



# Nanofibers doped with a novel red-emitting Europium complex: Synthesis, characterization, photophysical property and sensing activity toward molecular oxygen

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## ARTICLE INFO

### Article history:

Received 29 March 2011

Received in revised form 2 May 2011

Accepted 30 January 2012

### Keywords:

Eu(III) complex  
Photoluminescence  
Phosphorescence  
Oxygen sensing

## ABSTRACT

In this paper, we synthesize a novel diamine ligand of DIQ-Et and its corresponding Eu(III) complex of  $\text{Eu}(\text{TTA})_3\text{DIQ-Et}$ , where DIQ-Et = N-ethyl-10H-dipyrido-[f,h]-indolo-[3,2-b]-quinoxaline, and TTA = 2-thenoyltrifluoroacetate. The UV-vis absorption, photoluminescence, low temperature phosphorescence, energy transfer mechanism, and excited state lifetime of  $\text{Eu}(\text{TTA})_3\text{DIQ-Et}$  are investigated in detail. Data suggest that the emission of  $\text{Eu}(\text{TTA})_3\text{DIQ-Et}$  is quenched by molecular oxygen due to the back-energy transfer process. By doping  $\text{Eu}(\text{TTA})_3\text{DIQ-Et}$  into a polymer matrix of poly(vinylpyrrolidone) (PVP), oxygen sensing performance of the resulted nanofibers is investigated. Finally, the 0.7 wt% doped sample exhibits a linear response toward molecular oxygen, with a sensitivity of 2.4 and response/recovery time of 12 s/16 s.

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## 1. Introduction

In recent years, one-dimensional (1-D) nanostructures have drawn much attention since they may be utilized in the field of nanodevices with unique optoelectronic, electrochemical, and electromechanical properties [1]. Practicable approaches, such as drawing, template synthesis, phase separation, self-assembling, and electrospinning, have been proposed to construct such 1-D structures [2,3]. Among these approaches, electrospinning, which applies electric force to drive the spinning process and consequently to produce fibers, is a promising technique for fabricating long and uniform nanofibers, owing to its versatile, simple, and straightforward construction process, as well as the low cost [4]. Electrospinning nanofibers own unique properties, such as average fiber diameters in submicrometer range, high porosity, large surface area, fully interconnected pore structures, and sufficient mechanical strength, making themselves attractive for a wide range of potential applications, such as biomedical applications, solar cells, catalyst carriers, porous electrodes, light-emitting diodes, liquid crystal devices, as well as supporting matrixes for optical sensors [5–7].

Optical sensors for oxygen detection have attracted considerable attention in recent years due to their applications in different branches of chemical and food industries, medicine, analytical

chemistry, and environmental monitoring [8,9]. Such sensors can offer advantages in terms of size, electrical safety, costs, requiring no reference element. The analytical signals are free of influence from electromagnetic field and can be easily transmitted over a long distance [10,11]. For practical applications, it is necessary to embed the sensors into a solid matrix, allowing oxygen transportation from surroundings. Indeed, the supporting medium may have quite stringent criteria for suitable performances [12]. For example, a high diffusion coefficient is necessary for a rapid response, while, a highly effective quenching around the sensor molecule is necessary for good sensitivity. Meanwhile, long distance on-line monitoring necessitates a high degree of photostability. Thus, the exploration for sensors with intense luminescence, excellent anti-jam ability, high photostability, and good compatibility with supporting matrix is still a challenge.

Rare-earth (RE) based emitters seem to be promising candidates satisfying above requirements. Due to the unique antenna excitation mechanism and  $f-f$  radiative transitions,  $\text{RE}^{3+}$  based emitters can generate characteristically sharp and narrow emissions without being affected by surrounding environment or reagents, offering an excellent anti-jam ability [13]. In addition,  $\text{RE}^{3+}$  based emitters' good solubility in common solvents allow themselves to be easily loaded into various supporting matrixes. All these excellent characters make  $\text{RE}^{3+}$  based emitters promising candidates for oxygen-sensing materials. Guided by above results, in this paper, we synthesize a novel diamine ligand and its corresponding Eu(III) complex. The UV-vis absorption, photoluminescence, low temperature phosphorescence, energy transfer mechanism, and

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excited state lifetime of the resulting Eu(III) complex are investigated in detail. By doping it into a polymer matrix, the oxygen sensing performance of the resulted nanofibers is investigated, aiming at the exploration of a novel oxygen sensing material.

## 2. Experimental

A synthetic procedure for  $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$  and the corresponding nanofibers is shown in Scheme 1.

1,10-phenanthroline (Phen), indoline-2,3-dione, 2-thenoyltrifluoroacetate (TTA), and poly(vinylpyrrolidone) (PVP, K30) were purchased from Aldrich Chemical Co. and used without further purifications. Organic solvents, including N,N'-dimethylformamide (DMF), 1, 2-dichloroethane, ethanol, and  $\text{CH}_2\text{Cl}_2$ , were purified through standard procedures.

### 2.1. Synthesis of ligands

The starting materials of 1,10-phenanthroline-5,6-dione (Phen-O), 1,10-phenanthroline-5,6-dione-dioxime (Phen-NOH), and 1,10-phenanthroline-5,6-diamine (Phen-NH<sub>2</sub>) were synthesized exactly according to the literature procedures [12,14,15].

10H - dipyrido [*f,h*] indolo [3,2-*b*] quinoxaline (DIQ). DIQ was synthesized as follows: a mixture of 5 mmol of Phen-NH<sub>2</sub>, 5.5 mmol of indoline-2,3-dione, 25 mL of ethanol and 0.05 mmol of 4-methylbenzenesulfonic acid was heated under 80 °C for 10 h, the crude product was filtered and then recrystallized from ethanol to give the pure desired product. <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>, 25 °C): δ 10.08 (d, 1H, *J* = 8.5 Hz), 9.20 (d, 1H, *J* = 2.5 Hz), 9.12 (d, 1H, *J* = 2.0 Hz), 9.04 (d, 1H, *J* = 5.5 Hz), 8.51 (d, 1H, *J* = 5.5 Hz), 7.62–7.73 (m, 2H), 7.57 (d, 1H, *J* = 8.5 Hz), 7.31 (m, 2H). Anal. Calcd. for C<sub>20</sub>H<sub>11</sub>N<sub>5</sub>: C, 74.76; H, 3.45; N, 21.79. Found: C, 74.64, H, 3.63; N, 21.69.

N-ethyl-10H-dipyrido-*[f,h]*-indolo-*[3,2-b]*-quinoxaline (DIQ-Et). DIQ-Et was synthesized as follows. A mixture of 5 mmol of DIQ, 15 mmol of KOH, 15 mmol of EtBr, and 20 mL of DMF was stirred at room temperature for 72 h. Then the mixture was poured into cold water. Organic components were extracted with 30 mL of  $\text{CH}_2\text{Cl}_2$  and washed with water, then dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the residue was further purified by recrystallization from hot ethanol. <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>, 25 °C): δ 9.21 (d, 1H, *J* = 1.5 Hz), 9.10 (d, 1H, *J* = 1.2 Hz), 9.07 (d, 1H, *J* = 3.3 Hz), 8.51 (d, 1H, *J* = 3.3 Hz), 7.66–7.73 (m, 2H), 7.58 (d, 1H, *J* = 5.1 Hz), 7.35 (d, 1H, *J* = 4.2 Hz), 7.27 (s, 2H), 4.34 (t, 2H, *J* = 7.8 Hz), 1.37 (t, 3H, *J* = 8.4 Hz). Anal. Calcd. for C<sub>22</sub>H<sub>15</sub>N<sub>5</sub>: C, 75.63; H, 4.33; N, 20.04. Found: C, 75.44, H, 4.17; N, 20.31.

### 2.2. Synthesis of RE complexes

$\text{Eu}(\text{TAA})_3\text{DIQ-Et}$ .  $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$  was synthesized according a literature procedure except that the diamine ligand was replaced by DIQ-Et [16]. IR (KBr pellet): 3469, 2943, 1692, 1421, 1290, 845, 731, 570 cm<sup>-1</sup>. Anal. Calcd. for C<sub>46</sub>H<sub>27</sub>N<sub>5</sub>F<sub>9</sub>O<sub>6</sub>S<sub>3</sub>Eu: C, 47.43; H, 2.34; N, 6.01. Found: C, 47.51; H, 2.42; N, 5.94.

$\text{Gd}(\text{TAA})_3 \cdot (\text{H}_2\text{O})_2$ .  $\text{Gd}(\text{TAA})_3 \cdot (\text{H}_2\text{O})_2$  was synthesized according to the synthetic procedure for  $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$  and described as follows. The mixture of 3 mmol of TTA, 3 mmol of NaOH, 1 mmol of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ , and 50 mL of ethanol was heated to reflux for 3 h, offering the desired product as yellow powder which was recrystallized from hot ethanol and water. Anal. Calcd. for C<sub>24</sub>H<sub>16</sub>F<sub>9</sub>O<sub>8</sub>S<sub>3</sub>Gd: C, 33.64; H, 1.88. Found: C, 33.54; H, 2.07.

$\text{Gd}(\text{DIQ-Et})_2 \cdot \text{Cl}_3$ .  $\text{Gd}(\text{DIQ-Et})_2 \cdot \text{Cl}_3$  was synthesized as follows. The mixture of 4 mmol of DIQ-Et, 2 mmol of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ , and 30 mL of ethanol was heated to reflux for 3 h, giving the desired product as light yellow powder which was further purified by recrystallization

from hot ethanol and water. Anal. Calcd. for C<sub>44</sub>H<sub>30</sub>N<sub>10</sub>EuCl<sub>3</sub>: C, 55.21; H, 3.16; N, 14.63. Found: C, 55.16; H, 3.31; N, 14.58.

### 2.3. Fabrication of $\text{Eu}(\text{TAA})_3\text{DIQ-Et/PVP}$ nanofibers

A typical procedure for the electrospinning composite nanofibers is described as follows. 1 g of PVP was dissolved in the mixed solvent of 1,2-dichloroethane and ethanol (V:V = 1:1) to form a homogeneous solution. Then controlled amount of  $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$  (0.5 wt%, 0.7 wt%, and 0.9 wt%, respectively) were added into the solution under stirring to form  $\text{Eu}(\text{TAA})_3\text{DIQ-Et/PVP}$  homogeneous solutions. The final solutions were then electrospun to be composite nanofibers of  $\text{Eu}(\text{TAA})_3\text{DIQ-Et/PVP}$ . For electrospinning, the mixed solution was placed in a 5 mL glass syringe, with the opening end connected to a plastic needle (inner diameter = 0.6 mm) as the nozzle [17]. The anode terminal of a high-voltage generator was connected to a copper wire inserted into the polymer solution in the glass syringe. A piece of Al foil was used as the collector plate and connected to the grounding electrode. The driving voltage was 18 kV, with the tip-to-target distance of 25 cm.

### 2.4. Measurements

Luminescence decay data were obtained with a 355 nm light generated from the Third-Harmonic-Generator pumped, using pulsed Nd:YAG laser as the excitation source. The Nd:YAG laser possesses a line width of 1.0 cm<sup>-1</sup>, pulse duration of 10 ns and repetition frequency of 10 Hz. A Rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. All photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. UV-vis absorption spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 microscope. Fluorescence microscopy image was obtained with a Nikon TE2000-U fluorescence microscopy using the mercury lamp as the power supply. <sup>1</sup>H NMR spectra were obtained with a Varian INOVA 300 spectrometer. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. Oxygen-sensing performances were measured on the basis of steady emission intensity quenching. All measurements were carried out in the air at room temperature without being specified.

## 3. Results and discussion

### 3.1. Photophysical property of $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$

#### 3.1.1. UV-vis absorption

Fig. 1 shows the UV-vis absorption of  $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$  in  $\text{CH}_2\text{Cl}_2$  solution with a concentration of  $1 \times 10^{-4}$  mol/L, along with those for free ligands of TTA and DIQ-Et. It is observed that the absorption spectrum of  $\text{Eu}(\text{TAA})_3\text{DIQ-Et}$  is composed of a low energy absorption band centering at 338 nm and a high energy absorption band peaking at 272 nm. Compared with the absorption spectra of free TTA and DIQ-Et, we attribute the broad absorption band from 300 nm to 380 nm to the  $\pi \rightarrow \pi^*$  transitions of TTA, admixed with partial contribution from DIQ-Et, which is confirmed by the characteristic triple peaks of DIQ-Et centering at 324 nm, 337 nm, and 354 nm, respectively [16]. On the other hand, the  $\pi \rightarrow \pi^*$  transitions of DIQ-Et are responsible for the high-energy absorption band from 220 nm to 300 nm, along with small contribution from TTA fragment [16]. Even though the absorption intensity of  $\pi \rightarrow \pi^*$  transitions from DIQ-Et in high energy region from 220 nm to 300 nm is obviously higher than that from TTA in low energy

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