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A novel europium(III)-imidazol-diketonate-phenanthroline complex as a red phosphor applied in LED

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ABSTRACT

A β -diketone, 4-imidazol-4,4,4-trifluorobutane-1,3-dione (HIDTFBD) and the corresponding europium(III) complex Eu(IDTFBD)₃phen were designed and synthesized, where phen was 1,10-phenanthroline. The complex was characterized by IR, UV-visible, thermogravimetric analysis (TGA) and photoluminescence (PL) spectroscopy. Monitored at 610 nm, the Eu(III) complex exhibited a strong and wide excitation band between 320 and 420 nm due to the formation of a big π -conjugated system in the complex molecule. Under near UV-light excitation, the complex showed strong red emission of Eu³⁺ ion due to the ⁵D₀-⁷F_J (J=0-4) transitions. The fluorescence lifetime and the luminescence quantum yield were also measured. Finally, a bright red light-emitting diode was fabricated by coating the europium ternary complex onto an ~395 nm-emitting InGaN chip, and the LED exhibited appropriate CIE chromaticity coordinates in red area. All these results suggest that the Eu (III) complex is a promising candidate as red component for fabrication of near UV-based white light-emitting diodes.

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Compared with the traditional incandescent lamps and fluorescent lamps, lighting, light-emitting diodes (LEDs) show the advantages of high efficiency, low power consumption and being environment-friendly [1–3]. White light emission can be achieved by incorporation of tricolor phosphors (blue, green and red) with UV-InGaN chips or phosphors (green-yellow and red) with blue GaN [4,5] chips. Nowadays, most commonly used phosphors are inorganic compounds. However, the red inorganic phosphors currently used such as $Y_2O_2S:Eu^{3+}$ and CaS:Eu³⁺ have some disadvantages of having lower efficiency, being harmful to the environment [6], having low color-rendering index, low color reproducibility and low luminous efficiency of WLED [7]. Therefore, it is urgent to search for novel redemitting phosphors with high efficiency and color-rendering under near-UV excitation.

Europium(III) organic β -diketonate complexes have received considerable attention due to their potential applications in organic light-emitting diodes (OLED) [8,9]. There are many advantages such as excellent photoluminescent property, environment-independent emission wavelength, high color purity and theoretically high inner quantum efficiency. To obtain an excellent luminescent europium complex, an organic ligand must satisfy the following requirements: firstly, the ligand molecule must have suitable π -conjugated system to make the excitation wavelength shifted red till NUV; secondly, the ligand must keep good coordination stability to the central ion; thirdly, the europium complex must be stable to thermal and UV irradiation to be used in LED [10].

In this article, an imidazo-based β -diketone, HIDTFBD and the corresponding complex Eu(IDTFBD)₃phen were designed and synthesized. The photoluminescence (PL) and thermal stability of the complex were investigated. The PL mechanism was proposed as an "antenna effect", and the fluorescence lifetime and the quantum yield were also measured. At last, a bright red LED was fabricated by incorporation of Eu(IDTFBD)₃phen complex and an ~395 nm-emitting InGaN chip. All the results indicate that the complex is an efficient red phosphor under NUV excitation.

HIDTFBD was synthesized via the Claisen condensation. (4-imidazol-1yl) acetophenone (1.0 mmol) was added into the potassium tertbutoxide (1.2 mmol) toluene solution at 0 °C, and stirred for 0.5 h, then 1.2 mmol ethyl trifluoroacetate was added in the reaction solution. All processes of the reaction were under the nitrogen atmosphere protection. After 2 h reaction the solvent was acidified with HCl and extracted with ethyl acetate. The solvent was evaporated under vacuum, and then was purified by column chromatography (1:1 methanol/chloroform) and gave the product HIDTFBD as a yellow powder (yield 54.8%). The synthesis routine of HIDTFBD is shown in Fig. 1. ¹H NMR (300 M, CDCl₃) δ [ppm]: 3.721–3.929 (s, 2H), 6.708 (s, 1H), 7.229 (s, 1H), 7.357(s, 1H), 7.488(s, 2H), 8.051(s, 2H). MS(EI) *m/z*: 282 (M⁺H⁾⁺, 213 (M⁺–CF₃), 186 (M⁺–CH₂COCF₃), 143 (M⁺–COCH₂COCF₃). The elemental analysis (EA) data for HIDTFBD (C₁₃H₉F₃N₂O₂) were: found (calculated)%: C 55.29 (55.33); H 3.28 (3.21); N 9.97 (9.93).

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Fig. 1. The synthesis routine of the ligand HIDTFBD.

The europium(III) ternary complex was synthesized with a common method analogous to our earlier work [11] as shown in Fig. 2 (yield 61%). The EA data for Eu(IDTFBD)₃phen (EuC₅₁H₃₉F₉N₈O₆) were: found (calculated)%: C, 51.76 (51.79); H, 3.351 (3.32); N, 9.482 (9.47).

To measure the lowest triplet state energy level of the ligand HIDTFBD, gadolinium(III) binary complex $Gd(IDTFBD)_3 \cdot 2H_2O$, was also prepared in a similar method without phenanthroline (yield 61%). The EA data for $Gd(IDTFBD)_3 \cdot 2H_2O$ ($GdC_{39}H_{33}F_9N_6O_8$) were: found (calculated)%:C: 44.98 (44.96), H :3.16 (3.19), N:8.11 (8.07).

Compared to the free ligand HIDTFBD, a new and strong stretching vibration peak near 1532 cm⁻¹ in the complex reveals the presence of the new C-C bond in the Eu(III) complex, which is the characteristic of β -diketonate coordinated with rare earth ions. There were new weak bonds in the complex near 490 cm⁻¹ and 552 cm⁻¹, which were corresponding to the new bonds of Eu – N and Eu – O [12], respectively.

Thermogravimetric analysis (TG-DTG) showed that the decomposition temperature of the complex $Eu(IDTFBD)_3phen$ is 323 °C, which is high enough for the luminescence application since LEDs work commonly under a temperature below 150 °C.

The UV–visible absorption spectra for the free ligands, EuCl₃ and Eu (IDTFBD)₃phen in ethanol $(1 \times 10^{-5} \text{ mol L}^{-1})$ are shown in Fig. 3. Since the π -conjugated system in the complex molecule is expanded with coordination of Eu³⁺ to IDTFBD⁻ and phen, the absorption intensity of the complex is remarkably enhanced and the absorption bands of the complex appear in a wide range from 225 to 400 nm. Comparing the absorption spectra of HIDTFBD, phen and Eu(IDTFBD)₃phen, it is found that the absorption band centering at 330 nm of the complex is mostly attributed to the absorption of principal ligand IDTFBD⁻ and the absorption band of the secondary ligand phen is mainly located below 300 nm.

The photoluminescence excitation (PLE) and emission (PL) of the Eu(III) complex powder are shown in Fig. 4, and the Eu(III) complex exhibits high excitation intensity when monitored at 385 nm while the excitation bands of the complex remains in a wider range due to the formation of a big π -conjugated system in the complex molecule. Exited by the NUV light, five characteristic Eu³⁺ luminescence peaks appear at 578, 592, 610, 650 and 700 nm, which are due to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions, respectively. The relative intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 610 nm is the strongest. Most importantly, the complex shows the highest excitation intensity at around 370–395 nm, which is accurately matched with the NUV-emitting from the InGaN chips.

The coordination environment of Gd^{3+} ion in $Gd(IDTFBD)_3 \cdot 2H_2O$ is similar to that of Eu^{3+} ion in $Eu(IDTFBD)_3 \cdot 2H_2O$ as the radius of Gd^{3+} ion (94 pm) is close to that of Eu^{3+} ion (95 pm). The lowest excited state energy level of Gd^{3+} ion, ${}^{6}P_{7/2}$, is about 32,000 cm⁻¹, much higher than that of the lowest triplet energy level of the ligand IDTFBD⁻ [$T_1(L)$], so the



Fig. 2. The synthesis routine of the europium(III) complex Eu(IDTFBD)₃phen.



Fig. 3. The UV-visible absorption spectra of EuCl₃, the ligands and the Eu(III) complex in ethanol solution $(1 \times 10^{-5} \text{ mol } L^{-1})$: (a) EuCl₃, (b) phen, (c) HIDTFBD, (d) Eu(IDTFBD)₃phen.

absorbed energy by IDTFBD⁻ ligand cannot be transferred to Gd^{3+} ion, and phosphorescence of IDTFBD⁻ appears when $Gd(IDTFBD)_3 \cdot 2H_2O$ is excited by 430 nm light at 20 K. The lowest triplet state energy of the ligand IDTFBD⁻ $T_1(L)$, was determined by the shortest wavelength of the phosphorescence peak of $Gd(IDTFBD)_3 \cdot 2H_2O$ to be $E(T_1) = 18,416 \text{ cm}^{-1}$ (543 nm), which is higher than the lowest excited state of Eu^{3+} , 5D_0 (17,267 cm⁻¹) by 1149 cm⁻¹. So the mechanism of the photoluminescence of the corresponding europium(III) complex was proposed as a ligand-sensitized luminescence process (antenna effect) [13].

The fluorescence lifetime of Eu³⁺ in Eu(IDTFBD)₃phen was determined to be 357 µs by measuring the decay curve of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (610 nm) of the Eu³⁺. And the curve was fitted with a single exponential function, which indicates that the Eu³⁺ ions in Eu(IDTFBD)₃phen molecules are located in the same parity sites. The luminescence quantum yield for the Eu³⁺ complex was measured in solid state using an integrating sphere based on the method described by Lin [14]. And the luminescence quantum yield of the complex is $\varphi = 0.16$, which is good for a lanthanide organic complex. All the results indicate that the complex is an efficient red phosphor under NUV excitation.

Fig. 5 shows the emission spectra of the original LED without phosphor (a) and the LED fabricated with the complex Eu(IDTFBD)₃phen and a 395 nm-emitting InGaN chip (b) under excitation of 20 mA forward bias. The efficiency of the fabricated LED is 0.531 lm/W, much higher than that of the original LED without phosphor (0.33 lm/W). The CIE chromaticity coordinates of the LED are calculated as x = 0.65 and y = 0.32, which are very close to the National Television Standard Committee (NTSC) standard values for red (x = 0.67 and y = 0.33). A photograph of the lighting red LED with Eu(IDTFBD)₃phen is shown in



Fig. 4. PLE ($\lambda_{em} = 610 \text{ nm}$) and PL ($\lambda_{ex} = 385 \text{ nm}$) spectra of Eu(IDTFBD)₃phen.



Fig. 5. Emission spectra of the original LED without phosphor (a) and the LED with $Eu(IDTFBD)_3phen$ (b) and a photograph of the lighting LED (inset) under 20 mA forward bias.

Fig. 5 (inset). Bright purple-red light is observed, which is in accordance with its emission spectrum (Fig. 5b). As shown in Fig. 5b, only a little emission from the InGaN chip remains in the emission spectrum of the complex-LED, indicating that the NUV energy from the InGaN chip has been efficiently absorbed by the ligands and transferred to the central Eu^{3+} ions in the complex-LED can be used to excite a blue and a green phosphor to generate white light. The result indicates that $Eu(IDTFBD)_3$ phen is a good red component for fabrication of NUV-based white LEDs.

In summary, an imidazol-based β -diketone HIDTFBD and the corresponding europium(III) ternary complex were designed and synthesized. Eu(IDTFBD)₃phen exhibits good photoluminescence and high thermostability. A bright red LED was fabricated by coating Eu (IDTFBD)₃phen onto an ~395 nm-emitting InGaN chip, and all these results suggest that the Eu(III) complex is a promising candidate as red component for fabrication of near UV-based white light-emitting diodes.

Acknowledgments

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