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An efficient 2-linked carbazolyl β-diketonate europium(III) complex as red phosphor applied in LED

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Abstract An efficient 2-linked carbazolyl β-diketonate europium(III) complex Eu(ETFMCTFBD)$_3$phen was designed and synthesized, where ETFMCTFBD was 1-(9-ethyl-7-(trifluoromethyl)-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione and phen was 1,10-phenanthroline. Eu(ETFMCTFBD)$_3$phen exhibits high thermal stability and excellent photoluminescence properties. The CIE chromaticity coordinates ($x = 0.668$, $y = 0.331$) are close to the National Television Standard Committee (NTSC) standard values for red. The lowest triplet energy was measured and suggests the photoluminescence process as a ligand-sensitized luminescence process (antenna effect). A bright red light-emitting diode was fabricated by coating the complex phosphor onto a ∼395 nm-emitting InGaN chip. All the results indicate that Eu(ETFMCTFBD)$_3$phen is a good candidate as a red component in the fabrication of white LEDs with a high color-rendering index.

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1 Introduction

Light-emitting diode (LED) lamps using phosphor conversion of 350–480 nm LED radiation potentially can have higher efficiencies than traditional fluorescent lamps [1]. With the development of LED chip technology, the near UV light emission (∼400 nm) LED chips can offer higher energy to pump the phosphor [2], and the scheme of blue LED (∼460 nm) add yellow phosphor also appears to have many serious drawbacks such as color shift, low reproducibility and low color-rendering index (CRI) mainly due to the two-color mixing [3]. In order to obtain a higher efficiency white LED with an appropriate color temperature and a higher color-rendering index, a new approach using near UV (around 400 nm) InGaN-based LED chip coated with blue/green/red tricolor phosphors was introduced [4]. Presently, the main phosphors for near UV InGaN-based LEDs are $BaMgA_{11}0O_{17}:Eu^{2+}$ for blue, $ZnS:(Cu^{+}, Al^{3+})$ for green, and $Y_2O_2S:Eu^{3+}$ for red [5]. However, the efficiency of the $Y_2O_2S:Eu^{3+}$ red phosphor is much less than that of the blue and green phosphors [6]. Therefore, red-emitting phosphors with high luminance and satisfactory chromaticity become the key requirement to improve the lighting properties of white LEDs.

The primary interests of the present work are to search for a proper red-component phosphor for near-UV LEDs, which should show the following characteristics: proper thermal stability, good CIE chromaticity coordinates close to the NTSC (National Television Standard Committee) standard values, and strong absorption in LED chips emission region [4].

Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity [7–13]. Compared with other organic materials with a π-conjugated system, carbazole unit shows

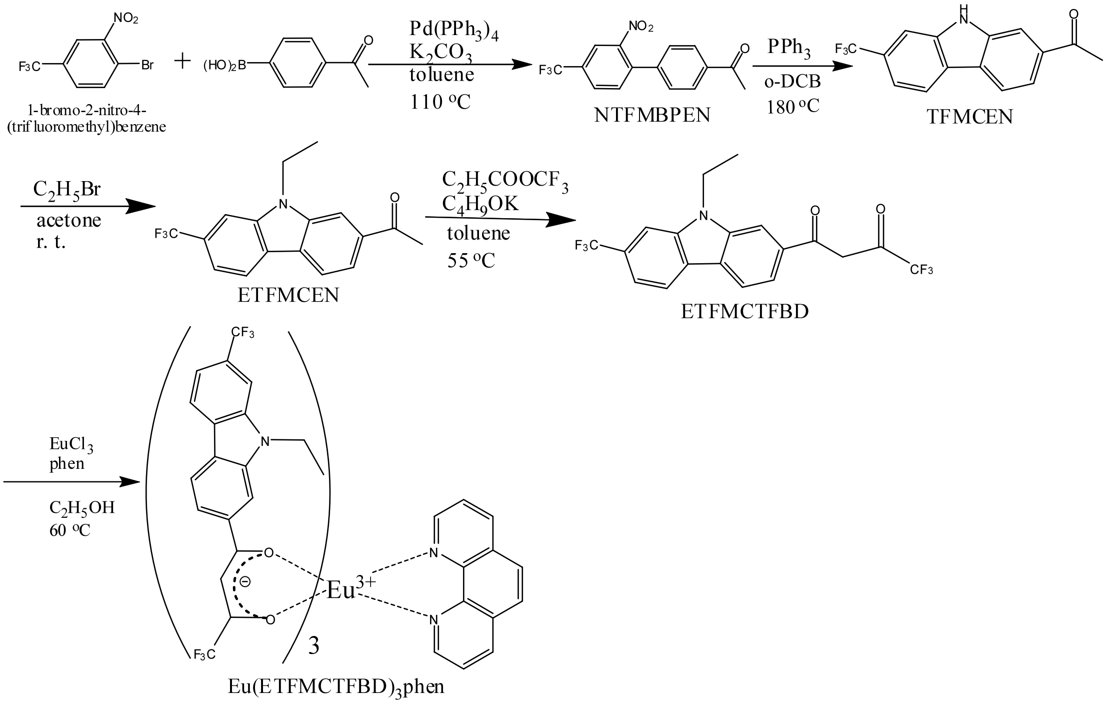

Fig. 1 Synthesis routine of ligand ETFMCTFBD and complex Eu(ETFMCTFBD)$_3$phen

special advantages, such as cheap starting material; better chemical and environmental stability, and easy substitution of nitrogen atom with a wide variety of functional groups for tuning the optical and electrical properties [14]. Consequently, in recent years, many organic materials containing a carbazole unit have been synthesized, but most of these compounds are photorefractive materials based on polymeric composites [15].

In our earlier work, 2- and 7-positional substituted β-diketonate europium complexes exhibited special photoluminescence properties [16]. In this article, a trifluoromethyl was introduced at 7-position in the 2-positional substituted carbazole β-diketone to observe the effect on the luminescence of the corresponding Eu(III) complex. 1-(9-ethyl-7-(trifluoromethyl)-9H-carbazol-2-yl)-4,4,4-trifluorobutane-1,3-dione (ETFMCTFBD) was designed and synthesized, and the corresponding complex Eu(ETFMCTFBD)$_3$ phen was prepared. The thermal stability and photoluminescence (PL) properties of the complex were investigated. A bright red LED was fabricated by coating the europium(III) complex onto an ~395 nm-emitting InGaN chip.

2 Experimental

All reagents and materials were analytical grade. Solvents were freshly distilled and dried by standard methods. Elemental analyses for the synthesized organic compounds and the complex were carried out with an Elementar vario EL elemental analyzer. Electron impact-mass spectrometer (EI-MS) spectra were determined on a Thermo DSQ EI-MS. ^{1}H NMR spectra were recorded on a Varian INOVA500NB. Excitation and emission spectra were measured with an Edinburgh FLS 920 combined fluorescence lifetime and steady-state spectrophotometer. UV-visible (UV-vis) absorption spectra were recorded on a UV-2501PC UV-vis spectrophotometer. IR spectra were recorded on a Nicolet Avatrar 330 Fourier transform infrared (FTIR) spectrometer with KBr method. Thermogravimetric analysis (TGA) was carried out up to 930°C with a heating speed of 10.0 K/min in air atmosphere on a Netzsch TG-209 thermogravimetric analyzer. The emission spectra of the fabricated LEDs and the quantum yield of the complex were measured with an Everfine PMS-50 PLUS UVvis- near-IR spectrophotocolorimeter.

The synthesis routine for ligand ETFMCTFBD and complex Eu(ETFMTFBD)$_3$phen is shown in Fig. 1.

1-(2′-nitro-4′-(trifluoromethyl)biphenyl-4-yl)ethanone (NTFMBPEN) was synthesized via a Suizuki-Miyaura cross-coupling reaction [17–19]. 1-bromo-2-nitro-4-(trifluoromethyl)benzene, 4-Acetylphenyl boronic acid, K_2CO_3 aqueous solution and $Pd(PPh_3)_4$ were solved in toluene and heated at 110°C for 2 days. The crude products were extracted with CH_2Cl_2 and purified by column chromatography (dichloromethane - petroleum ether with a 1:2 volume ratio) to give NTFMBPEN:

^{1}HNMR (CDCl$_3$) δ 2.674 (s,3H,-CH$_3$);
δ 7.440–7.466 (m,2H,PhH); δ 7.621–7.641 (d,1H,PhH);
δ 7.932–7.954 (q,1H,PhH); δ 8.058–8.088 (m,2H,PhH);
δ 8.229–8.231 (d,1H,PhH).
MS(EI)m/z: 309(M$^+$), 294(M$^+$-CH$_3$), 294(M$^+$-CH$_3$). The elemental analysis data for $C_{15}H_{10}F_3NO_3$ were: found (calculated) %: C, 58.24 (58.26); H, 3.37 (3.26); N, 4.43 (4.53).

The method preparing 1-(7-(trifluoromethyl)-9H-carbazol-2-yl)ethanone (TFMCEN) is commonly referred to as the Cadogan cyclization [20]. TFMCEN and PPh$_3$ were added into o-dichlorobenzene (o-DCB) and refluxed for 6.5 h. The most byproducts and impurities have been removed by precipitation from hexane. No further purification was executed, considering that the major remained impurity PhPh$_3$ and PPh$_3$O, could be easily removed by chromatography in the last products because of the large difference of polarity, and they would not influence the following reactions. TFMCEN:

MS(EI)m/z: 277(M$^+$), 262(M$^+$-CH$_3$),
208(M$^+$-COCH$_3$), 234(M$^+$-COCH$_3$-CH$_3$).

1-(9-ethyl-7-(trifluoromethyl)-9H-carbazol-2-yl)ethanone (ETFMCEN) and C$_2$H$_5$Br were added into the mixture of KOH and acetone. The reaction solution was refluxed for 3 days. The solution was poured into water, stirred continuously until a white precipitate was deposited completely. The precipitate was then filtered, washed with distilled water, and recrystallization from alcohol to remove remained TFMCEN and ETFMCEN was achieved. No further purification was executed. ETFMCEN:

MS (EI)m/z: 305(M$^+$), 290(M$^+$-methyl),
262(M$^+$-COCH$_3$), 247(M$^+$-COCH$_3$-CH$_3$).

ETFMCTFBD was synthesized via a Claisen condensation reaction from ketone and esters with a similar method described in literature [21]. A mixture of ETFMCEN, toluene, CF$_3$COOC$_2$H$_5$ and C$_4$H$_9$OK was stirred under room temperature, and reflux for 6 h in N$_2$ atmosphere. Then the mixture was treated with diluted hydrochloric acid and extracted with toluene. The solvent was evaporated in vacuum. The ETFMCTFBD crude product was purified by recrystallization in alcohol after separated by column chromatography (dichloromethane—petroleum ether with a 1:10 volume ratio). ETFMCTFBD:

^{1}HNMR (CDCl$_3$) δ 1.523–1.560 (t,3H,-CH$_3$);
δ 4.493–4.548 (q,2H,-CH$_2$-); δ 6.759 (s,1H,enol-γ-CH-);
δ 7.547–7.567 (d,1H,ArH); δ 7.745 (s,1H,ArH);
δ 7.832–7.856 (q,1H,ArH); δ 8.138–8.141 (d,1H,ArH);
δ 8.220–8.260 (t,2H,ArH).
MS(EI)m/z: 401(M$^+$), 486(M$^+$-CH$_3$), 332(M$^+$-CF$_3$), 290(M$^+$-CH$_2$COCF$_3$). The elemental analysis data for $C_{19}H_{13}F_6NO_2$ were found (calculated)%: C, 56.89(56.87); H, 3.3.26(3.27); N, 3.52(3.49).

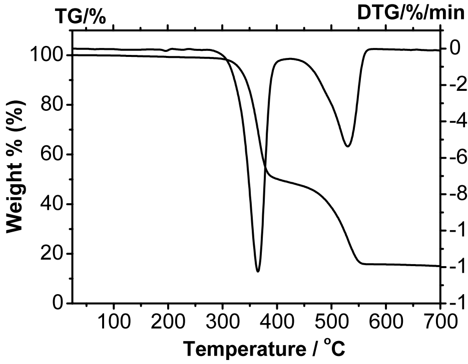

Fig. 2 TGA and DTG curves of the complex Eu(ETFMCTFBD)$_3$phen

ETFMCTFBD, phen and EuCl$_3$ were mixed with a molar ratio of 3:1:1 in alcohol and stirred, and heated at 60°C for 6 h. An orange precipitate was obtained for Eu(ETFMCTFBD)$_3$phen. IR spectra of ETFMCTFBD and Eu(ETFMCTFBD)$_3$phen show that the peak at 1535 cm^{-1} in the ETFMCTFBD spectrum was shifted to 1529 cm^{-1} in the complex spectrum, and a stretching vibration peak of C=C appeared at 1427 cm^{-1}. This is the characteristic of β-diketonate coordinated with rare-earth ions; the C=O bond was converted into a vibrating structure of C–O–Eu bond and C=O–Eu bond. The elemental analysis data for Eu(ETFMCTFBD)$_3$phen ($C_{69}H_{44}EuF_{18}N_5O_6$) were found (calculated)%: C, 53.83 (54.06); N, 4.33 (4.57); H, 3.06 (2.89). FTIR (KBr): $v = 1610$(s); 1564(s); 1529(s); 1500(s); 1477(s); 1457(s); 1427(w); 1382(w) cm^{-1}.

For measuring the lowest triplet state energy level of the ligand ETFMCTFBD, gadolinium(III) binary complex with ETFMCTFBD, Gd(ETFMCTFBD)$_3 \cdot 2H_2O$, was also synthesized with a similar procedure except using phen. The elemental analysis data for Gd(ETFMCTFBD)$_3 \cdot 2H_2O$ ($C_{57}H_{40}GdF_{18}N_3O_8$) were found (calculated)%: C, 48.82 (49.11); H, 2.71 (2.89); N, 2.86 (3.01).

3 Results and discussion:

3.1 Thermal stability of the complex

As well known, device temperature would rises up when an LED is working, so proper thermal stability is an essential requirement for phosphors used in LEDs. The differential TGA (DTG) curve (Fig. 2) shows that the decomposition temperature of Eu(ETFMCTFBD)$_3$phen is 365.9°C, which is thermally stable enough to be fabricated in LEDs.

3.2 UV-vis absorption spectra

The UV-vis absorption spectra of Eu(ETFMCTFBD)$_3$phen, ETFMCTFBD, phen, and EuCl$_3$ in alcohol solution

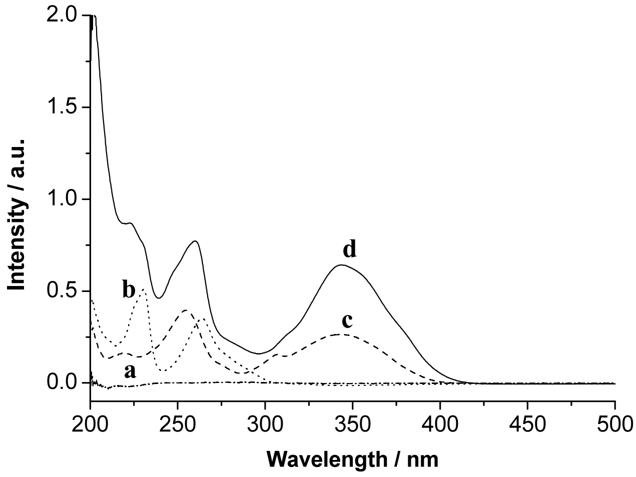

Fig. 3 UV-vis absorption spectra of the ligands and the Eu^{3+} complex in alcohol (1×10^{-5} mol/L): (**a**) $EuCl_3$, (**b**) phen, (**c**) ETFMCTFBD, and (**d**) Eu(ETFMCTFBD)$_3$phen

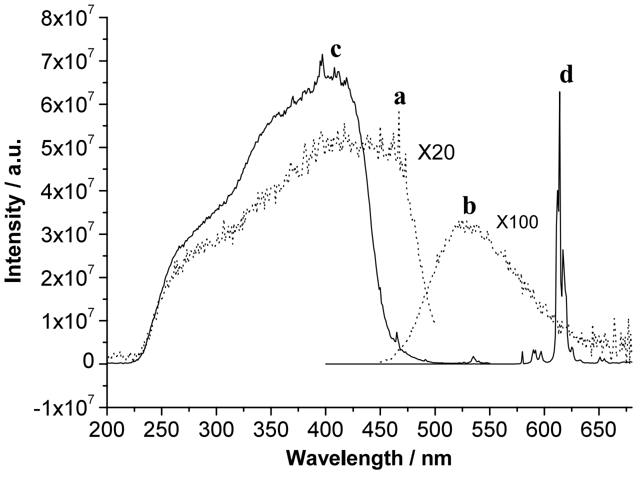

Fig. 4 Excitation and emission spectra of ligand ETFMCTFBD. ((**a**) $\lambda_{em} = 530$ nm, blown up by 20 times; (**b**) $\lambda_{ex} = 417$ nm, blown up by 100 times) and complex Eu(ETFMCTFBD)$_3$phen ((**c**) $\lambda_{em} = 613$ nm; (**d**) $\lambda_{ex} = 397$ nm)

(1×10^{-5} mol/L) are shown in Fig. 3. The strong absorption peaks for Eu(ETFMCTFBD)$_3$phen are located at 223, 260 and 343 nm. As shown in Fig. 3, there are wide range absorption band from 200 to 400 nm, however the absorption from 300 to 400 nm is only attributed to the π–π^* transition absorption of ETFMCTFBD; and the absorption of the secondary ligand phen is very weak in this region. The absorption intensity was enhanced remarkably in the complex spectrum, because of the expanded π-conjugated system in the complex molecule. The existence of the secondary ligand phen not only provided larger π-conjugated system, but also satisfied the high coordination number (8) for the central Eu^{3+} ion, and thus improves the coordination stability and thermal stability of the complex.

3.3 Photoluminescence properties

The excitation and emission spectra of ligand ETFMCTFBD and the complex Eu(ETFMCTFBD)$_3$phen powder samples, measured in the same experimental condition, are shown in Fig. 4. The excitation spectrum of ligand ETFMCTFBD (Fig. 4a) exhibits a broad band between 225 and 500 nm with low intensity, and the ligand emits weak green light under near 417 nm light excitation (Fig. 4b). As a comparison, formation of the complex Eu(ETFMCTFBD)$_3$phen enhanced both the intensity of excitation and emission spectra remarkably (Fig. 4c and d). The excitation band of the complex stays in a wide range (225–450 nm), due to the formation of a large π-conjugated system in the complex molecule; and the strong and narrow red emission at 613 nm appears,attributed to the transmission $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ions. Compared with the complex without the trifluoromethyl at 7-position in our earlier work [17], the integrated emission intensity of Eu(ETFMCTFBD)$_3$phen is about 2.2 times higher, while it is 6 times higher than that of the $Y_2O_2S{:}Eu^{3+}$, a commercial red phosphor applied in LEDs, synthesized as the method reported by Reddy [22]. Importantly, the highest excitation intensity of the complex appears at around 395 nm, which is accurately matched with the emission wavelength of a near UV-emitting InGaN chip. This fact reveals that the complex is a good candidate as a red phosphor in the fabrication of near UV-based white LEDs.

The CIE chromaticity coordinates for Eu(ETFMCTFBD)$_3$ phen are calculated to be $x = 0.668$, $y = 0.331$ based on its emission spectrum. Compared with the widely used commercial red phosphor $Y_2O_2S{:}Eu^{3+}$ ($x = 0.63$, $y = 0.35$) for LED, the CIE chromaticity coordinates of Eu(ETFMCTFBD)$_3$phen are closer to the National Television Standard Committee standard CIE values for red ($x = 0.67$, $y = 0.33$) [23].

The quantum yield of the complex was measured in the solid state using an integrating sphere based on the method described by Lin [24]. The quantum yield of Eu(ETFMCTFBD)$_3$phen is 0.34, which is good for a europium(III) organic complex due to the ligand-sensitized luminescence mechanism and the parity-forbidden f–f transitions of Eu^{3+} ions. In fact, the quantum efficiency is about 0.20–0.30 for a common rare-earth organic complex, and the best quantum efficiency is 0.49 for Eu(TTA)$_3$phen. Deuteration can significantly decrease the quenching capacity of C–H oscillators on luminescence in an organic complex, therefore it is a possible route to improve the efficiency.

3.4 The photoluminescence mechanism of the complex

To investigate the photoluminescence mechanism of the complex Eu(ETFMCTFBD)$_3$phen, the phosphorescence

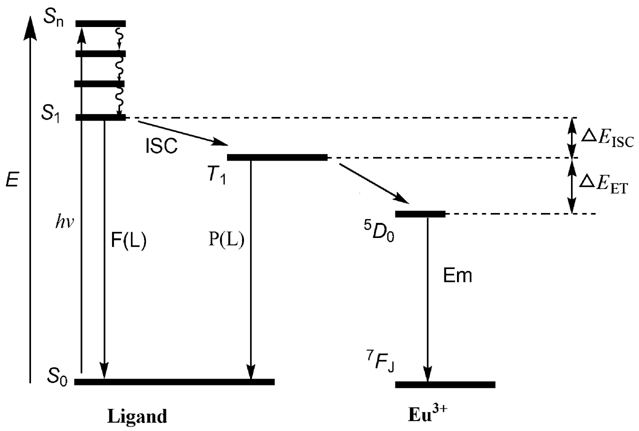

Fig. 5 Schematic representation of the photophysical process of the Eu(III) complex

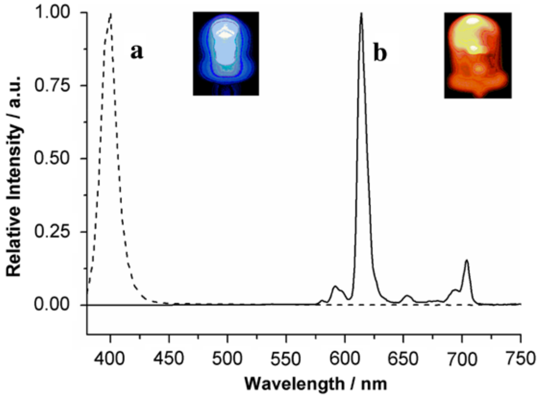

Fig. 6 Emission spectra of the original InGaN LED without phosphor (**a**) and the LED with Eu(ETFMCTFBD)$_3$phen (**b**) under excitation of 20 mA forward bias (*insert*: photographs of the lighting LEDs)

spectrum of a Gd(ETFMCTFBD)$_3$·2H$_2$O solid sample was measured at 23 K. The radius of the Gd^{3+} ion is similar to the Eu^{3+} ion, however, the lowest excited state energy level of the Gd^{3+} ion, ^{6}P$_{7/2}$, was about 32,000 cm^{-1}, much higher than that of the lowest triplet energy level of ETFMCTFBD [$T_1(L)$], so the energy absorbed by ETFMCTFBD cannot be transferred to the Gd^{3+} ion, and the lowest triplet state energy level was determined by the shortest wavelength of the phosphorescence peak to be 18,416 cm^{-1} (543 nm), which was higher than the lowest excited state of Eu^{3+}, $^5D_0$ (17,267 cm^{-1}). So the photophysical process can be described as follows. Firstly, the principal ligand ETFMCTFBD absorbed energy of the near UV light and the electrons transferred to their excited state S_n; secondly, the $S_n \to S_1$ quick nonradiative transitions happened, then the energy fell to the triplet state of ETFMCTFBD through spin flip because of the heavy atom effect; finally, the energy transferred to the lowest excited state ($^5D_0$) of the central Eu^{3+} ion in the complex; subsequently $^5D_0 \to {}^7F_J$ ($J = 0$–6) transitions happened, and the characteristic and narrow fluorescence peaks of Eu^{3+} ion appeared. The photophysical process in the Eu(III) complex can be called as a ligand-sensitized luminescence process (antenna effect), and is schematically represented in Fig. 5 [25, 26].

3.5 Emission spectra of the fabricated LED

Eu(ETFMCTFBD)$_3$phen was used as a phosphor to fabricate LEDs in a mass ratio of 1:40 of phosphor to silicone gel with ~395 nm-emitting InGaN chips. The emission spectra and photographs of the original ~395 nm LED without phosphor (a) and the LED fabricated with the complex and an ~395 nm chip (b) under 20 mA forward bias are shown in Fig. 6. The emission around 395 nm from the chip was completely absorbed in the spectrum of the LED with the complex, and the sharp and intense peak at 613 nm is due to the Eu^{3+} emission from the complex, confirming that the complex can be efficiently excited by the NUV light from the chip. This result indicates that Eu(ETFMCTFBD)$_3$phen is a good candidate as a red component in the fabrication of white LEDs with a high color-rendering index.

Thermal quenching of the Eu^{3+} luminescence or photobleaching of the phosphor within the LED package is a common problem to organic complexes. We think that incorporation of the organic complexes with SiO$_2$ may be a route for reducing the thermal quenching or photobleaching of the organic phosphor.

4 Conclusions

An efficient europium(III) carbazole-containing organic complex Eu(ETFMCTFBD)$_3$phen was designed and synthesized. Eu(ETFMCTFBD)$_3$phen exhibits a high thermal stability, excellent photoluminescence properties and a good quantum yield. The CIE chromaticity coordinates are close to the NTSC standard values for red. A bright red LED was fabricated by coating the complex phosphor onto an ~395 nm-emitting InGaN chip All the results indicate that Eu(ETFMCTFBD)$_3$phen is a good candidate as a red component in fabrication of white LEDs with high color-rendering index.

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