

Synthesis and characterization of novel thermoresponsive fluorescence complexes based on copolymers with rare earth ions



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ABSTRACT

The thermo-sensitive and fluorescent complexes containing Eu(III) or Tb(III) were synthesized and characterized, in which cholesterol-*g*-poly(*N*-isopropylacrylamide) (PNIPAM) copolymer was used as a polymer ligand. The results from the experiments indicated that Eu(III) or Tb(III) was bonded to nitrogen and oxygen atoms in the polymer chain. The fluorescence lifetimes of the powdered Eu(III) and Tb(III) complexes was 11.48 ms and 10.71 ms, respectively. The maximum emission intensity of the PNIPAM–Eu(III) complex at 613 nm and the PNIPAM–Tb(III) complex at 545 nm were enhanced about 11.1 and 11.3 times compared with that of the corresponding rare earth ions, respectively. Additionally, the lower critical solution temperature (LCST) of complexes were slightly higher than those of the copolymers.

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1. Introduction

The rare earth ions in a ligand-free cationic state, have a lower absorption/emission efficiency in the visible region of the spectrum, but when they bound to organic ligands of high molar absorption coefficients and form the rare earth complexes, their luminous intensity can be enhanced drastically [1–4]. This phenomenon is mainly attributed to the organic ligands which absorb ultraviolet ray energy and transfer to central rare earth ions, so that the characteristic fluorescence will be enhanced. Due to the unique long luminescence lifetimes, sharp emission bands and photostability [5–10], the lanthanide-based complexes have generated much research interest as a new optical components, especially those containing europium (III) or terbium (III), which possess high color purity and produce red-emission (Eu³⁺) and green-emission (Tb³⁺) are often used as probes and labels in many fields such as materials science, biological technology and photoluminescent devices [11–15].

It is an attractive idea to functionalize lanthanide-based complexes with stimuli-responsive polymers, and the obtained materials can be used to control the release of guest molecules in immunodiagnostic assays under external stimuli, such as temperature, pH, ionic strength [16–18]. Perhaps the most extensively

studied stimuli-responsive complexes are these modified poly(*N*-isopropylacrylamide) (PNIPAM). PNIPAM is a well-known thermoresponsive polymer which that can change its appearance from a clear solution to a turbid suspension in water at a relatively lower critical solution temperature (LCST) of 32 °C (near that of the human body) [19]. Herein we synthesized a new class of composite complexes via conjugating the fluorescent Eu³⁺ or Tb³⁺ with thermosensitive and biocompatible cholesterol-*g*-PNIPAM copolymers. Some polymers such as polymethylmethacrylate [20,21], styrene-*co*-butylmethacrylate [22], and polyvinylpyrrolidone (PVP) [23,24] were doped with Eu³⁺ and Tb³⁺ forming the complexes, in our previous papers we have reported a new composite materials from cellulose-*g*-PNIPAM polymers doped with Eu³⁺ ions [25], which had large Stokes shifts and long luminescence lifetimes. Once coupled to cholesterol-*g*-PNIPAM, the complexes should become a robust functional probe and is suitable for optical imaging applications.

2. Experimental

2.1. Materials and instrumentation

N-isopropylacrylamide (Aldrich, 98%) was recrystallized twice from a hexane/benzene mixture (3/2, v/v). Tris(2-(dimethylamino)ethyl)amine (Me₆TREN) was synthesized from tris(2-ami-

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no) ethyl amine (TREN, Aldrich, 99%) according to the literature [26]. CuCl (Aldrich, 99%) was washed successively with acetic acid and ether and then dried and stored under nitrogen. Eu_2O_3 and Tb_2O_3 (Aldrich, 99.99%), 2-Chloropropionyl chloride (Acros, 97%) and Cholesterol (Aldrich, 98%) were obtained commercially.

The ^1H nuclear magnetic resonance (NMR) spectra of monomers and polymers in CDCl_3 were obtained on a Varian Unity 400 NMR spectrometer. The molecular weights (M_n) and polydispersity (M_w/M_n) were measured by a gel permeation chromatograph (GPC) using a Waters 510 pump and a Model 410 differential refractometer at 25 °C. THF was used as a mobile phase at a flow rate of 1.0 mL min^{-1} . The LCSTs of the polymer solutions were determined by turbidimetry, using Shimadzu-1240 UV-Vis spectrophotometer with a heating rate of 0.1 °C min^{-1} . FTIR spectra were recorded on a Shimadzu IR-8400S spectrometer. Raman studies have been carried out at the wavelength excitation of 1064 nm using a FT Raman Bruker RFS 100 spectrophotometer. A Shimadzu RF-5301PC fluorescence spectrophotometer was used to obtain fluorescence spectra and lifetime measurements. Quantum yields were determined by comparison of the total light emitted from the solutions to the total light emitted from a known standard $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ [27]. The XPS spectra (Mg $K\alpha$) were recorded with a VG Scientific ESCALAB instrument. Elemental analysis (C, H, N) was performed on a (American Perkin-Elmer) 2400II CHNS/O elemental analyzer. The lanthanide content was determined by EDTA titration.

2.2. General procedure for cholesterol-g-PNIPAM synthesis

Cholesterol-g-PNIPAM was synthesized as follows (Scheme 1). A mixture of CuCl and Me_6TREN in 7:1 (v/v) DMF/ H_2O (1.0 mL)

was placed on one side of an H-shaped ampoule glass and stirred at room temperature. NIPAM and initiator in DMF (3.0 mL) were placed on the other side of the ampoule. Nitrogen was bubbled through both mixtures for 5 min to remove any oxygen. Three freeze-pump-thaw cycles were performed to degas the solution. Both mixtures were placed in an oil bath and thermostated at 80 °C for 2 h. The polymerization was terminated by exposing the mixture to air. The reaction mixture was diluted with DMF and purified using a neutral Al_2O_3 column. Next, the solvent was evaporated, and the remainder was dialyzed in DMF using a cellophane tube (Spectra/Por6, Membrane). Finally, the solvent was evaporated and a white product was collected by filtration and dried in a vacuum oven overnight (conversion rate 30.2%, $M_n = 4000 \text{ g mol}^{-1}$, $M_w/M_n = 1.08$).

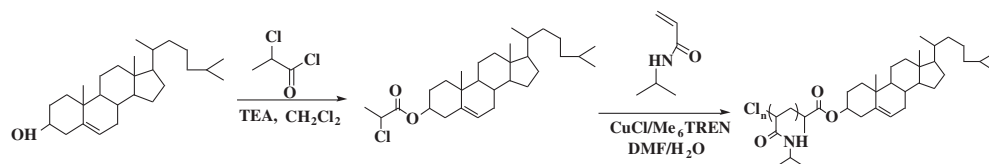
2.3. Synthesis of cholesterol-g-PNIPAM/Eu(III) or Tb(III) complexes

A solution of EuCl_3 or TbCl_3 and PNIPAM ($W_{\text{RE}^{3+}} : W_{\text{PNIPAM}} = 0.08 : 1$) in ethanol was added to a flask. The mixture was stirred with a magnetic stirring bar for 24 h. The product was purified and then dried under vacuum at room temperature, yielding the cholesterol-g-PNIPAM/Eu(III) complexes.

3. Results and discussion

3.1. Synthesis and characterization of complexes

Fig. 1 showed the ^1H NMR spectra of 2-chloropropionate cholesterolyl initiator and the product. In Fig. 1A, the peaks located at 4.42 ppm and 1.65 ppm corresponded to the protons next to the



Scheme 1. Cholesterol-g-PNIPAM synthesis by ATRP.

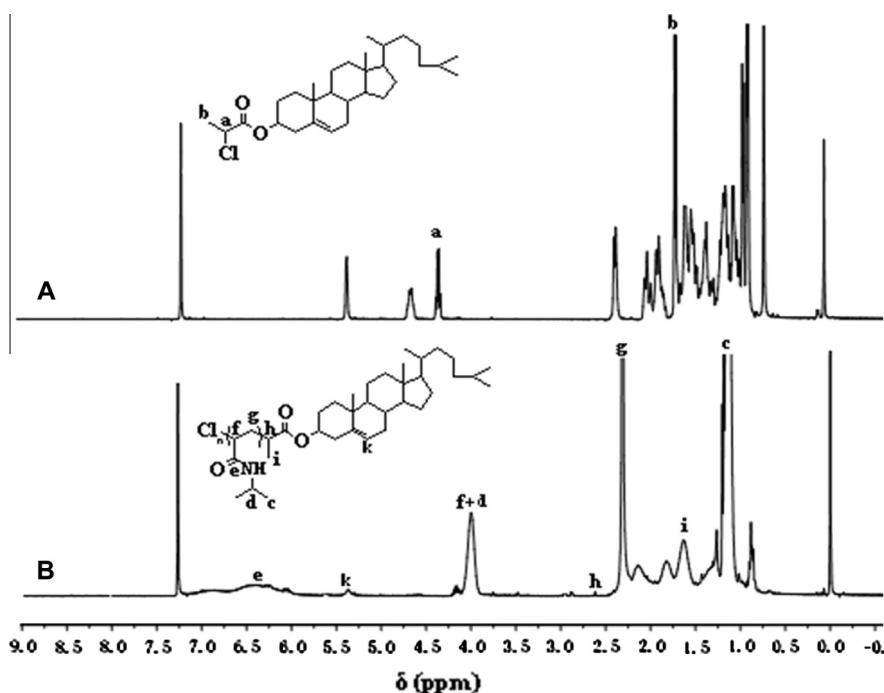


Fig. 1. ^1H NMR spectra in CDCl_3 of the (A) 2-chloropropionate cholesterolyl initiator and (B) cholesterol-g-PNIPAM polymer.

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