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

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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 J = 0 → 7FJ (J = 0–4) emission bands of Eu3+ 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.

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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 [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

Dibenzothiophene was purchased from Alfa Aesar. The other reagents and GaInN chip were commercially available. The solvent CH2Cl2 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 CDCl3 as solvent and TMS as internal reference. Excitation and emission spectra and was measured by PerkinElmer
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 N2 atmosphere. Luminescence quantum yield was measured according to the reported method using Eu(TTA)$_3$(phen) (Φ = 0.365 in DMF, TTA = 2-thienyltrifluoroacetone) 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$_3$COOC$_2$H$_5$ (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$_9$F$_3$O$_2$S 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; 1HNMR (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$_2$O (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$_9$N$_2$O$_6$S$_3$) 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)$_3$·2H$_2$O

The gadolinium (III) complex was synthesized with a similar method to the europium complex except for GdCl$_3$·6H$_2$O instead of EuCl$_3$·6H$_2$O and absence of phen. The elemental analysis data for Gd(dbt)$_3$·2H$_2$O. [C$_{48}$H$_{28}$F$_9$GdO$_8$S$_3$] 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$_3$·6H$_2$O (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 $1 \times 10^{-5}$ mol/L ligand and the complex in DMF (Fig. 2) exhibited a broad band within $\lambda_{max} = 320$ nm, attributed to singlet-singlet $\pi \rightarrow \pi^*$ enol absorption, characteristic of the enol form of $\beta$-diketone. The shape of the absorption spectra of complex is similar to the free ligand, which shows that the $\beta$-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. 2. Absorption spectra of the ligand and the complex in DMF (1 × 10⁻⁵ mol/L).

level of dbt [\(T_1(L)\)], so the energy absorbed by dbt ligand cannot be transferred to Gd³⁺ ion, and the phosphorescence of dbt appears when Gd (dbt)₃ 2H₂O is excited by NUV-light (\(\lambda_{exc} = 370\) nm). In this case, the lowest triplet state energy of the ligand dbt, \(T_1(L)\), was determined by the shortest wavelength of the phosphorescence peak to be 18518 cm⁻¹ (540 nm), which is higher than the lowest excited state of Eu³⁺, \(5D_0\) (17267 cm⁻¹), confirming the suitability of the ligand as a sensitizer to Eu³⁺-emission. The luminescence quantum yield of the complex in DMF was measured at room temperature to be 39%.

Light excitation into the ligand \(\pi\pi^*\) state at 320 nm of complex in DMF is followed by strong red luminescence, characteristic of the \(5D_0 \rightarrow 7F_j\) \((J = 0–4)\) emission bands of Eu³⁺. The most strong emission peak is located 614 nm. The emission spectrum of powder sample of complex is depicted in Fig. 3. Its maximum excitation wavelength centered at 392 nm, which is well suite to the emission wavelength of ~395 nm-GaInN chip. The luminescent properties of this complex suggested us to employ it as red phosphor incorporation of ~395 nm-GaInN chip.

Luminescence decay curve of Eu³⁺ related to the \(5D_0 \rightarrow 7F_2\) emission in complex powder sample is presented in Fig. 4. The lifetime measurements for the excited state of the Eu(III) ion were recorded under the excitation at 395 nm at room temperature. The luminescence lifetime of the emitting \(5D_0\) level is 539 us. The decay curve for the complex can be fit with a single exponential model.

3.3. Fabrication of red lighting emitting diodes

A red light-emitting diode was fabricated by combination of a ~395 nm-emitting InGaN chip with the complex as a phosphor, while an original LED without phosphor was also made for a comparison. Fig. 5 shows the emission spectra of the InGaN–complex LEDs and the original InGaN LED without phosphor under 20 mA forward bias excitation. The sharp and intense peak at 614 nm for the complex-LEDs is due to the Eu³⁺ emission from the complex in the LEDs. Comparison of the excitation spectra of the Eu³⁺ complex and the emission band of the original InGaN chip confirms that the complex can be efficiently excited by the ~395 nm-light emitted from the InGaN chip. The remained emission intensity from the InGaN chip in the emission spectra of the complex-LEDs is related to the mass ratio of the phosphor to the silicone. At a higher ratio of the red phosphor to the silicone, more emitting light from the InGaN chip was absorbed and more red light is emitted. When the mass ratio of the red phosphor to the silicone is 1:25, bright red light can be observed by naked eye under 20 mA forward bias, and the CIE chromaticity coordinates of the complex-LEDs are calculated to be \(x = 0.5835\), \(y = 0.2857\) based on their emission spectra. The efficiency of the original LED without phosphor is only 0.29 lm/w.
however, the efficiency of the fabricated LED with the europium complex achieves 1.29 lm/w when the mass ratio of the red phosphor to the silicone is 1:25. The intensity of remained ~395 nm emission light from the InGaN chip in the complex-LEDs is relate to the mass ratio of the red phosphor to the silicone, and can be used to excite blue and green phosphor to generate white light. Therefore, this europium complex may act as a red component in fabrication of white LEDs with high color-rendering index if appropriate blue and green phosphors with a suitable mass ratio are chosen.

4. Conclusions

A europium complex based on 2-(4′, 4′, 4′-trifluoro-1′, 3′-dioxobutyl)-dibenzothiophene was synthesized. The complex exhibits high thermal stability and excellent photoluminescence properties. Bright red light-emitting diode was fabricated by coating the complex onto ~395 nm-emitting InGaN chip. All the results indicate that the complex may act as a promising red component in the fabrication of white LEDs.

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References