



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)

# Synthesis and strong luminescence of water soluble lanthanide complexes sensitized by a new tridentate organic ligand

Bao-Li An<sup>a,\*</sup>, Xiao-Di Huang<sup>a</sup>, Ji-Ming Zhang<sup>b</sup>, Xiao-Ya Zhu<sup>a</sup>, Jia-Qiang Xu<sup>a</sup><sup>a</sup> Department of Chemistry, College of Science, Shanghai University, Shanghai 200444, China<sup>b</sup> Periodicals Agency, Shanghai University, Shanghai 200444, China

## ARTICLE INFO

### Article history:

Received 26 September 2016

Received in revised form

2 March 2017

Accepted 21 March 2017

Available online 22 March 2017

### Keywords:

Optical materials

Chemical synthesis

Luminescence

## ABSTRACT

Sensitive biological analysis requires optical labels have good water solubility and relative longer excitation wavelength. Herein, two water-soluble lanthanide (Ln) organic complexes,  $\text{Na}_3\text{Ln}(\text{DIEDPA})_3$  (Ln=Eu, Tb) have been synthesized with a new tridentate ligand, 4-[2-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-ethoxy]-pyridine-2,6-dicarboxylic acid ( $\text{H}_2\text{DIEDPA}$ ). The two lanthanide complexes showed characteristic emissions of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions with high quantum yields of  $11 \pm 1.1\%$  and  $13 \pm 1.5\%$  respectively. Moreover, compared with those for the europium and terbium complexes with pyridine-2,6-dicarboxylic acid as a ligand, the effective excitation wavelengths for the two complexes shifted more than 60 nm to longer wavelengths by decoration of the molecular structure of the organic ligand. The results might provide reference for design and synthesis of organic luminescent lanthanide bioprobes with longer excitation wavelengths.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Lanthanide chelates, especially  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  complexes, have drawn considerable interests due to their peculiar luminescent properties: narrow emission peaks, long lifetimes of the excited states, large Stokes shift and high quantum yields [1–3]. They can be used as time-resolved luminescence probes for the imaging analysis of cell and tissues [4,5], sensing metal ions and small molecules [6], oxygen sensor [7], multiplex detection in complex biological systems [8] and bimodal contrast agents for magnetic resonance and optical imaging [9], etc.

Pyridine-2,6-dicarboxylic acid ( $\text{H}_2\text{DPA}$ ) is an efficient tridentate ligand, the europium and terbium complexes,  $\text{Na}_3\text{Ln}(\text{DPA})_3$  (Ln=Eu, Tb), showed good stability in dilute water solution with high luminescent quantum yields [10,11], they can also be used as convenient paramagnetic shift reagents for protein NMR images [12]. However, the maximum excitation wavelengths for  $\text{Na}_3\text{Ln}(\text{DPA})_3$  (Ln=Eu, Tb) locate at 270–280 nm [13–15], and some biomolecules absorb ultraviolet light around 260–300 nm. Usually, serum is commonly used in immune assay, the maximum emissions of the protein molecules in serum locate in 325–350 nm excited by 280 nm, and the emissions for bilirubin and nicotinamide adenine dinucleotide (NADH) in serum locate in 430–470 nm. The excitation wavelengths for fluorescent probes are required accordingly to be longer than 330 nm, and the emission

wavelengths should be longer than 500 nm [1]. The competitive adsorption of the excitation light between the biomolecules and the lanthanide luminescent bioprobes can decrease the sensitivity of detection. By modification of the structures of organic ligands, the excitation wavelengths of the lanthanide complexes can be shifted to longer wavelengths, even to visible light regions [16–18]. Recently, we have successfully synthesized two water soluble europium and terbium complexes, and their effective excitation wavelengths shifted about 70 nm to longer wavelengths compared with those of the europium and terbium complexes with DPA as a ligand by configuration of the structure of DPA [19].

The luminescence intensity for lanthanide complexes is related to the absorption efficiency of the complexes, which depends on the expanded  $\pi$ -conjugated structures of the organic lanthanide complexes. Meanwhile, the maximum excitation bands could be shifted to longer wavelengths even to visible regions by expansion of the  $\pi$ -conjugated structure of the organic ligand. But if the  $\pi$ -conjugated structure is too large, the lowest triplet level ( $T_1$ ) of the organic ligand will be close to the lowest excited  $f$  state of the lanthanide ions. In this case, the electron on the lowest excited  $f$  state of the lanthanide ions can back to the  $T_1$  levels of the organic ligand, this process can decrease the luminescent efficiency of the lanthanide complex [20]. Presently, it is a challenging work to synthesize an efficient luminescent organic lanthanide complex with longer maximum excitation wavelength and good water solubility.

In this paper, by modification of the structure of pyridine-2,6-dicarboxylic acid, two water-soluble lanthanide organic complexes,

\* Corresponding author.

$\text{Na}_3\text{Ln}(\text{DIEDPA})_3$  (Ln=Eu, Tb) have been synthesized. The maximum excitation wavelengths for solid  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  complexes shifted more than 60 nm to longer wavelengths compared with those for solid  $\text{Na}_3\text{Ln}(\text{DPA})_3$  (Ln=Eu, Tb) compounds, and the lanthanide complexes also showed high luminescent quantum yields and good water-soluble properties.

## 2. Experiment

### 2.1. Syntheses of $\text{H}_2\text{DIEDPA}$

Water molecules in tetrahydrofuran (THF), toluene, acetone and diethyl oxalate were removed by conventional experimental methods; other chemicals used in the experiments are analytical grade or better without further purification.  $\text{Eu}_2\text{O}_3$  (99.95%) and  $\text{Tb}_2\text{O}_3$  (99.95%) were purchased from Guangdong Pearl River Rare Earth Co. The synthetic route is showed in Fig. 1.

#### 2.1.1. Synthesis of 2-(2-bromo-ethyl)-isoindole-1,3-dione

4.41 g phthalimide (30 mmol) was dissolved in 50 ml THF, 12.44 g  $\text{K}_2\text{CO}_3$  (90 mmol) and 0.3 mol% tetrabutylammonium bromide (TBAB) were added into the solution. The mixture was stirred at 50 °C for 3 h in  $\text{N}_2$  atmosphere, then 7.77 g 1,2-dibromoethane (41 mmol) in 50 ml THF solution was dropped into the mixed solution. The solution was stirred continuously for 24 h at 50 °C. After most of the THF and superfluous 1,2-dibromoethane was evaporated in vacuum, 6.1 g light yellow crystals were obtained by filtration with yield of 80%. Melting point: 81–83 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz),  $\delta$ : 7.884 (2H, d, d,  $^3J=6.6$  Hz,  $^4J=3.0$  Hz), 7.753 (2H, t, d,  $^3J=6.6$  Hz,  $^4J=3.0$  Hz), 4.119 (2H, t,  $^3J=6.5$  Hz), 3.623 (2H, t,  $^3J=6.5$  Hz).

#### 2.1.2. Synthesis of 4-pyranone-2,6-dicarboxylic acid

Sodium ethoxide was prepared by adding 12 g sodium (0.51 mol) into 180 ml absolute ethanol until the sodium was completely dissolved in ethanol. 19 ml acetone (0.25 mol) and 72 ml diethyl oxalate (0.53 mol) were added into the pre-prepared sodium ethoxide solution, and the mixed solution was stirred at 60 °C for 1 h in  $\text{N}_2$  atmosphere. Then, a mixture of 100 ml concentrated hydrochloric acid and 50 ml water was added into the solution, the solution was stirred continuously at 50 °C for 24 h. After the ethanol was removed under reduced pressure, a mixture of 25 ml concentrated hydrochloric acid and 150 ml water was added, the mixed solution was stirred at 50 °C for another 72 h. The solid crystals were filtered and washed with water and acetone. Yield: about 63%, melting point: 256–257 °C.  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 500 MHz),  $\delta$ : 5.712 (2H, s), 6.893 (2H, s).

#### 2.1.3. Synthesis of diethyl 4-hydroxy-2,6-pyridinedicarboxylate

6 g 4-pyranone-2,6-dicarboxylic acid (32 mmol) was added into 200 ml concentrated ammonia water, and the solution was stirred at room temperature for 4 h. After most of the ammonia was removed under reduced pressure, the pH value of the solution was adjusted to 1–2 by adding concentrated hydrochloric acid. The white precipitate was filtered and washed with water for three times. After the precipitate was dissolved into 120 ml absolute ethanol, 1 ml concentrated sulfuric acid was added slowly. The mixed solution was refluxed for 12 h, then, the pH value of the solution was adjusted to 5–6 by sodium hydroxide solution. The product was extracted with ethyl acetate for four times, later, the ethyl acetate solution was dried with anhydrous magnesium sulfate. 5.2 g product was obtained by removing the solvent by rotary evaporation under reduced pressure. Yield: about 68%, melting

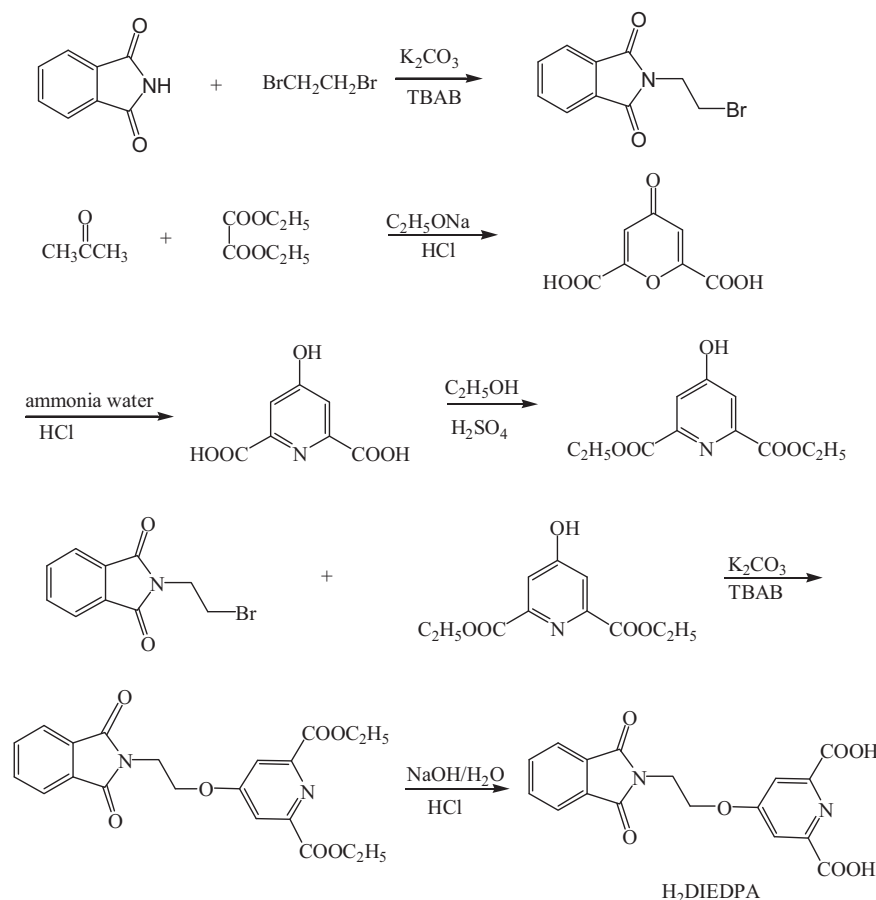


Fig. 1. Synthetic route of  $\text{H}_2\text{DIEDPA}$ .

Download English Version:

<https://daneshyari.com/en/article/5397917>

Download Persian Version:

<https://daneshyari.com/article/5397917>

[Daneshyari.com](https://daneshyari.com)