

ARTICLE

Red Emission of Eu(III) Complex Based on 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione Excited by Blue Light

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A new Eu(III) complex, $\text{EuL}_3(\text{phen})$, was synthesized, where L is the abbreviation of deprotonated 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione (HL), phen is the abbreviation of 1,10-phenanthroline. The Eu(III) complex was characterized by element analysis, IR, ^1H NMR, UV-visible absorption spectroscopy, thermogravimetric analysis (TGA), and photoluminescence measurements (PL). TGA shows that thermal stability of the complex is up to 325 °C. PL measurement indicates that the Eu(III) complex exhibits intense red-emission and extends their excitation bands to visible region. LEDs device was successfully fabricated by precoating complex $\text{EuL}_3(\text{phen})$ onto 460 nm blue-emitting InGaN chip. The emission of device shows that the complex can act as red phosphor in combination with 460 nm blue-emitting chips. This europium complex based on 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione is a kind of interesting red-emitting material excited by blue light, which could avoid the damage of excitation by UV light.

Key words: Carbazole β -diketone, Lanthanide complex, Chemical synthesis, Luminescence

I. INTRODUCTION

Eu(III) β -diketonato complexes have been widely studied with the advantages of excellent photoluminescent properties with high color purity, high quantum yield and the environment-independent emission wavelength [1–7]. Generally, Eu(III) β -diketonato complexes give wide excitation bands in near ultraviolet (UV) region, they show low photochemical stability under UV irradiation [8]. Extending β -diketonato Eu(III) complex excitation band to visible region is an alternative path of avoiding UV irradiation damage.

There are two ways to extend β -diketonato complex excitation band to visible region. One method is to introduce 4d- or 5d-transition metal ion, such as Ir(III), Fe(II) into the Eu(III) complex molecule. Unfortunately, the photoluminescence efficiency of this kind of Eu(III) complex based on the MMLCT (metal-metal-to-ligand charge transfer) was always very low [9, 10]. The other method is to modify ligand molecule with expanded π -conjugated system. The size of π -conjugated system of ligand is very crucial. If the π -conjugated system is too small, it will not absorb visible-light, if it is too big, it will not sensitize the europium ion to emit because that the energy of triplet state of the ligand is higher than $^5\text{D}_0$, the lowest excited state energy level of the central Eu^{3+} [11, 12].

Carbazole group is an attractive unit of molecule

with interesting photoconducting, charge-transporting property, and thermal stability, which was widely introduced to polymers [13–16]. In our previous research, we found that 2-(β -diketonato)carbazole ligand can effectively sensitize europium ion to emit red emission and shift the excitation bands of its Eu(III) complexes to visible-light band comparing with 3-(β -diketonato)carbazole ligand [17–21]. *Tert*-butyl group is often introduced into molecules to change photochemistry property of substance because it arouses big volume substitute effect and space effect [22–24]. Herein we synthesize 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione (HL) and its Eu(III) complex to investigate its thermal stability and luminescence property.

The solid lighting technology is especially expected to replace incandescent bulbs and fluorescent lamps. One path of getting white LEDs is combining 460 nm blue-emitting InGaN chip with broad-band yellow-emitting phosphor, *e.g.* Ce^{3+} -doped yttrium aluminum garnet (YAG: Ce^{3+}) [25]. However, such white LEDs show low color-rendering index, low color reproducibility, and low luminous efficiency because of the deficiency of red emission light. It is urgent to find red-emitting phosphor that can be excited by blue light [26]. In order to investigate whether complex, $\text{EuL}_3(\text{phen})$, could be acted as red-emitting phosphors excited by blue light, LEDs device was successfully fabricated by precoating complex $\text{EuL}_3(\text{phen})$ onto 460 nm emitting InGaN chips. The europium complex based on 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione is a kind of interest-

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ing red-emitting material excited by blue light, which could avoid the damage of excitation by UV light.

II. EXPERIMENTS

A. Materials and characterization

1-(4-bromo-3-nitrophenyl)ethanone, ethyl trifluoroacetate, (4-(*tert*-butyl)phenyl)boronic acid, and Pd(PPh₃)₄ were purchased from Shenzhen Meryer Chemistry Technology Company. All reagents and materials were analytical grade. Solvents were freshly distilled and dried by standard methods. Elemental analyses for the synthesized ligand and the Eu(III) complex were carried out with an Elementar vario EL elemental analyzer. Electrospray ionisation mass spectra (ESI-MS) were acquired on a Thermo Finnigan LCQ DECA XP ion trap mass spectrometer, equipped with an ESI source. ¹H NMR spectra were recorded on a Bruker AVANCE 400. Photoluminescence excitation and emission spectra were measured with an EDINBURGH FLS 920 combined fluorescence lifetime and steady state spectrophotometer. UV-visible absorption spectra were recorded on a UV-2501PC UV-visible spectrophotometer. IR spectra were recorded on a Nicolet Avatrar 330 FT-IR Spectrometer. Thermogravimetric analysis (TGA) was carried out up to 600 °C with a heating speed of 10.0 °C/min in atmosphere on a NETZSCH TG-209 Thermogravimetric Analyzer. The emission spectrum of the fabricated LEDs and the overall quantum yield of the Eu(III) complex were measured with an EVERFINE PMS-50 PLUS UV-VIS-near IR spectrophotometer. All measurements were made at room temperature.

B. 1-(4'-(*tert*-butyl)-2-nitro-[1,1'-biphenyl]-4-yl)ethanone

1-(4'-(*tert*-butyl)-2-nitro-[1,1'-biphenyl]-4-yl)ethanone was synthesized by Suzuki-Miyaura cross-coupling reaction [27]. 1-(4-bromo-3-nitrophenyl)ethanone (4.88 g, 0.02 mol), (4-(*tert*-butyl)phenyl)boronic acid (3.56 g, 0.02 mol), K₂CO₃ (2.76 g, 0.02 mol), and Pd(PPh₃)₄ (0.22 g, 0.02 mmol) were solved in 150 mL toluene and 30 mL water, then heated at 110 °C for 24 h. The crude product was extracted with CH₂Cl₂ and purified by column chromatography (ethyl acetate-petroleum ether) to give 1-(2'-nitrobiphenyl-4-yl)ethanone (5.1 g, yield of 86%). The elemental analysis data for C₁₈H₁₉NO₃ were found (calculated): C 72.52%(72.71%), H 6.57%(6.44%), N 4.60%(4.71%). ¹H NMR (300 Hz, CDCl₃, δ) 1.38 (s, 9H, -C(CH₃)₃), 2.70 (s, 3H, -COCH₃), 7.31 (s, 2H, Ph-H), 7.47–7.50 (d, 2H, Ph-H), 7.58–7.60 (d, 1H, Ph-H), 8.16–8.20 (d, 1H, Ph-H), 8.37–8.38 (d, 1H, Ph-H). ESI-MS: *m/z*=298 (M+H⁺).

C. 1-(7-(*tert*-butyl)-9H-carbazol-2-yl)ethanone

The synthesis of 1-(7-(*tert*-butyl)-9H-carbazol-2-yl)ethanone is realized by Cadogan cyclization reaction [28, 29]. 1-(4'-(*tert*-butyl)-2-nitro-[1,1'-biphenyl]-4-yl)ethanone (4.6 g, 15 mmol) and PPh₃ (11.8 g, 45 mmol) were added into *o*-dichlorobenzene (*o*-DCB) and refluxed for 8 h. The most byproducts and impurities have been removed by precipitation from hexane. No further purification was executed, since the major impurity, PhPh₃ and PPh₃O, didn't take part in the next step reaction. The ESI-MS was used to monitor the formation of 1-(7-(*tert*-butyl)-9H-carbazol-2-yl)ethanone, ESI-MS: *m/z*=264 (M-H⁺).

D. 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)ethanone

1-(7-(*tert*-butyl)-9H-carbazol-2-yl)ethanone and 4.0 mL C₂H₅Br were added into the mixture of NaOH (0.8 g, 0.02 mol) and 200 mL acetone. The reaction solution was reduced after being stirred for 2 days at room temperature. Then the solution was poured into water. The precipitate was then filtered, washed with water, and recrystallized from alcohol to give crude 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)ethanone. The pure product was obtained by column chromatography (dichloromethane-petroleum ether). (2.46 g, yield of 56%). The elemental analysis data for C₂₀H₂₃NO were found (calculated): C 81.81%(81.87%), H 7.74%(7.90%), N 4.78%(4.77%). FT-IR (KBr): ν=3429, 2962, 1671, 1625, 1471, 1434, 1326, 1251, 809, 657, 586 cm⁻¹. ¹H NMR (300 Hz, CDCl₃, δ) 1.48 (s, 9H, -C(CH₃)₃) 1.67 (m, 3H, -CH₃), 2.76 (s, 3H, CO-CH₃), 4.43–4.50 (q, 2H, -CH₂), 7.35–7.44 (s, 1H, Ar-H), 7.36–7.38 (d, 1H, Ar-H), 7.82–7.85 (d, 1H, Ar-H), 8.06–8.12 (t, 3H, ArH). ESI-MS: *m/z*=294 (M+H⁺).

E. 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione

1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione was synthesized by Claisen condensation reaction from ketone and ester. The mixture of 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)ethanone (1.45 g, 5 mmol), CF₃COOC₂H₅ (1.42 g, 0.01 mol) and C₄H₉OK (0.73 g, 6 mmol) was refluxed for 6 h in toluene. Then the mixture was treated with diluted hydrochloric acid and extracted with toluene. The solvent was evaporated in vacuum. The crude product was recrystallized from ethanol. The pure 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione (1.13 g, yield of 78%) was obtained by column chromatography (dichloromethane-petroleum ether). The elemental analysis data for C₂₂H₂₂F₃NO₂ were found (calculated): C 67.81%(67.86%), H 5.74%(5.69%), N 3.58%(3.60%). FT-IR (KBr): ν=3449, 2968, 1583, 1496, 1443, 1330, 1265, 1206, 1153, 1110, 791, 704,

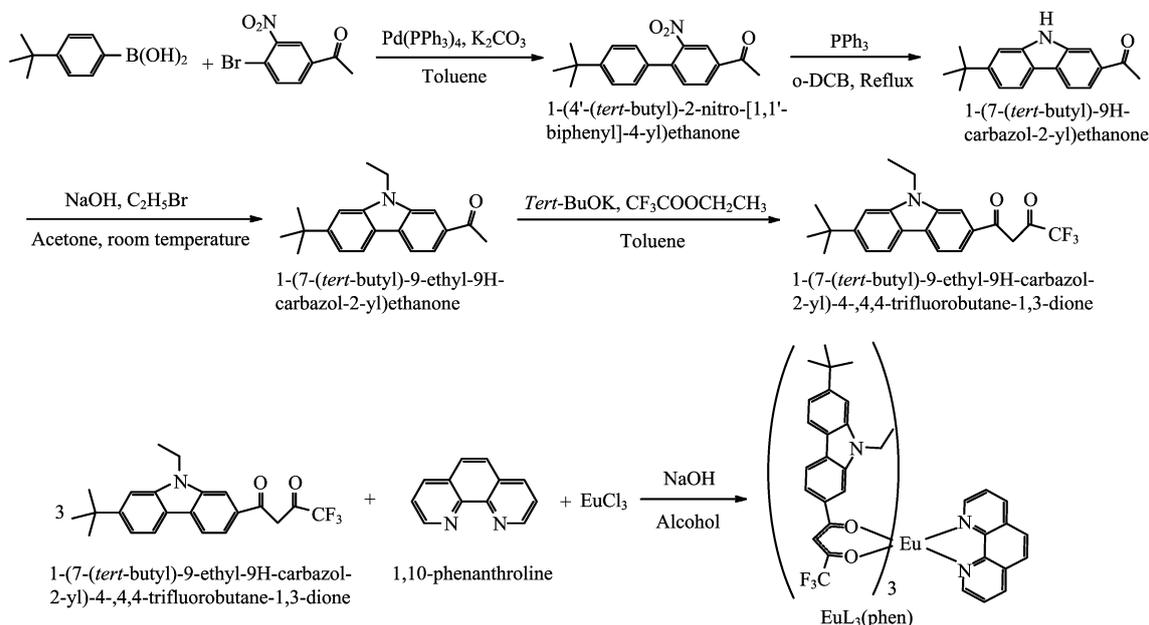


FIG. 1 The synthesis routine of the ligand and the europium complex $\text{EuL}_3(\text{phen})$.

582 cm^{-1} . $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 1.48 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.54–1.52 (m, 3H, $-\text{CH}_3$), 4.45–4.52 (q, 2H, $-\text{CH}_2-$), 6.75 (s, 1H, $\text{C}(\text{OH})=\text{C}-\text{H}$), 7.38–7.45 (m, 2H, Ar-H), 7.77–7.80 (m, 1H, Ar-H), 8.07–8.10 (m, 2H, Ar-H), 8.13–8.15 (d, 1H, Ar-H). ESI-MS: $m/z=388$ ($\text{M}-\text{H}^+$).

F. $\text{EuL}_3(\text{phen})$

1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione (116.7 mg, 0.3 mmol), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (36.6 mg, 0.1 mmol), 1,10-phenanthroline (phen) (19.8 mg, 0.1 mmol) were mixed with a molar ratio of 3:1 in alcohol. The solution was adjusted to pH=8–9 by NaOH solution, and heated at 60 °C for 2 h under stirring. The precipitate was filtered and washed with alcohol, dried at 50 °C, yellow complex product was obtained (0.11 g, yield of 73%). The elemental analysis data for $\text{EuL}_3(\text{phen})$ ($\text{C}_{78}\text{H}_{74}\text{EuF}_9\text{N}_5\text{O}_6$) were found (calculated): C 62.48%(62.44%), H 4.89%(4.97%), N 4.56%(4.67%), FT-IR (KBr): 3440, 2962, 1610, 1531, 1469, 1296, 1257, 1137, 958, 789, 580 cm^{-1} . $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 1.40 (s, 27H, $-\text{C}(\text{CH}_3)_3$), 1.70 (t, 9H, $-\text{CH}_3$), 3.54 (s, 3H, $=\text{C}-\text{H}$), 4.67 (d, 6H, $-\text{CH}_2$), 6.09 (d, 3H, Ar-H), 7.33–7.36 (d, 3H, Ar-H), 7.51 (d, 6H, Ar-H), 7.90 (d, 3H, Ar-H), 8.14 (d, 2H, Ar-H), 8.48 (d, 2H, py-H), 10.16 (s, 2H, py-H), 10.64 (s, 2H, py-H).

G. Fabrication of LEDs

Light-emitting diodes device was fabricated by combination of 460 nm-emitting InGaN chip with the

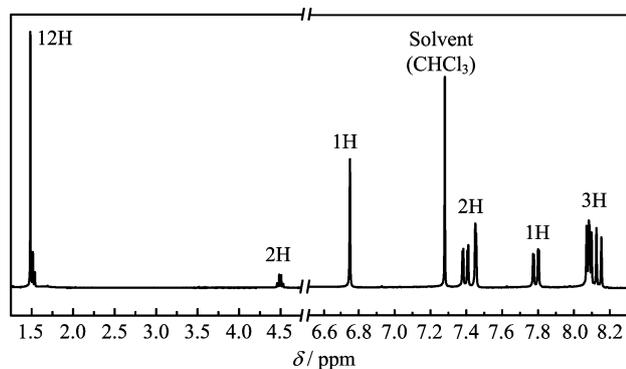
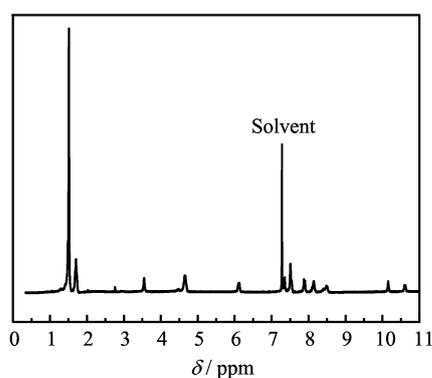
$\text{Eu}(\text{III})$ complex as phosphor. The phosphor was blended with commercially available silica gels (6175A and 6175B, purchased from Sil-More Industrial Ltd., China) in order to be precoated onto the LED chip. The thickness of the admixture precoated onto the chip was the same due to the fixed size of the reflector cup. In order to prevent the phosphor from dispersing into the epoxy resins, the admixture was firstly cured in an oven at 150 °C for 1 h. Then, the admixture and chip were encapsulated with transparent epoxy resin. Eventually, the LEDs device was obtained by transparent epoxy resin cured in oven at 150 °C for 1 h.

III. RESULTS AND DISCUSSION

A. Synthesis, $^1\text{H NMR}$, IR, and thermal stability

The key steps in the synthesis routine (see Fig.1) are the synthesis of 1-(4'-(*tert*-butyl)-2-nitro-[1,1'-biphenyl]-4-yl)ethanone by a Suzuki-Miyaura cross-coupling reaction, and 1-(7-(*tert*-butyl)-9H-carbazol-2-yl)-ethanone by Cadogan cyclization. The formation of β -diketone group was adopted by common Claisen condensation reaction from ketone and ester. The europium complex was obtained from europium ion and β -diketone in the base alcohol solution.

The $^1\text{H NMR}$ spectrum of 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluoro-butane-1,3-dione confirms the structure of ligand (Fig.2). Only one $-\text{CH}-$ hydrogen atom in β -diketone group is detected, which suggests that β -diketone adopt enol configuration form in CDCl_3 solution. The shift values and numbers of all the other hydrogen atoms are in good agreement with

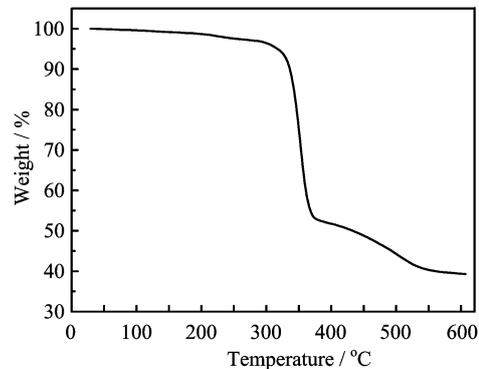
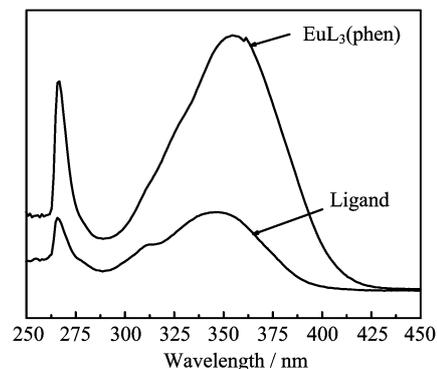
FIG. 2 The ^1H NMR spectrum of the ligand.FIG. 3 The ^1H NMR spectrum of the complex $\text{EuL}_3(\text{phen})$.

the theoretically calculated hydrogen of ligand structure.

The ^1H NMR spectrum of complex is shown in Fig.3, which confirms the structure of complex. The peaks at 10.16 (s, 2H) and 10.64 (s, 2H) show the 1,10-phenanthroline coordinated to the europium ion. The peak 6.75 of $=\text{C}-\text{H}$ in the free ligand shifts to 3.54 in the complex suggest that β -diketonato group oxygen atoms of L-1 coordinated to europium ion.

Comparison of the IR absorption spectra of ligand and complex shows that the peaks in ligand are all red shifted in the complex. 1583 cm^{-1} of $\text{C}=\text{O}$ was shifted to 1610 cm^{-1} , 1496 cm^{-1} of $\text{C}=\text{C}$ of ligand appearing on 1532 cm^{-1} in complex. This is the characteristic of β -diketonato coordinated with rare earth ions since the $\text{C}=\text{O}$ bond was converted into vibrating structure of $\text{C}-\text{O}-\text{Eu}$ bond and $\text{C}=\text{O}-\text{Eu}$ bond. The element analyses for ligand and europium complex are also in good agreement with theoretically calculation.

High thermal stability is an essential requirement for most application. TGA curve of the complex $\text{EuL}_3(\text{phen})$ is shown in Fig.4. TGA results show that the decomposition temperatures of the complex is up to $325\text{ }^\circ\text{C}$, which meets with the requirement for normal working temperature of LEDs [30].

FIG. 4 The TGA curve of the complex $\text{EuL}_3(\text{phen})$.FIG. 5 The UV-visible absorption spectra of the ligand and the complex $\text{EuL}_3(\text{phen})$ in alcohol ($10\text{ }\mu\text{mol/L}$).

B. UV-visible absorption and photoluminescence

The UV-visible absorption spectra of the ligand and the complex $\text{EuL}_3(\text{phen})$ in alcohol solution ($10\text{ }\mu\text{mol/L}$) are shown in Fig.5. All the profile of the absorption spectra of the complex is similar to the free ligand, suggesting that the ligand contributes to the key absorption for the complex, since the aqueous Eu^{3+} shows very weak absorption in this range. The absorption band from 300 nm to 400 nm is attributed to the $\pi-\pi^*$ transition absorption of ligand. The absorption band centered at 265 nm is attributed to the $n-\pi^*$ transition absorption of ligand. The absorption bands of the complex extend to the visible region, which are favorable to being excited by visible-light.

The emission and excitation spectra of ligand, complex $\text{EuL}_3(\text{phen})$ powder sample are shown in Fig.6. The ligand emits green-yellow light with the peak at 512 nm under $250-500\text{ nm}$ wavelength light. The complex emit red light under $230-500\text{ nm}$ wavelength light. In the complex, no green-yellow light remains, which shows that the ligand could effectively absorb energy to sensitize the europium ions to emit red light. Compared with the similar 3-(β -diketonato)carbazole complexes, the excitation bands of the complex show remarkable red-shift by about 30 nm and were extended to 500

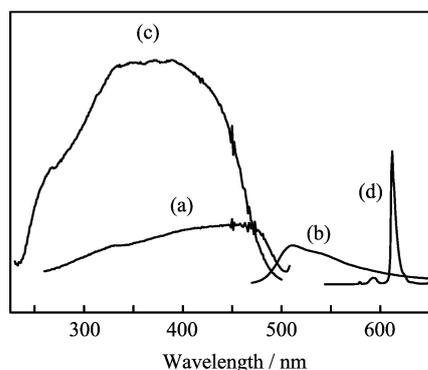


FIG. 6 The excitation and emission spectra of ligand and complex $\text{EuL}_3(\text{phen})$. (a) Excitation spectra of ligand, monitored at $\lambda_{\text{em}}=512$ nm, (b) emission spectra of ligand $\lambda_{\text{ex}}=460$ nm, magnified by 2.5 times, (c) excitation spectra of complex monitored at $\lambda_{\text{em}}=613$ nm, (d) emission spectra of complex $\lambda_{\text{ex}}=395$ nm.

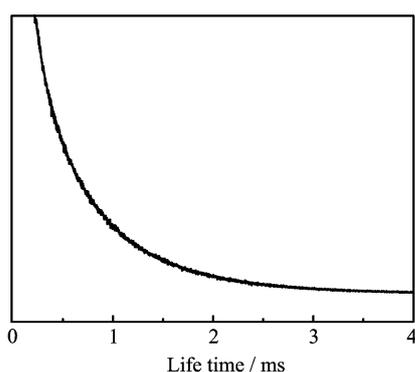


FIG. 7 The decay curve of $\text{Eu}^{3+} \ ^5\text{D}_0$ excited state of complex $\text{EuL}_3(\text{phen})$.

nm [17–19]. This red-shift would make the complex avoid UV irradiation-induced photodecomposition in photoluminescence applications. Monitored at 613 nm, the excitation band of complex $\text{EuL}_3(\text{phen})$ extends to 500 nm, the complex can emit red light by excitation of 460 nm-emitting InGaN chips light.

The decay curve of $\text{Eu}^{3+} \ ^5\text{D}_0$ excited state of complex $\text{EuL}_3(\text{phen})$ is shown in Fig.7. The luminescence decay time of the $^5\text{D}_0$ state in complex $\text{EuL}_3(\text{phen})$ is 604 μs . The curve fit with a single exponential function, indicating that the Eu^{3+} in complex molecule is only located at the same parity site. The europium complex has been of importance for fluorometric applications in biochemistry and molecular biology owing to its longer luminescence lifetime [31].

The overall quantum yield of the complex was measured in solid state using an integrating sphere according to the method described by Lin *et al.* [32]. The overall quantum yields is 14% for $\text{EuL}_3(\text{phen})$. The reduction of overall quantum yield for this complex than complex $\text{Eu}(\text{2-TFDBC})_3(\text{phen})$ (28%, where, 2-TFDBC, 1-(9-ethyl-9H-carbazol-2-yl)-4,4,4-

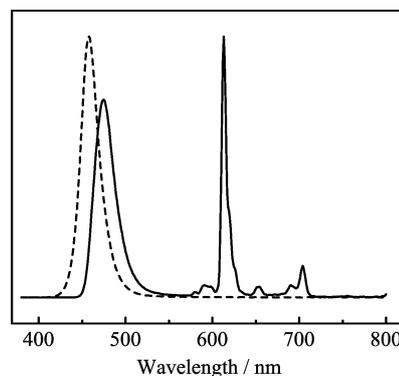


FIG. 8 The emission spectra of the original InGaN LEDs without phosphor (broken line) and the LEDs with $\text{EuL}_3(\text{phen})$ (solid line) under excitation of 20 mA forward bias.

trifluorobutane-1,3-dione) is due to the C–H oscillation of *tert*-butyl group [17].

C. Emission spectra of the fabricated LEDs

Complex $\text{EuL}_3(\text{phen})$ was employed as a phosphor to fabricate LEDs in a mass ratio of 1:20 of phosphor to silicone gel with 460 nm-emitting InGaN chips. The emission spectra of the original 460 nm LEDs without phosphor and the LED fabricated with the complex and a 460 nm chip under 20 mA forward bias are shown in Fig.8. The sharp peak at 613 nm is due to the Eu^{3+} emission from the complex in the LEDs chip. Based on the emission spectrum, the CIE chromaticity coordinates of the LED are calculated as $x=0.28$ and $y=0.20$, confirming that the complex can be excited by blue light from the LEDs. The remained exciting light from 460 nm chips could be used to excite other color-emitting phosphors to obtain white-emitting LEDs. This result suggests that this complex can be used as red component in the fabrication of white LEDs excited by 460 nm chips.

IV. CONCLUSION

A new ligand which contains carbazole group, 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione was synthesized. Deprotonated 1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione and 1,10-phenanthroline coordinate to europium ion and result in a new complex, $\text{EuL}_3(\text{phen})$, which emits red emission and extends its excitation bands to blue region. LEDs device is successfully fabricated by the complex with 460 nm emitting chips. The emission spectra of device indicate that the europium complex can be employed as red component in the fabrication of white LEDs excited by 460 nm chips. The europium complex based on

1-(7-(*tert*-butyl)-9-ethyl-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione is a kind of interesting red-emitting material excited by blue light, which can avoid the damage of excitation by UV light.

V. ACKNOWLEDGMENT

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