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A luminescent Eu(III) complex based on 2-(4′, 4′, 4′-trifluoro-1′, 3′-dioxobutyl)-dibenzothiophene for light-emitting diodes

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ABSTRACT

Complex Eu(dbt)$_3$(phen) (Hdbt = 2-(4′, 4′, 4′-trifluoro-1′, 3′-dioxobutyl)-dibenzothiophene, phen = 1,10-phenanthroline) was synthesized. The complex emits red luminescence, characteristic of the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) emission bands of Eu^{3+} under near ultraviolet. A red conversion light-emitting diode (LED) device was fabricated by coating complex onto InGaN-based-LED chip that emits 395 nm ultraviolet light. When the mass ratio of the red phosphor to the silicone is 1:25, the LED device's CIE chromaticity coordinates are x = 0.5835, y = 0.2857, and the luminescence efficiency is 1.29 lm/w. All the results show that this europium complex may act as a red component in fabrication of white LEDs with high color-rendering index.

1. Introduction

Since white light-emitting diodes (LEDs) can offer benefits in terms of high luminous efficiency, maintenance and environmental protection, they are called the next-generation solid-state light [1]. In the past years, white LEDs are obtained mainly by combining an ~465 nm blue-emitting InGaN chip with yellow-emitting phosphor [2]. Such white LEDs show low color-rendering index, low color reproducibility and low luminous efficiency because of the lack of red light. Recently, the emission bands of LED chips shifted to near ultraviolet (NUV) range (~370–400 nm), the NUV light can offer higher energy to pump the phosphor. A near UV chip plus blue-, green- and red-emitting tricolor phosphors to produce white light was developed. The commonly used red-emitting phosphor for NUV InGaN-based white LEDs is $Y_2O_2S:Eu^{3+}$, which exhibits lower efficiency compared with that of the blue (e.g. $BaMgAl_{10}O_{17}:Eu^{2+}$) and the green (e.g. $ZnS:Cu^+$, Al^{3+}) phosphors and shorter working-lifetime under NUV irradiation [3]. Thus, it is urgent to search for new red phosphors that can be efficiently excited by around ~400 nm-light.

Organic phosphors usually possess strong absorptions in NUV region, which are produced by π–π^* transitions and the emission colors can be easily adjusted by molecular design and structural modifications [4]. In our previous research, some europium (III) β-diketonate complexes were used as a red phosphor to fabricate red LEDs with NUV-emitting chips [5,6].

2-(4′, 4′, 4′-trifluoro-1′, 3′-dioxobutyl)-dibenzothiophene (Hdbt) has some advantages as ligand: (1) It bears a β-diketone unit, which could coordinate effectively to europium ions to form a stable Eu(III) complex; (2) Dibenzothiophene unit has a suitable π-conjugated system and could absorb the NUV energy effectively and then transfer it to the europium ion; (3) It has no absorption in the blue and green emission range. Therefore, we synthesized Eu (III) complex based on Hdbt and employed it as red phosphor to fabricate red LEDs.

2. Experimental

2.1. Reagents and measurements

Dibenzothiophene was purchased from Alfa Aesar. The other reagents and GaInN chip were commercially available. The solvent CH_2Cl_2 and toluene were dried before used 2-Acetyldibenzothiophene was synthesized according to the literature method [7].

Elemental analyses were performed on an Elementar vario EL elemental analyzer. Infrared spectra (400–4000 cm^{-1}) were recorded with samples as KBr pellets using a Nicolet NEXUS 670 FTIR spectrophotometer. ^1H NMR spectra was measured using a Mercury–Plus 300 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent and TMS as internal reference. Excitation and emission spectra and was measured by PerkinElmer

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LS-55 Luminescence spectrometer. Fluorescence lifetime was measured with Edinburgh FLSP920 Combined Fluorescence Lifetime and Steady State Spectrometer. Thermogravimetric analyses (TG) were performed on a TG 209 F3 Tarsus Thermogravimetry from 30 to 800 °C in the N_2 atmosphere. Luminescence quantum yield was measured according to the reported method using $Eu(TTA)_3(phen)$ (Φ = 0.365 in DMF, TTA = 2-thenoyltrifluoroacetonate) as a standard [8]. The emission spectrum of the fabricated LEDs was measured with an Everfine PMS-50 Plus UV–vis-near IR Spectrophotocolorimeter at room temperature.

2.2. Synthesis of 2-(4′, 4′, 4′-trifluoro-1′, 3′-dioxobutyl)-dibenzothiophene (Hdbt)

2-Acetyldibenzothiophene (1.34 g, 5 mmol), $CF_3COOC_2H_5$ (0.60 g, 5 mmol), and Potassium tert-butoxide (0.34 g, 6 mmol) was stirred in 30 mL dry toluene for 3 h at room temperature, then reaction mixture was poured into 30 mL 15% HCl. The organic phase was separated, toluene was removed by distillation. The light yellow solid was recrystalized from ethanol and further purified by column chromatography. (1.1 g, 66.2% yield). The elemental analysis data for $C_{16}H_9F_3O_2S$ was found (calculated): C, 59.36 (59.62); H, 2.85 (2.81); S, 9.89 (9.95). IR (KBr, cm^{-1}): 3436, 3057, 1577, 1424, 1270, 1198, 1126, 737; ^{1}HNMR (300 MHz, $CDCl_3$) δ(ppm): 8.741(1H, s), 8.255 (1H,s), 8.137(1H, m) 7.966 (1H, m) 7.853 (1H, m), 7.544(1H, m), 7.431(1H, m) 6.718(1H, s).

2.3. Synthesis of $Eu(dbt)_3(phen)$

0.97 g (0.3 mmol) Hdbt and 1, 10-phenanthroline monohydrate (0.20 g, 0.1 mmol) were dissolved in 10 mL ethanol. 0.30 mmol of a 1.0 mol/L NaOH was then added while stirring. A solution of $EuCl_3.6H_2O$ (0.37 g, 0.1 mmol) in 4 mL pure water was added dropwise to the mixture. The mixture was stirred for 2 h at 60 °C under PH = 7.0–8.0 (adjusted by adding 0.1 mol/L NaOH) and then cooled. The light yellow precipitate deposited from the solution was collected and washed with water and ethanol, and vacuum drying at 60 °C for 24 h (yield: 0.64 g, 49%). The elemental analysis data for $Eu(dbt)_3(Phen)$. ($C_{60}H_{32}EuF_9N_2O_6S_3$) were found (calculated)/%: C, 56.39 (56.09), H, 3.06 (3.11), and N 2.37 (2.47). IR (KBr, cm^{-1}): 3420, 1618, 1536, 1301, 1195, 1137, 796, 755.

2.4. Synthesis of $Gd(dbt)_3{\cdot}2H_2O$

The gadolinium (III) complex was synthesized with a similar method to the europium complex except for $GdCl_3{\cdot}6H_2O$ instead of $EuCl_3{\cdot}6H_2O$ and absence of phen. The elemental analysis data for $Gd(dbt)_3.2H_2O$. [$C_{48}H_{28}F_9GdO_8S_3$] were found (calculated)/%: C, 49.75 (49.82), H 2.46 (2.44), 8.27 (8.31).

2.5. Fabrication of red lighting emitting diodes

A red light-emitting diode was fabricated by combination of an ~395 nm-emitting InGaN chip with complex as a phosphor. The phosphor was blended with silicone in order to be precoated onto the LED chip. The thickness of the admixture precoated onto the chip was the same due to the fixed size of the reflector cup. The admixture was cured in an oven at 150 °C for 1 h. In order to prevent the phosphor to disperse into the epoxy resins, another silicone layer was coated onto the phosphor and was cured for another 1 h. The whole LED lamp was encapsulated with transparent epoxy resin.

3. Results and discussion

3.1. Synthesis and thermal stability of complex

The complex was obtained from reaction between the ligand Hdbt and $EuCl_3{\cdot}6H_2O$ (Fig. 1). In IR spectra, there is a typical vibrations of C=O at 1610 cm^{-1} for ligand, but in the complex this peak split two peaks at about 1620 cm^{-1} and 1530 cm^{-1}, which shows that C = O coordinated to Eu(III) ions. Thermogravimetric analysis (TGA) showed that the complex is stable up to 230 °C.

3.2. Photoluminescence of the complex

The UV-vis absorption spectra for 1×10^{-5} mol/L ligand and the complex in DMF (Fig. 2) exhibited a broad band within λ_{max} = 320 nm, attributed to singlet-singlet $\pi \rightarrow \pi^*$ enol absorption, characteristic of the enol form of β-diketone. The shape of the absorption spectra of complex is similar to the free ligand, which shows that the β-diketonate ligands contribute to the absorption of the complex.

The lowest excited state energy level of Gd^{3+} ion, $^6P_{7/2}$, is about 32000 cm^{-1}, much higher than that of the lowest triplet energy

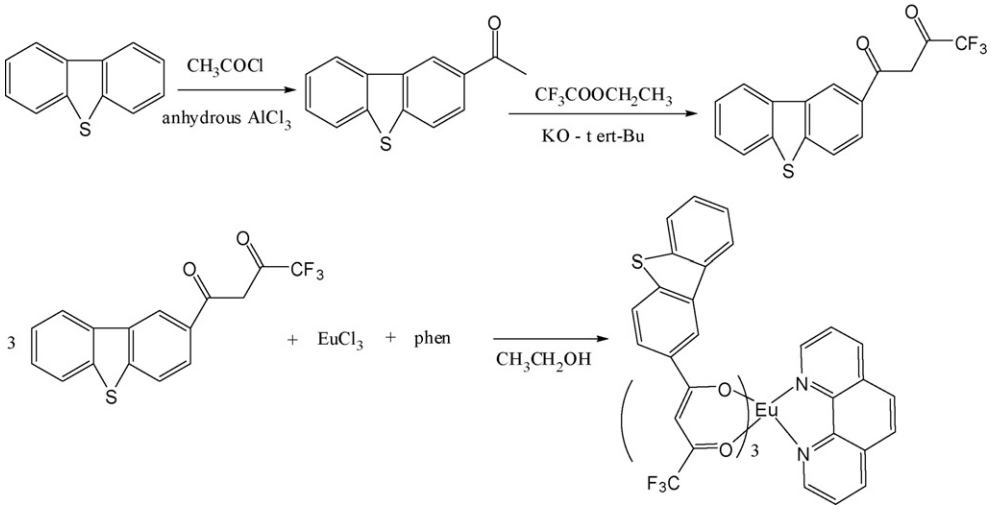

Fig. 1. Synthesis route of the ligand and the europium complex.