Accepted Manuscript

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

Dan Liu, Chengjian Li, Yaling Xu, Dapeng Zhou, Hongmei Wang, Ping Sun, Huasheng Jiang

PII: S0032-3861(17)30185-4

DOI: 10.1016/j.polymer.2017.02.061

Reference: JPOL 19462

To appear in: *Polymer*

Received Date: 5 October 2016

Revised Date: 26 January 2017

Accepted Date: 20 February 2017

Please cite this article as: Liu D, Li C, Xu Y, Zhou D, Wang H, Sun P, Jiang H, Near-infrared luminescent erbium complexes with 8-hydroxyquinoline-terminated hyperbranched polyester, *Polymer* (2017), doi: 10.1016/j.polymer.2017.02.061.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





Erbium Complexes with 8-hydroxyquinoline-terminated Hyperbranched Polyester

Macromolecular ligand



Near-infrared Luminescent Erbium Complexes with 8-Hydroxyquinoline-terminated Hyperbranched Polyester

Dan Liu^{*}, Chengjian Li, Yaling Xu, Dapeng Zhou, Hongmei Wang, Ping Sun, Huasheng Jiang

College of Biological, Chemcial Sciences and Engineering, Jiaxing University, Jiaxing 314001, P. R. China

^{*} Corresponding author.

E-mail address: liudan1029@126.com

ABSTRACT

Novel 8-hydroxyquinoline-terminated hyperbranched polyesters (1-HBPQ and 2-HBPQ) were synthesized and characterized by ¹H-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 1530nm, which corresponds to the ${}^{4}I_{13/2}{}^{-4}I_{15/2}$ 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.

Keywords: Near-infrared; Erbium complexes; Hyperbranched polyester; 8-Hydroxyquinoline; Luminescence

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 ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er^{3+} ion exactly corresponding to the low-loss transmission window of optical fibers (1500-1650 nm) [6-10]. Thus, 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 good energy matches well with Er^{3+} ion, and 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 HO and then coordinating with Er³⁺ ions to achieve erbium complexes would resolve problems associated with ErQ₃ 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 Yb³⁺ ions in the near-infrared region. In addition, Luo et al. [20] synthesized a polymer ligand by copolymerization of a polymerizable HQ derivative with N-vinylcarbazole (NVK), which was then coordinated with Er³⁺ ions to form erbium complexes. The resulting erbium complexes displayed intense near-infrared luminescence of the Er³⁺ ions when excited by UV-Vis light. However, the reported polymer ligands reported 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 interchain 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-Er³⁺-HQ or 2-HBPQ-Er³⁺-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*-dimethlyacetamide (DMAc), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetone, anhydrous ether, ethyl acetate, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,1,1-T ris (hydroxymethyl) propane (TMP), 4,4-bis(4-hydroxyphenyl) valeric acid (DPA), 2,2-bis(hydroxymethyl) propionic acid (DMPA), tetra-n-butyl titanate (TBT), sussinic anhydride and tin chloride were obtained from Aladdin Reagent Co.. Erbium nitrate hexahydrate ($Er(NO_3)_3 \cdot 6H_2O$) 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 а 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 13 C-NMR) were obtained in deuterated dimethyl sulfoxide (DMSO-d₆) on a Varian ADVENCE 400M spectrometer with tetramethylsilane (TMS) as internal reference. The ultraviolet-visible (UV-Vis) absorption spectra were measured by a Cary5000 spectrophotometer at room temperature. The Er³⁺ 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 DMF solution of the Er^{3+} complexes 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 CISO₃H (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) v/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-d₆) 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-d₆) 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: 0.2000 g 2-HBP (0.2000 g, 0.21 mmol) was dissolved in 8.00 ml dry pyridine, and then a solution of (0.3114 g, 1.28 mmol) HQ-SO₂Cl 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

 $Er(NO_3)_3 \cdot 6H_2O$ (0.3021 g, 0.65 mmol) and HQ (0.2831 g, 1.95 mmol) in 2.00 ml dry DMF was added under constant stirring. The reaction solution was stirred for 2 h at 80 °C, and then 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- Er^{3+} -HQ as a yellow powder.

The synthesis procedure for 2-HBPQ- Er^{3+} -HQ was as follows: 2-HBPQ (0.2000 g, 0.09 mmol) was dissolved in 3.00 ml dry DMF, and then a solution of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2537 g, 0.55 mmol) and HQ (0.2394 g, 1.65 mmol) in 2.00 ml dry DMF was added under constant stirring. The reaction solution was stirred for 2 h at 80 °C, and then precipitated in ethyl acetate. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to 2-HBPQ- Er^{3+} -HQ as a yellow powder.

2.3.5. Synthesis of other erbium complexes $(1-HBPQ-Er^{3+}, 2-HBPQ-Er^{3+})$ and $Er^{3+}-HQ$

For comparison purposes, 1-HBPQ- Er^{3+} , 2-HBPQ- Er^{3+} and Er^{3+} -HQ were also prepared. The synthesis procedure for 1-HBPQ- Er^{3+} was as follows: 1-HBPQ (0.2000 g, 0.05 mmol) was dissolved in 3.00 ml dry DMF. Then a solution of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.3021 g, 0.65 mmol) in 2.00 ml dry DMF was added. The mixture was stirred for 2 h at 80 °C, and then 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- Er^{3+} as a yellow powder.

The synthesis procedure for 2-HBPQ- Er^{3+} was as follows: 2-HBPQ (0.2000 g, 0.09 mmol) was dissolved in 3.00 ml dry DMF. Then a solution of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2537 g, 0.55 mmol) in 2.00 ml dry DMF was added. The mixture was stirred for 2 h at 80 °C, and then precipitated in ethyl acetate. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to obtain 2-HBPQ- Er^{3+} as a yellow powder.

The synthesis procedure for Er^{3+} -HQ was as follows: HQ (0.2831 g, 1.95 mmol) was dissolved in 3.00 ml dry DMF. Then a solution of $Er(NO_3)_3 \cdot 6H_2O$ (0.3021 g, 0.65 mmol) in 2.00 ml dry DMF was added. The reaction solution was stirred for 2 h at 80 °C, and then precipitated in ethanol. The precipitate was filtered off, and dried at 80 °C for 12 h in the vacuum oven to obtain Er^{3+} -HQ as a light yellow powder.

3. Results and discussion

3.1. Design, synthesis and characterization of 8-hydroxyquinoline-terminated hyperbranched polyester (1-HBPQ and 2-HBPQ)

In order to obtain new organic ligands with many HQ end-groups capable of coordinating with Er^{3+} ions, two novel hyperbranched polyester ligands, 1-HBPQ and 2-HBPQ, have been designed and synthesized as shown in Scheme 1.



Scheme 1. Synthesis of 1-HBPQ and 2-HBPQ.

HQ-SO₂Cl was prepared by chlorosulfonation reaction of HQ with ClSO₃H as a chlorosulfonation agent. The structure of HQ-SO₂Cl was characterization by FTIR, ¹H-NMR and ¹³C-NMR spectra, as shown in Fig. S1 to Fig. S3, which are consistent with the reported literature [32]. It can be confirmed that HQ-SO₂Cl is successfully synthesized from HQ.



Fig. 1. FTIR spectra of (a) TMP, (b) DMPA and (c) 1-HBP.

Fig. 1 displays the FTIR spectrum of 1-HBP, as well as the spectra of the two reactants, TMP and DMPA. The absorption peak located at 1691 cm⁻¹ corresponding to the C=O stretching vibration of carboxyl group of DMPA was absent in the spectrum of 1-HBP; while a new peak at 1727 cm⁻¹ appeared, which belonged to the C=O stretching vibration of ester group of 1-HBP. Fig. 2 presents the FTIR spectra of TMP, DPA and 2-HBP, respectively. Similarly, the absorption peak at 1703 cm⁻¹ attributed to the C=O stretching vibration of carboxyl group of DPA disappeared in the spectrum of 2-HBP, while a new peak at 1712 cm⁻¹ corresponding to the C=O stretching vibration of eater group of 2-HBP was observed. Furthermore, the ¹H-NMR spectra of 1-HBP and 2-HBP and the peak assignments are given in Fig. 3a and Fig. 4a, respectively. The above FTIR and ¹H-NMR results confirmed that 1-HBP and 2-HBP were successfully synthesized.

Then, 1-HBP and 2-HBP were reacted with HQ-SO₂Cl to afford the desired products, 1-HBPQ and 2-HBPQ, respectively. Fig. 3b and Fig. 4b exhibit the ¹H-NMR spectra of 1-HBPQ and 2-HBPQ, respectively. In Fig. 3b, the peaks at 4.952 ppm and 4.639 ppm corresponding to the chemical shifts of terminal hydroxyl group

proton of 1-HBP were absent; while new peaks between 7.1 ppm to 12.5 ppm attributed to HQ structure appeared. The results demonstrated that the terminal hydroxyl groups of 1-HBP reacted with the -SO₂Cl groups of HQ-SO₂Cl, and HQ groups were successfully connected to the ends of 1-HBP molecules. The similar phenomenon was also observed in Fig. 4b. The new peaks in the range of 7.1 ppm to 12.5 ppm corresponding to HQ structure appeared, while the peak at 9.203ppm attributed to terminal hydroxyl group proton of 2-HBP disappeared, showing that 2-HBPQ was also successfully synthesized.



Fig. 2. FTIR spectra of (a) TMP, (b) DPA and (c) 2-HBP.



Fig. 3. ¹H-NMR spectra of (a) 1-HBP and (b) 1-HBPQ.



Fig. 4. ¹H-NMR spectra of (a) 2-HBP and (b) 2-HBPQ.

It is speculated that the UV-Vis absorption behaviors of 1-HBP and 2-HBP would change after attaching a large number of HQ groups with conjugated structures on the

hyperbranched polyester molecular structures. Hence, the UV-Vis absorption spectra of 1-HBPQ and 2-HBPQ were measured, as well as those of HQ, 1-HBP and 2-HBP. The results were presented in Fig. 5 and Fig. 6. As shown in Fig. 5, 1-HBP exhibits an absorption band from 200 nm to 270 nm due to the $n \rightarrow \pi^*$ electronic transition of carbonyl group of 1-HBP. HQ had a wide band from 200 nm to 400 nm corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of quinoline ring. Relative to 1-HBP and HQ, the absorption band of 1-HBPQ became obviously wider and was red-shifted. This could be attributed to the decrease in electron density around 1-HBP due to the introduction of a large number of the conjugated quinoline rings and the decrease of transition energy, which also indicates that the HQ structures had been successfully attached onto 1-HBP. Similarly, as shown in Fig. 6, 2-HBPQ displays a wider absorption band in comparison with 2-HBP because of the formation of a more conjugated system by the introduction of HQ structures into 2-HBP molecule. The ¹H-NMR spectra and the UV-Vis absorption spectrum results of 1-HBPQ and 2-HBPQ confirmed that HQ structures had been successfully attached onto 1-HBP and 2-HBP.



Fig. 5. UV-Vis spectra of (a) 1-HBP, (b) HQ and (c) 1-HBPQ.



Fig. 6. UV-Vis spectra of (a) 2-HBP, (b) HQ and (c) 2-HBPQ.

3.2. Synthesis and characterization of erbium complexes based on 8-hydroxyquinoline-terminated hyperbranched polyester $(1-HBPQ-Er^{3+}-HQ)$ and 2-HBPQ-Er³⁺-HQ)



1-HBPQ-Er³⁺-HQ or 2-HBPQ-Er³⁺-HQ

Scheme 2. Synthesis of 1-HBPQ-Er³⁺-HQ and 2-HBPQ-Er³⁺-HQ.

Two novel erbium complexes based on 8-hydroxyquinoline functional hyperbranched polyester (1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ) were prepared by using 1-HBPQ and 2-HBPQ as the macromolecular ligands, respectively, and HQ as a second ligand. The synthesis route of 1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ is given in Scheme 2. The Er^{3+} contents in the complexes prepared were measured by

ICP, and were founded to be 13.91 wt% for 1-HBPQ- Er^{3+} -HQ and 13.49 wt% for 2-HBPQ- Er^{3+} -HQ, as shown in Table 1. The results suggested that the obtained complexes have high Er^{3+} contents, which are much higher than the Er^{3+} complexes based on the linear polymer with 8-hydroxyquinoline end-groups (lower than 1.6 wt%) [20]. This can be due to the fact that the globular molecular structure ends of hyperbranched polyesters have abundant 8-hydroxyquinoline groups, which can chelate more Er^{3+} ions than traditional linear polymers. High Er^{3+} ion content is benefit for the Er^{3+} complexes to yield intense near-infrared luminescence.

Table 1. ICP^a and Elemental analysis data^a of 1-HBPQ-Er³⁺-HQ and

2-HBPQ-Er ³⁺ - 2	HQ.
-------------------------------	-----

Complexes	1-HBPQ-Er ³⁺ -HQ			2-HBPQ			
Element	С	Н	N	Er C	Н	N	Er
Found	45.13	2.80	8.58	13.91 48.49	3.02	8.19	13.49

a All the values are given in percentages.



Fig. 7. FTIR spectra of (a) HQ, (b) Er^{3+} -HQ, (c) 2-HBPQ and (d) 2-HBPQ- Er^{3+} -HQ.



Fig. 8. UV-Vis spectra of (a) HQ, (b) Er^{3+} -HQ, (c) 2-HBPQ, (d) 2-HBPQ- Er^{3+} and (e) 2-HBPQ- Er^{3+} -HQ.



Fig. 9. UV-Vis spectra of (a) HQ, (b) Er^{3+} -HQ, (c) 1-HBPQ, (d) 1-HBPQ- Er^{3+} and (e) 1-HBPQ- Er^{3+} -HQ.

In order to confirm the existence form of Er^{3+} ions in the complexes, the FTIR spectra of the complexes were investigated. Fig. 7 shows the FTIR spectra of HQ, Er³⁺-HQ, 2-HBPQ and 2-HBPQ-Er³⁺-HQ. Compared with the spectrum of HQ, a new peak at 494 cm⁻¹ attributed to the Er³⁺-O stretching vibration appeared in the spectrum of Er³⁺-HQ. Moreover, the peak ascribed to the C-O stretching vibration of HQ shifted to 1110cm⁻¹ from 1093 cm⁻¹. These results indicated that the O atom of HQ coordinated with Er^{3+} ion [33, 34]. In addition, the peak at 740 cm⁻¹ corresponding to the Er^{3+} -N stretching vibration appearing in the spectrum of Er^{3+} -HO suggested that the N atom of HQ also coordinated with Er^{3+} ion [35]. These results verified that both O and N atoms of HQ coordinated with Er^{3+} ion in the Er^{3+} -HQ system. Similar to the spectrum of Er³⁺-HQ, a new peak at 495 cm⁻¹ attributed to the Er³⁺-O stretching vibration was observed in the spectrum of 2-HBPQ-Er³⁺-HQ. Also, the relative intensity of the peak at 742 cm⁻¹ in the spectrum of 2-HBPQ-Er³⁺-HQ increased significantly in comparison with that of 2-HBPQ, which might be due to the formation of the Er^{3+} -N bonds. The above results verified that the Er^{3+} ions in the 2-HBPQ-Er³⁺-HQ system were not simply doped in the organic ligands, but coordinated with the O and N atoms of the ligands. However, it was difficult to ascertain whether the O and N atoms coordinated with Er³⁺ ions were from the second ligand HQ or the HQ groups of the macromolecular ligand 2-HBPQ. To further investigate the coordinated environment of Er³⁺ ions in the 2-HBPQ-Er³⁺-HQ system, the UV-Vis absorption spectrum of 2-HBPQ-Er³⁺-HQ was measured, as shown in Fig. 8. The UV-Vis absorption spectra of HO, Er^{3+} -HO and 2-HBPO- Er^{3+} are also presented in Fig. 8 for comparison. Relative to HQ, the absorption band of Er³⁺-HQ was obviously red-shifted due to the decrease electron density around HQ as a result of the formation of the coordination bonds between Er^{3+} ion and HQ [36]. In addition, two new weak peaks at 520 and 653 nm appeared in the absorption spectrum of Er^{3+} -HQ, which were attributed to the 4*f*-4*f* transitions of Er^{3+} ions corresponding to the ${}^{4}I_{15/2} \rightarrow {}^{2}H_{11/2}$ and ${}^{4}I_{15/2} \rightarrow {}^{4}F_{9/2}$ transitions, respectively. The results suggested that the absorption of Er^{3+} ions themselves was rather weak and the absorption of Er^{3+} -HQ was mainly from organic ligand HQ. Moreover, the absorption band of 2-HBPQ-Er³⁺

was red-shifted in comparison with that of 2-HBPQ, which indicated that 2-HBPQ coordinated successfully with Er^{3+} ion in the 2-HBPQ- Er^{3+} system. Compared with 2-HBPQ- Er^{3+} , the absorption band of 2-HBPQ- Er^{3+} -HQ was further red-shifted, indicating that HQ coordinated with Er^{3+} ion in the 2-HBPQ- Er^{3+} -HQ system. On the other hand, 2-HBPQ- Er^{3+} -HQ also showed a red-shifted absorption band in comparison with that of Er^{3+} -HQ, suggesting that 2-HBPQ was also involved in coordination reaction with Er^{3+} ion in the 2-HBPQ- Er^{3+} -HQ system. Therefore, it can be concluded that both the HQ groups of 2-HBPQ and the second ligand HQ coordinated with Er^{3+} ions in the 2-HBPQ- Er^{3+} -HQ system. Fig. 9 presents the UV-Vis spectra of 1-HBPQ- Er^{3+} -HQ, Er^{3+} -HQ, 1-HBPQ- Er^{3+} , HQ and 1-HBPQ, from which the similar conclusion could be drawn.

Based on the above results, it is evident that both the HQ groups of the macromolecular ligands and the second ligand HQ coordinated with Er^{3+} ions in the complexes. In order to ascertain the molecular structures of the complexes, the C, H and N contents in the complexes were measured by elemental analysis, and the results are listed in Table 1. Combining the results from FTIR, UV-Vis, ICP and elemental analysis, the possible molecular formula of the complexes is depicted in Scheme 2. The x/y values were calculated approximately and were close to 3:1 for 1-HBPQ- Er^{3+} -HQ and close to 4:1 for 2-HBPQ- Er^{3+} -HQ. The results indicated that the HQ groups of the macromolecular ligands could not be fully coordinated with Er^{3+} ions due to steric hindrance [20].

Furthermore, the solubility properties of 1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ were investigated. As seen from Table 2, the coordination reactions of 8-hydroxyquinoline-terminated hyperbranched polyesters and Er^{3+} ions had some influence on the solubilities of these polyesters in 7 conventional solvents. 1-HBPQ- Er^{3+} -HQ and 2-HBPQ- Er^{3+} -HQ displayed a slightly decreased solubility in comparison with non-coordinated polyester 1-HBPQ and 2-HBPQ. The results could be attributed to the increased rigidity of the polyester molecule due to the formation of many chelate rings after coordinating with Er^{3+} ions, which led to the difficult diffusion of solvent molecules in the polyester molecules. Nevertheless,

1-HBPQ-Er³⁺-HQ and 2-HBPQ-Er³⁺-HQ could still easily dissolve in DMF, DMAc and DMSO at room temperature, suggesting that the erbium complexes prepared have good solubility. As is well known, the excellent solubility is very important for the practical application of these luminescence materials. In addition, 1-HBPQ-Er³⁺-HQ could also dissolve in THF and acetone on heating. The above results confirmed that two new erbium complexes 1-HBPQ-Er³⁺-HQ and 2-HBPQ-Er³⁺-HQ with stable coordination structures, high Er³⁺ ion contents and excellent solubilities were successfully prepared.

Samples	DMF	DMAc	DMSO	THF	Acetone	Ethanol	Water
1-HBPQ	+	+	+	+	+	_	—
1-HBPQ-Er ³⁺ -HQ	+	+	+	+-	+-	—	—
2-HBPQ	+	+	+	+	_	—	—
2-HBPQ-Er ³⁺ -HQ	+	+	+	~	_	_	_

Table 2 Solubilities^a of 1-HBPQ-Er³⁺-HQ and 2-HBPQ-Er³⁺-HQ.

^a +, soluble; -, insoluble; +-, soluble on heating.

3.3. Near-infrared luminescence properties of erbium complexes based on 8-hydroxyquinoline-terminated hyperbranched polyester $(1-HBPQ-Er^{3+}-HQ)$ and 2-HBPQ-Er³⁺-HQ)



Fig. 10. (a) Excitation and (b) emission spectra of 1-HBPQ-Er³⁺-HQ.

Fig. 10 presents the excitation and emission spectra of 1-HBPQ-Er³⁺-HQ. The strong and broad excitation band centered at 403 nm in the excitation spectrum of 1-HBPQ-Er³⁺-HQ could be attributed to the absorption of ligands, while the weak and

sharp peaks at 527, 654 and 987 nm are due to the 4*f*-4*f* transitions of Er^{3+} ions, corresponding to the ${}^{4}I_{15/2} \rightarrow {}^{2}H_{11/2}$, ${}^{4}I_{15/2} \rightarrow {}^{4}F_{9/2}$ and ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$ transitions, respectively. This result indicated the emission of 1-HBPQ- Er^{3+} -HQ was mainly sensitized by the absorption of ligands rather than that of Er^{3+} ions themselves. Under excitation at 403nm, 1-HBPQ- Er^{3+} -HQ exhibited a broad emission band centered at 1528 nm attributed to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er^{3+} ion. This emission band corresponds to the wavelength of the low-loss transmission window in silica telecommunication fibers, which suggests that 1-HBPQ- Er^{3+} -HQ would have the potential applications in the optical amplification field. Moreover, it is worth pointing out that the full width at half maximum (FWHM) of 1-HBPQ- Er^{3+} -HQ was as wide as 85 nm, which is much wider than that of other reported Er^{3+} -containing materials, such as Er^{3+} -doped tellurite glass (66 nm) [37] and polydentate hemispherand organic cage complexes (70 nm) [38]. Such wide FWHM could enable a wide gain bandwidth for optical amplification.





Fig. 11. (a) Excitation and (b) emission spectra of 2-HBPQ-Er³⁺-HQ.

The excitation and emission spectra of 2-HBPQ- Er^{3+} -HQ are shown in Fig. 11. The maximum excitation peak of 2-HBPQ-Er³⁺-HQ located at 428 nm corresponding to the absorption of the ligands, and three other small peaks at 522, 653 and 984 nm were attributed to the 4f-4f transitions of Er^{3+} ions, which were very similar to the spectrum of 1-HBPQ-Er³⁺-HQ. Under excitation at 428 nm, excitation 2-HBPQ-Er³⁺-HQ emitted the characteristic luminescence of Er³⁺ ion centered at 1533 nm. It could be observed that 2-HBPQ-Er³⁺-HQ showed much higher luminescence intensity than 1-HBPQ-Er³⁺-HQ, which could be because 2-HBPQ has more rigid polyester backbone structures than 1-HBPQ, as shown in Scheme 1, resulting in the more stable coordination structure of 2-HBPQ-Er³⁺-HQ. This was beneficial for the enhancement of the emission intensity of Er^{3+} ions. Besides, the FWHM of 2-HBPQ-Er³⁺-HQ was 88 nm, which was also wider than that of 1-HBPQ-Er³⁺-HQ. Therefore, 2-HBPQ-Er³⁺-HQ with strong emission at around 1530 nm and wide FWHM is very promising as a new optical amplification luminescence material.



Fig. 12. Emission spectra of (a) 2-HBPQ-Er³⁺-HQ, (b) Er³⁺-HQ and (c) 2-HBPQ-Er³⁺.

In order to further investigate the effects of the macromolecular ligand and second ligand on the luminescence emission of 2-HBPQ- Er^{3+} -HQ, the emission spectra of Er^{3+} -HQ and 2-HBPQ- Er^{3+} were measured, as presented in Fig. 12. Obviously, the emission intensity of 2-HBPQ- Er^{3+} -HQ was much higher compared to Er^{3+} -HQ and 2-HBPQ- Er^{3+} . This could be due to the fact that the simultaneous coordination of both 2-HBPQ and HQ with Er^{3+} ions could not only meet the coordination number of Er^{3+} ion but also form a more stable coordination structure. This synergistic effect of 2-HBPQ and HQ was beneficial for the decrease in the non-radiative transition of Er^{3+} ions and the increase in the emission intensity of the complex, thus resulting in the intense near-infrared luminescence of 2-HBPQ- Er^{3+} -HQ. Therefore, a kind of novel Er^{3+} complexes base on 8-hydroxyquinoline-terminated hyperbranched polyester was successfully prepared, which had high Er^{3+} contents and showed quite strong near-infrared luminescence.

4. Conclusions

Two new hyperbranched polymer ligands containing HQ end-groups 1-HBPQ

and 2-HBPQ were designed and synthesized. Furthermore, the corresponding erbium complexes 1-HBPQ-Er³⁺-HQ and 2-HBPQ-Er³⁺-HQ were successfully prepared. In these complex systems, both the macromolecular ligand 1-HBPQ or 2-HBPQ and the second ligand HQ participated in the coordination reaction with Er³⁺ ions. Due to the synergistic effects of the two ligands, the as-prepared erbium complexes showed intense near-infrared luminescence at around 1530 nm corresponding to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er³⁺ ion. The FWHM values of 1-HBPQ-Er³⁺-HQ and 2-HBPQ-Er³⁺-HQ were as wide as 85 nm and 88 nm, respectively. These erbium complexes with excellent near-infrared luminescence properties are promising materials for optical amplification applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21306062, and 51402126); Zhejiang Provincial Natural Science Foundation of China (LQ13E030007, and LY16E050010); Program for Science and Technology of Jiaxing (2014AY21013); and National Training Programs of Innovation and Entrepreneurship for Undergraduates (201510354010).

References

- [1] J.D.B. Bradley, M. Pollnau, Laser Photonics Rev. 5 (2011) 368-403.
- [2] Y.L. Zhang, F. Wang, Y.B. Lang, J. Yin, M.L. Zhang, X.H. Liu, D.M. Zhang, D. Zhao, G.S. Qin, W.P. Qin, J. Mater. Chem. C, 3 (2015) 9827-9832.
- [3] S. Serna, W.W. Zhang, X. Leroux, D.S. Gao, D.M. Zhang, L. Vivien, E. Cassan,
 J. Opt. Soc. Am. B: Opt. Phys. 31 (2014) 2021-2028.
- [4] O. Mahran, Aust. J. Basic Appl. Sci. 9 (2015) 84-92.
- [5] Y.H. Wang, Y.X. Sun, C.X. Wang, G.F. Wang, M.X. Song, Z.K. Qin, C.S. Ma, Optik 125 (2014) 6778-6784.
- [6] Y. Zheng, C.H. Chen, Y.L. Gu, J.H. Wang, S.Z. Yang, X. Fei, X.B. Wang, Y.J. Yi, X.Q. Sun, F. Wang, D.M. Zhang, RSC Adv. 6 (2016) 3224-3230.

- [7] P. Martín-Ramos, V. Lavín, M. Ramos Silva, I. R. Martín, F. Lahoz, P. Chamorro-Posada, J. A. Paixão, J. Martín-Gil, J. Mater. Chem. C, 1 (2013) 5701-5710.
- [8] A. Mech, A. Monguzzi, F. Meinardi, J. Mezyk, G. Macchi, R. Tubino, J. Am. Chem. Soc. 132 (2010) 4574-4576.
- [9] Q.Y. Sun, P.F. Yan, W.Y. Niu, W.Y. Chu, X. Yao, G.H. An, G.M. Li, RSC Adv. 5 (2015) 65856-65861.
- [10] S. Sarkar, V.N. Adusumalli, V. Mahalingam, J.A. Capobianco, Phys. Chem. Chem. Phys. 17 (2015) 17577-17583.
- [11] Y. Tian, T. Wei, F.Z. Chen, X.F. Jing, J.J. Zhang, S.Q. Xu, J. Quant. Spectrosc. Ra. 133 (2014), 311-318.
- [12] F. Cabelloa, S. Sanchez-Cortesb, M. Jiménez de Castroa, J Non-Cryst. Solids 445-446 (2016) 110-115.
- [13] R. Van Deun, P. Fias, P. Nockemann, A. Schepers, T.N. Parac-Vogt, K. Van Hecke, L.Van Meervelt, K. Binnemans, Inorg. Chem. 43 (2004) 8461-8469.
- [14] F. Artizzu, L. Marchio, M.L. Mercuri, L. Pilia, A. Seroe, F. Quochi, R. Orru, F. Cordella, M. Saba, A. Mura, G. Bongiovanni, P. Deplano, Adv. Funct. Mater. 17 (2007) 2365-2376.
- [15] S. Dang, Q.H. Liu, K. Liu, Z.Y. Guo, L.N. Sun, S.Y. Song, H.J. Zhang, Cryst. Growth Des. 10 (2010) 4662-4667.
- [16] J.X. Luo, C.Y. Zhang, C.H. Li, W.G. Wang, H.X. Hu, B.N. Hu, J. Chin. Soc. Rare earths 31 (2013) 49-54.
- [17] X.C. Qi, Z.L. Wang, S.M. Ma, L.J. Wu, S.G. Yang, J. Xu, Polymer 55 (2014) 1183-1189.
- [18] D.F. Fan, X. Fei, J. Tian, L.Q. Xu, X.Y. Wang, S.Q. Fan, Y. Wang, Polym. Chem. 6 (2015) 5430-5436.
- [19] A. Meyers, A. Kimyonok, M. Weck, Macromolecules 38 (2005) 8671-8678.

- [20] J.X. Luo, C.Y. Zhang, C.H. Li, H.X. Hu, B.N. Hu, RSC Adv. 4 (2014) 57393-57401.
- [21] A. I. Ismail, K. A. K. Ebraheem, M. S. Mubarak & F. I. Khalili, Solvent Extr. Ion Exc. 21 (2003) 125-137.
- [22] B. Su, F.H. Bai, J. Chin. Soc. Rare earths 29 (2011) 396-401.
- [23] D. Konkolewicz, M. J. Monteiro, S Perrier, Macromolecules 44 (2011) 7067-7087.
- [24] J.M. Giussi, O. Azzaroni, S. Hensel-Bielowka, Z. Wojnarowska, J. Knapik, M. Paluch, Polymer 100 (2016) 227-237.
- [25] A. Hult1, M. Johansson, E. Malmström, Adv. Polym. Sci. 143 (1999) 1-34.
- [26] B.I. Voit, A. Lederer, Chem. Rev. 109 (2009) 5924-5973.
- [27] B. Voit, J. Polym. Sci. Pol. Chem. 38 (2000) 2505-2525.
- [28] C. Gao, D. Yan, Prog. Polym. Sci. 29 (2004) 183-275.
- [29] Y. Liu, C.Y. Yu, H.B. Jin, B.B. Jiang, X.Y. Zhu, Y.F. Zhou, Z.Y. Lu, D.Y. Yan, J. Am. Chem. Soc. 135 (2013) 4765-4770.
- [30] A.F. Ghanem, A. El-Gendi, M.H. Abdel Rehim, K. M. El-Khatib, RSC Adv. 6 (2016) 32245-32257.
- [31] S. Boye, H. Komber, P. Friedel, A. Lederer, Polymer 51 (2010) 4110-4120.
- [32] A. Badiei, H. Goldooz, G.M. Ziarani , A. Abbasi, J. Colloid Interf. Sci. 357 (2011) 63-69.
- [33] Q.G. Li, X. Li, Y. Huang, S.X. Xiao, D.J. Yang, L.J. Ye, D.L. Wei, Y. Liu, Thermochim. Acta 441 (2006) 195-198.
- [34] J.T. Wang, X.X. Zhou, Chin. J. Inorg. Chem. 5 (1989) 102-105.
- [35] Y.Z. Zhang, Y. Huang, Chin. Textile Auxiliaries 20 (2003) 12-14.
- [36] L.M. Zhao, B.Yan, J. Non-Cryst. Solids 353 (2007) 4654-4659.
- [37] H. Chen, Y.H. Liu, Y.F. Zhou, Z.H. Jiang, J. Alloy. Compd. 397 (2005) 286-290.
- [38] L.H. Slooff, A. Polman, M.P. Oude Wolbers, F.C.J.M. van Veggel, D.N.

Reinhoudt, J.W. Hofstraat, J. Appl. Phys. 83 (1998) 497-503.

- Two novel 8-hydroxyquinoline-terminated hyperbranched polyesters were synthesized.
- Erbium complexes based on modified hyperbranched polyesters were prepared.
- Erbium complexes show intense near-infrared luminescence and wide FWHM.

CHR MAN