta)$_3$·mbpt in toluene. Excitation maximal wavelengths (λ_{ex}), extinction coefficients (ε_{max}), fluorescence quantum yields (Φ), excitation maximal window (λ_T).

Compounds	λ_{ex} (nm)	Φ[a] (%)	λ_T (nm)	ε_{max} ($\times 10^4$ L·mol^{-1}·cm^{-1})
Eu(tta)$_3$·dpbt	402	0.35	443	6.3
Eu(tta)$_3$·dmbpt	409	0.40	460	1.1
Eu(tta)$_3$·mpbt	404	0.31	450	9.7
Eu(tta)$_3$·bpt	410	0.43	450	6.9

[a] The experimental uncertainty on δ is 10–15 (%).

Keeping the above problems in mind, in this work we prepared a new kind of hybrid nanoparticle based on the Eu(tta)$_3$·bpt complex (EuHNPS) by a co-precipitation-condensation method [42,43], in which 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyltrimethoxysilane (PFOTS) and poly(styrene-co-methyl methacrylate) [P(ST-co-MMA)] were used as matrix materials. The results demonstrated the nanoparticles displayed excellent long-wavelength-sensitized luminescent properties. Their maximal excitation wavelength was located at 425 nm, and their luminescence quantum yield was measured to be 0.22 (room temperature). The photostability of the prepared nanoparticles was also measured to check its future application in bio-detection.

2. Experimental

Materials and methods: 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyltrimethoxysilane (PFOTS) (PFOTS, 97%) was purchased from Matrix Scientific. Poly(styrene-co-methyl methacrylate) (P(ST-co-MMA), 40% styrene, Mw ~ 100,000–150,000) was purchased from Sigma–Aldrich. Hexadecyltrimethyl ammonium bromide (CTAB) (≥99%) was obtained from Acros Organics. Other chemicals of AR grade were used as received. Elemental analysis of EuHNPS was carried out with an Elementarvario EL elemental analyzer. Eu and Si contents of EuHNPS were determined by an inductively coupled plasma atomic emission spectrometer (ICP). Transmission electron microscopy (TEM) was taken on a transmission electron microscope (JEM 2000FX, Hitachi). Energy dispersive X-ray spectroscopy (EDX) measurements, scanning transmission electron microscope (STEM), and elemental mapping were carried out on a field emission transmission electron microscope (Tecnai G2F20 U-TWIN) with an energy dispersive X-ray spectroscope (EDX, EPMA-1600). UV–vis absorption and photoluminescence measurements were carried out on an absorption spectrometer (UV-2550, SHIMADZU) and a fluorescence spectrophotometer (RF-5301PC, SHIMADZU). The photoluminescence decay kinetics of EuHNPS colloidal nanoparticles were measured by FLS920 (Edinburgh Instruments). Luminescence quantum yield (Φ) of the prepared nanoparticles was determined according to the method described by Demas and Grosby [44], using DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran) in *n*-propanol ($\Phi = 0.57 \pm 0.02$) as the reference. The photo-bleaching experiments were carried out on a fluorescence spectrophotometer using a 150 W xenon lamp as an excitation source. Eu(tta)$_3$·bpt was synthesized according to the method reported previously [30].

Preparation of EuHNPS: A colloidal solution of EuHNPS was synthesized by a co-precipitation-condensation method [42,43]. In a typical experiment, 2.0 mL of acetone solution containing PFOTS (1.14×10^{-3} mol L^{-1}), P(ST-co-MMA) (0.12 g L^{-1}), and Eu(tta)$_3$·bpt (1.20×10^{-4} mol L^{-1}) was dropwise added into an aqueous solution of CTAB (7.0 mL, 1.40×10^{-3} mol L^{-1}) with stirring at room temperature. The mixture was then stirred for another 30 min to obtain a yellow colloidal solution. Subsequently, the as-prepared colloidal solution was centrifuged at $10,000 \times g$ to remove large particles. The supernatant was then centrifuged at $35,000 \times g$, and the obtained precipitation was re-dispersed in 8 mL of water to prepare a colloidal solution of EuHNPS. This process was repeated to remove most of the CTAB and produce a stable colloid solution of EuHNPS (about 50.2 mg L^{-1}, corresponding to a yield of EuHNPS of 26 wt%) with an average diameter of 60 nm as measured by TEM. A colloidal solution of nanoparticles was also prepared by the aforementioned processes except for the addition of P (ST-co-MMA) and PFOTS, respectively.

PFOTS and Silicon content determination of EuHNPS: the 25 mL EuHNPS solution was centrifuged at $35,000 \times g$ to collect the resulting EuHNPS precipitate, which was then placed in the