



Near-infrared luminescent erbium complexes with 8-hydroxyquinoline-terminated hyperbranched polyester

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ABSTRACT

Novel 8-hydroxyquinoline-terminated hyperbranched polyesters (1-HBPQ and 2-HBPQ) were synthesized and characterized by $^1\text{H-NMR}$ and UV-Vis analyses. Then, two erbium complexes (1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ) were prepared by using 1-HBPQ or 2-HBPQ as the macromolecular ligand and 8-hydroxyquinoline (HQ) as a second ligand. The FTIR spectra and UV-Vis absorption spectra confirmed that both the macromolecular ligand and the second ligand were successfully coordinated with Er^{3+} ions. The erbium complexes emitted intense near-infrared luminescence at about 1530 nm, which corresponds to the $^4I_{13/2}$ - $^4I_{15/2}$ transition of Er^{3+} ions. Moreover, their full width at half maximum (FWHM) values were greater than 80 nm. The erbium complexes exhibited good solubility in conventional solvents and excellent near-infrared luminescence properties, indicating their promising potential as gain medium materials in optical amplification devices.

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1. Introduction

Optical waveguide amplifier is an important device in the optical transmission field, which can be used to amplify light signals [1,2]. Gain medium is a key material in optical waveguide amplifier device and has been widely investigated [3–5]. Luminescence materials containing trivalent erbium ion (Er^{3+}) are regarded as excellent gain medium materials due to their near-infrared luminescence emission around 1550 nm attributed to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ion exactly corresponding to the low-loss transmission window of optical fibers (1500–1650 nm) [6–10]. It is crucial to prepare luminescence materials with high Er^{3+} ion content and strong absorption to obtain high gain. At present, Er^{3+} ions are usually doped directly in inorganic matrixes (glass, oxides films) while fabricating amplifiers [11,12]. In these Er^{3+} -doped inorganic materials, Er^{3+} ion content is very low due to the poor compatibility between Er^{3+} ions and the inorganic bases. Moreover, the 4f-4f transitions of the Er^{3+} ions are partly forbidden, leading to low absorption intensity of Er^{3+} -doped inorganic materials. Consequently, Er^{3+} -doped inorganic gain materials often show weak luminescence and low gain. A useful strategy to overcome these drawbacks is to design and prepare suitable organic ligands

to coordinate with Er^{3+} ions to obtain erbium complexes. In these complex systems, the organic ligands can absorb energy efficiently and excite the Er^{3+} ions via an energy transfer from the organic ligands to Er^{3+} ions, and then the complexes can emit strong luminescence of Er^{3+} ions, which is known as the “antenna effect”.

8-Hydroxyquinoline (HQ) is a highly suitable chelating ligand for the Er^{3+} ions as its energy matches well with that of the Er^{3+} ion, and also the corresponding Er^{3+} complex exhibits strong near-infrared emission [13–16]. However, the low-molecular lanthanide complexes often display poor physicochemical stability, poor processability and limited photostability. On the other hand, polymer materials are ideal as organic ligands for lanthanide ions due to their many outstanding properties, such as excellent thermal and chemical stability, versatility, processability, etc. [17,18]. Thus, developing new polymer ligands covalently bonded with HQ and then coordinating with Er^{3+} ions to achieve erbium complexes would resolve problems associated with the Er^{3+} complex coordinated with HQ alone. Some attempts have been made to synthesize polymer molecules bonded with HQ structure and investigate luminescence properties of their corresponding lanthanide complexes in recent years. For example, Meyers et al. [19] reported the preparation of poly(norbornene) and poly(cyclooctene) bearing 8-hydroxyquinoline side chains. The corresponding ytterbium complex showed the characteristic luminescence of Yb^{3+} ions in the near-infrared region. In addition, Luo et al. [20] synthesized a polymer ligand by copolymerization of a polymerizable HQ

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derivative with N-vinylcarbazole (NVK), which was then coordinated with Er^{3+} ions to form erbium complexes. The resulting erbium complexes displayed intense near-infrared luminescence of the Er^{3+} ions when excited by UV-Vis light. However, the reported polymer ligands containing HQ structures are usually based on linear polymer backbones [19–22].

Different from linear polymers, hyperbranched polymers have globular molecular structures, which make them show excellent solubility and low melt viscosities due to lack of restrictive inter-chain entanglements [23–27]. More importantly, hyperbranched polymers usually have a multitude of highly reactive ends, such as hydroxyl group and amino group, which could be easily modified by covalently attaching desirable functional groups. Therefore, our aim here is to attach HQ functional groups to the ends of a hyperbranched polymer by chemical reactions so as to produce a hyperbranched polymer ligand with a large number of HQ end-groups, which are expected to chelate more Er^{3+} ions than traditional linear polymers. Also, the new erbium complexes based on hyperbranched polymer are expected to have intense near-infrared luminescence, as well as good solubility.

Among hyperbranched polymers, hyperbranched polyesters (HBP) are the most extensively investigated type due to their ease of synthesis and large number of highly reactive hydroxyl end-groups [28–31]. Here, we developed a new approach to prepare 8-hydroxyquinoline-terminated hyperbranched polyesters (1-HBPQ and 2-HBPQ) by attaching HQ groups on the end branches of HBP by the reaction of sulphonyl chloride groups of 8-hydroxyquinoline-5-sulphonyl chloride (HQ-SO₂Cl) and hydroxyl end groups of HBP. Furthermore, two novel erbium complexes (1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ) were prepared and characterized. The near-infrared luminescence properties of these erbium complexes were further investigated.

2. Experimental

2.1. Materials

8-Hydroxyquinoline (HQ) was obtained from Shenyang Chemical Reagent Factory. Chlorosulfonic acid (ClSO₃H), *p*-toluenesulfonic acid (*p*-TSA), pyridine, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetone, anhydrous ether, ethyl acetate, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,1,1-Tris (hydroxymethyl) propane (TMP), 4,4-bis(4-hydroxyphenyl) valeric acid (DPA), 2,2-bis(hydroxymethyl) propionic acid (DMPA), tetra-*n*-butyl titanate (TBT), succinic anhydride and tin chloride were obtained from Aladdin Reagent Co.. Erbium nitrate hexahydrate ($\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was purchased from Shandong Qingda Fine Chemical Factory. All chemical reagents were of analytical reagent grade.

2.2. Measurements

Fourier transform infrared spectra (FTIR) were recorded on a Thermo Nicolet Nexus 470 FT-IR spectrophotometer in the 4000–400 cm^{-1} region using KBr pellets at room temperature. Nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were obtained in deuterated dimethyl sulfoxide (DMSO-*d*₆) on a Varian ADVANCE 400 M spectrometer with tetramethylsilane (TMS) as internal reference. The ultraviolet-visible (UV-Vis) absorption spectra were measured by a Cary5000 spectrophotometer at room temperature. The Er^{3+} ion contents were determined by a Leeman Prodigy inductively coupled plasma spectrometer (ICP). Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. The fluorescence excitation and emission spectra were measured

on a QM/TM steady state and transient state fluorescence spectrometer. The concentrations of the Er^{3+} complex solutions in DMF were 1×10^{-4} mol/L.

2.3. Synthesis procedure

2.3.1. Synthesis of 8-hydroxyquinoline-5-sulphonyl chloride (HQ-SO₂Cl)

A mixture of HQ (0.4000 g, 2.76 mmol) and ClSO₃H (5.00 ml, 75.22 mmol) was heated to 45 °C under nitrogen atmosphere and stirred for 4 h. Then, the reaction mixture was poured into ice water and a yellow precipitate was formed. The precipitate was filtered off and dried at 80 °C for 12 h in the vacuum oven to obtain HQ-SO₂Cl as a pale yellow powder. IR (KBr) ν/cm^{-1} 3404 (OH), 3081 (C-H), 1627, 1603, 1556, 1503, 1416 (8-HQ ring), 1384 (S=O, *asym.*), 1229 (C-O), 1191 (S=O, *sym.*); ¹H NMR (DMSO-*d*₆) δ 7.32 (d, 1H, 8-HQ), 8.05 (d, 1H, 8-HQ), 8.11 (q, 1H, 8-HQ), 9.06 (d, 1H, 8-HQ), 9.77 (d, 1H, 8-HQ), 12.09 (s, 1H, OH); ¹³C NMR (DMSO-*d*₆) δ 113.88, 122.89, 126.54, 128.69, 130.08, 135.80, 144.63, 145.57, 149.60.

2.3.2. Synthesis of hydroxyl-terminated hyperbranched polyester (1-HBP and 2-HBP)

1-HBP was synthesized by the following procedure: A mixture of TMP (2.0000 g, 14.91 mmol), DMPA (17.9946 g, 134.16 mmol) and *p*-TSA (0.1000 g, 0.53 mmol) was heated to 140 °C under nitrogen atmosphere and stirred for 1 h. Then, the reaction mixture was stirred continuously for 1 h under reduced pressure, and then was purified by dissolution and precipitation with acetone and anhydrous ether. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to obtain 1-HBP as a white powder.

2-HBP was synthesized by the following procedure: A mixture of TMP (2.0000 g, 14.91 mmol), DPA (12.8041 g, 44.72 mmol) and TBT (2.00 ml, 5.85 mmol) were heated to 200 °C under nitrogen atmosphere and stirred for 5 h. Then, the reaction mixture was stirred continuously for 2 h under reduced pressure, and then was purified by dissolution and precipitation with THF and deionized water. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to obtain 2-HBP as a yellow powder.

2.3.3. Synthesis of 8-hydroxyquinoline-terminated hyperbranched polyester (1-HBPQ and 2-HBPQ)

The synthesis procedure for 1-HBPQ was as follows: 1-HBP (0.2000 g, 0.17 mmol) was dissolved in 6.00 ml dry pyridine, and then a solution of HQ-SO₂Cl (0.4960 g, 2.04 mmol) in 4.00 ml dry pyridine was added dropwise with stirring. The resulting mixture was heated to 30 °C under nitrogen atmosphere and stirred for 16 h, and then was precipitated in ethyl acetate. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to obtain 1-HBPQ as a yellow powder.

The synthesis procedure for 2-HBPQ was as follows: 2-HBP (0.2000 g, 0.21 mmol) was dissolved in 8.00 ml dry pyridine, and then a solution of HQ-SO₂Cl (0.3114 g, 1.28 mmol) in 4.00 ml dry pyridine was added dropwise with stirring. The resulting mixture was heated to 30 °C under nitrogen atmosphere and stirred for 16 h, and then was precipitated in anhydrous ether. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to obtain 2-HBPQ as a yellow powder.

2.3.4. Synthesis of erbium complexes base on 8-hydroxyquinoline-terminated hyperbranched polyester (1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ)

The synthesis procedure for 1-HBPQ- Er^{3+} -HQ was as follows: 1-HBPQ (0.2000 g, 0.05 mmol) was dissolved in 3.00 ml dry DMF, and then a solution of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.3021 g, 0.65 mmol) and HQ (0.2831 g, 1.95 mmol) in 2.00 ml dry DMF was added under

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