

Synthesis and electroluminescence properties of europium (III) complexes with new second ligands

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Abstract

Two novel second ligands, 9,9-Di-(4-methoxyphenyl)-9-*H*-4,5-Diazafluorene (OMe-Spiro-DF) and 9,9-Di-(2-(4-(4-butyloxy)phenyl)-5-phenyl-1,3,4-oxadiazolyl)-phenyl-9-*H*-4,5-Diazafluorene (OXD-Spiro-DF), were successfully prepared. Europium complexes, Eu(DBM)₃(OMe-Spiro-DF) and Eu(DBM)₃(OXD-Spiro-DF) (DBM=dibenzolymethane) based on the two ligands were designed and synthesized. For a double-layer device with configuration of indium tin oxide (ITO)/*N*, *N*'-diphenyl-*N*,*N*'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD)/Eu(DBM)₃(OXD-Spiro-DF) or Eu(DBM)₃(OMe-Spiro-DF)/Mg/Ag, compared with the device based on complex Eu(DBM)₃(OMe-Spiro-DF), the brightness and electroluminescent (EL) efficiency of device based on complex Eu(DBM)₃(OXD-Spiro-DF) with oxadiazole-functionalized ligand OXD-Spiro-DF are significantly improved due to the improvement of electron-transporting ability. A maximum brightness of 154 cd/m² was obtained at 17 V in the complex Eu(DBM)₃(OXD-Spiro-DF), about four times brighter than the corresponding complex Eu(DBM)₃(OMe-Spiro-DF).

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1. Introduction

Organic electroluminescent devices (OLEDs) based on organic thin film are one of the most promising next generation full color flat panel display systems [1,2]. Also, a variety of organic materials, including fluorescent dyes [3,4], metal complexes [1,5,6] and polymers [7,8] have been reported to show electroluminescence. However, the OLEDs using organic materials and polymers as the emissive layers generally produce emission due to their π - π^* transition, whose emission spectra have a full-width at half-maximum wavelength of ca. 100 nm. Among red emission materials, the europium (III) complexes have drawn tremendous attention because pure red emission near 615 nm can be produced by electronic transition of the

europium central ion. Therefore, it is well suited for actual multicolor display applications [9–15]. In addition, the other advantage is that up to 100% of internal quantum efficiencies for devices is theoretically possible because both singlet and triplet excitations can transfer their energy to the europium (III) ions [16,17].

However, there is a key problem with OLEDs containing these europium (III) complexes, that is low electroluminescent (EL) efficiency of europium (III) complexes when incorporated into OLEDs due to the poor carrier transporting ability reported so far [18–20]. Therefore, several groups have devoted to the application of europium (III) complexes as red emitters in OLEDs and higher brightness more than 1000 cd/m² has been achieved by using a doping europium (III) complexes with hole-transporting materials as an active layer or introducing electron-transporting and hole-blocking layer to fabricate a multilayer device [21–25]. However, doping usually leads to phase separation when the doping device undergoes operation, and emission from the electron

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or hole-transporting materials often appears due to the complicated device fabrication processes in multilayer devices. Therefore, in general, more efficient method to solve this problem is to introduce the charge-transporting group into the complex by molecular design. Wang et al. [18] synthesized a new terbium complex containing oxadiazole-functionalized β diketone ligand with a light output of 100 cd/m^2 with an external quantum efficiency as high as 1.1% at 15 V, and Liang et al. [26] reported a highly efficient double-layer OLEDs with current efficiency 1.7 cd/A using a europium (III) complex with oxadiazole-functionalized second ligand. Xin et al. [27] designed a carbazole-functionalized second ligand, and high power efficiency of 2.7 lm/W at 5 V was obtained from europium (III) complex with carbazole-functionalized second ligand as emitter layer.

In this paper, we present the synthesis and characterization of europium (III) complexes, as shown in Scheme 1, with the aim of realizing highly efficient red light emission. In order to improve the electron-transporting property of the europium (III) complexes, oxadiazole units are introduced to the second ligand because oxadiazole unit is known to be of electron-transporting character and has been used for the europium (III) complexes. In addition, the second ligand is also designed to be a bulky molecular with spiro-structure derived from 1,10-phenanthroline, which can coordinate with the europium (III) ion via two nitrogen atoms to improve the volatility and stability of the europium (III) complex, and should give the complex topological attributes to discourage crystallization.

2. Experimental details

2.1. Materials and instrumentation

2.1.1. Synthesis

Phenanthroline, phenol, 1,4-dichlorobutane, europium (III) oxide (Eu_2O_3) (Shanghai Chemical Reagent), benzoyl hydrazine, 4-anisyl chloride and dibenzoylmethane (DBM) (Acros Chemical Reagent) were used without any further purification. All solvents were purified by standard procedures. The elemental analysis of the europium (III) complex was carried out with a Perkin-Elmer 240 C elemental analyzer for C, H and N determinations. UV–visible (UV–vis) absorption spectra were recorded on a Shimadzu Model 310 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 300 MHz spectrometer in chloroform-*d* or dimethyl sulfoxide (DMSO)-*d*₆.

Compound 2-(4-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole (1) was synthesized according to the procedures in Ref. [26].

2.1.1.1. (2-(4-(4-Chlorobutyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole). Compound 2. To a mixture of compound 1 (2.38 g 10 mmol) dissolved in 50 mL of *N,N*-Dimethyl-

formamide (DMF) was added (5.52 g 40 mmol) of potassium carbonate. The mixture was heated at 120 °C for 1 h, and then 3.81 g 30 mmol of 1,4-dichlorobutane was added. The mixture was further reacted for 10 h and then cooled, the reaction mixture was poured into 100 mL of 0.2 M HCl and extracted with CH_2Cl_2 . The extract was washed with water three times, with brine once, and then was dried over anhydrous Na_2SO_4 . After removal of the solvent, the residue was subjected to purification by chromatography on silica gel to afford 2.73 g (74%) of a white powder product. Mp: 107–109 °C ^1H NMR (CDCl_3) δ 2.01 (m, 4H), 3.63 (t, 2H), 4.09 (t, 2H), 7.03 (d, 2H), 7.56 (d, 3H), 8.18 (m, 4H).

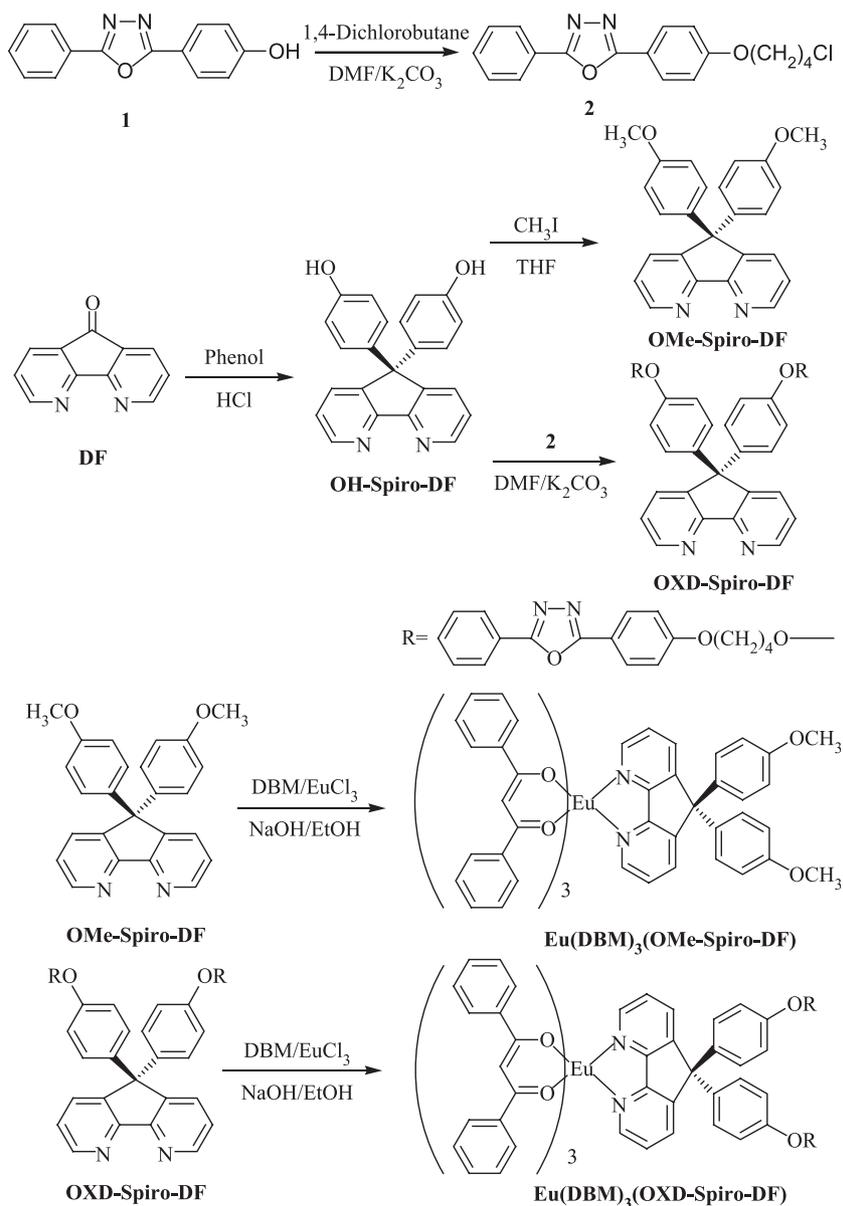
2.1.1.2. 9,9-Di-(4-hydroxyphenyl)-9-H-4,5-Diazafluorene. Compound OH-Spiro-DF. 9-H-4,5-Diazafluorene-9-one DF (1.82 g 10 mmol) was dissolved in 9.4 g 100 mmol of molten phenol. The mixture was heated at 50 °C and then dry hydrogen chloride was bubbled for about 3 h. The system became very dark but it was clear. The mixture was reacted for 8 h and then diluted with solution of NaOH to pH=8 to give a white solid, which was collected and washed with hot water. The product was further purified by crystallization from ethanol gave white crystal. The yield was 1.4 g (40%). ^1H NMR (DMSO-*d*₆) δ 6.66 (d, 4H), 6.92 (d, 4H), 7.42 (dd, 2H), 7.93 (d, 2H), 8.67 (d, 2H), 9.44 (s, 2H). ^{13}C NMR (DMSO-*d*₆) 114.0, 116.1, 123.5, 126.4, 128.6, 129.2, 131.6, 160.8, 163.2, 164.1.

2.1.1.3. 9,9-Di-(4-methoxyphenyl)-9-H-4,5-Diazafluorene. Compound OMe-Spiro-DF [28]. To a mixture of 3.5 g 10 mmol of compound OH-Spiro-DF dissolved in 50 mL of THF was added 4.88 g 0.40 mol of sodium hydroxide. The mixture was stirred for 5 h at room temperature, and then 10.92 g 30 mmol of iodomethane was added. The mixture was further reacted for 10 h, the reaction mixture was quenched with 0.2 M HCl and extracted with CH_2Cl_2 . The extract was washed with water three times, with brine once, and then was dried over anhydrous Na_2SO_4 . After removal of the solvent, the residue was subjected to purification by chromatography on silica gel to afford 7.25 g (72%) of a white powder product. ^1H NMR (CDCl_3) δ 3.62 (s, 6H), 6.79 (d, 4H), 7.06 (d, 4H), 7.08 (m, 4H), 7.32 (dd, 2H), 7.52 (m, 2H), 7.54 (m, 2H), 7.80 (d, 2H), 8.07 (d, 4H), 8.13 (m, 4H), 8.75 (m, 2H).

2.1.1.4. 9,9-Di-(2-(4-(4-butyloxy)phenyl)-5-phenyl-1,3,4-oxadiazolyl)-phenyl-9-H-4,5-Diazafluorene. Compound OXD-Spiro-DF. To a mixture of 3.52 g 10 mmol of compound OH-Spiro-DF dissolved in 50 mL of *N,N*-Dimethylformamide (DMF) was added 5.52 g 40 mol of potassium carbonate. The mixture was heated at 120 °C for 1 h, and then 9.85 g 30 mmol of 2-(4-(4-chlorobutyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole was added. The mixture was further reacted for 10 h and

then cooled, the reaction mixture was quenched with 0.2 M HCl and extracted with CH_2Cl_2 . The extract was washed with water three times, with brine once, and then was dried over anhydrous Na_2SO_4 . After removal of the solvent, the residue was subjected to purification by chromatography on silica gel to afford 7.25 g (72%) of a white powder product. Mp: 220–222 °C ^1H NMR (CDCl_3) δ 1.98 (m, 4H), 3.99 (t, 2H), 4.08 (t, 2H), 6.79 (d, 4H), 7.06 (d, 4H), 7.08 (m, 4H), 7.32 (dd, 2H), 7.52 (m, 2H), 7.54 (m, 2H), 7.80 (d, 2H), 8.07 (d, 4H), 8.13 (m, 4H), 8.75 (m, 2H). ^{13}C NMR (CDCl_3) 60.38, 67.35, 67.66, 114.43, 114.92, 116.35, 123.62, 124.06, 126.78, 128.65, 128.86, 129.00, 131.49, 133.85, 135.43, 146.49, 149.74, 156.86, 158.23, 161.70, 164.09, 164.49.

2.1.1.5. Europium (III) Complex $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ and $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$. To a solution of dibenzoylmethane (0.673 g 3 mmol) and OXD-Spiro-DF or OMe-Spiro-DF (1 mmol) in 5 mL hot chloroform, 1 N solution of NaOH (0.12 g 3 mmol) was added before dropwise addition of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution (0.366 g 1 mmol). Then the reaction mixture was heated at 60 °C for 6 h, and the precipitate was obtained by the addition of ethanol to the mixture. These complexes were further purified by washing with ethanol for three times before device fabrication. Elemental analysis for $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ $\text{C}_{106}\text{H}_{79}\text{EuO}_7\text{N}_4$ Calc. C, 76.12; H, 4.73; N, 3.35. Found: C, 76.48; H, 4.61; N, 3.33. For $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ $\text{C}_{70}\text{H}_{53}\text{EuO}_8\text{N}_2$ Calc. C, 69.94; H, 4.41; N, 2.33. Found: C, 69.18; H, 4.44; N, 2.43.



Scheme 1. Synthesis of the ligands and the complexes.

2.2. Devices fabrication and measurements

The indium tin oxide (ITO) glass is about 150 nm thick with a sheet resistance of 15 Ω /square. The cleaning procedure included sonication in detergent solution, pure water, acetone and ethanol. All the materials and cathode were evaporated at a pressure of 10^{-7} Torr. The layer thickness is controlled in vacuo with a quartz crystal monitor. The double-layer device was fabricated as ITO/N, N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) (40 nm)/Eu(DBM)₃(OXD-Spiro-DF) or Eu(DBM)₃(OMe-Spiro-DF) (80 nm)/Mg/Ag (10:1) (200 nm). The emitting area was about 9 mm². All measurements were carried out at room temperature under ambient atmosphere. The photoluminescence (PL) and EL spectra were measured with a Perkin-Elmer LS 50 B luminescence spectrometer. The luminance (*L*)–Current density (*J*) and luminance (*L*)–Voltage (*V*) curves were obtained from a source meter (Keithley 2400) and an optical meter (Newport 1835-C) equipped with a silicon photodiode (Newport 818-ST).

3. Results and discussion

3.1. Optical properties in film

The complexes Eu(DBM)₃(OMe-Spiro-DF) and Eu(DBM)₃(OXD-Spiro-DF) are all soluble in common organic solvents, such as chloroform tetrahydrofuran. Either in the solution or in the film, both complexes emit strong red fluorescence under ultraviolet irradiation. Fig. 1 shows the UV–vis absorption and PL spectra of thin films of complex Eu(DBM)₃(OMe-Spiro-DF) and Eu(DBM)₃(OXD-Spiro-DF). It can be seen that the absorption spectrum of complex Eu(DBM)₃(OMe-Spiro-DF) has a maximum peak at 345 nm, which is associated with DBM ligand. Thus, the absorption spectrum is caused by the π – π^* transition of

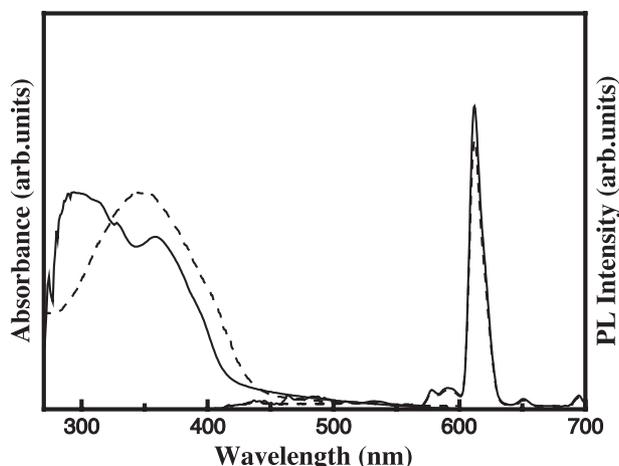


Fig. 1. UV–vis absorption and PL spectra of Eu(DBM)₃(OMe-Spiro-DF) (dashed curve) and Eu(DBM)₃(OXD-Spiro-DF) (solid curve) in film.

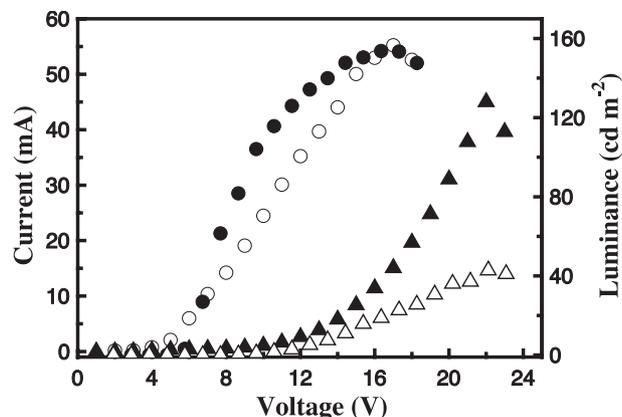


Fig. 2. Current–voltage characteristics of the double-layer device based on complex Eu(DBM)₃(OMe-Spiro-DF) (▲) and Eu(DBM)₃(OXD-Spiro-DF) (○), and brightness–voltage characteristics of the double-layer device based on complex Eu(DBM)₃(OMe-Spiro-DF) (△) and Eu(DBM)₃(OXD-Spiro-DF) (●).

DBM. Compared to complex Eu(DBM)₃(OMe-Spiro-DF), the absorption spectrum of complex Eu(DBM)₃(OXD-Spiro-DF) exhibits two absorption peaks, one at 355 nm and the other at 310 nm. The former peak is also contributed to the π – π^* transition of DBM ligand, and the latter peak is related to the absorption of oxadiazole units [26]. The PL spectra of the two complexes in film on quartz substrates are also shown in Fig. 1. It can be found that the emission spectra are very similar and both complexes show five sharp emission peaks at 580, 590, 612, 651 and 696 nm, indicating the emission only originated from electronic energy 5D_0 – 7F_J ($J=0$ –4) transitions of europium (III) ion [21].

3.2. EL properties

Fig. 2 illustrates the typical current–light–voltage characteristics of the double-layer devices based on Eu(DBM)₃(OMe-Spiro-DF) and Eu(DBM)₃(OXD-Spiro-DF). It can be found that the luminance increases with increasing injection

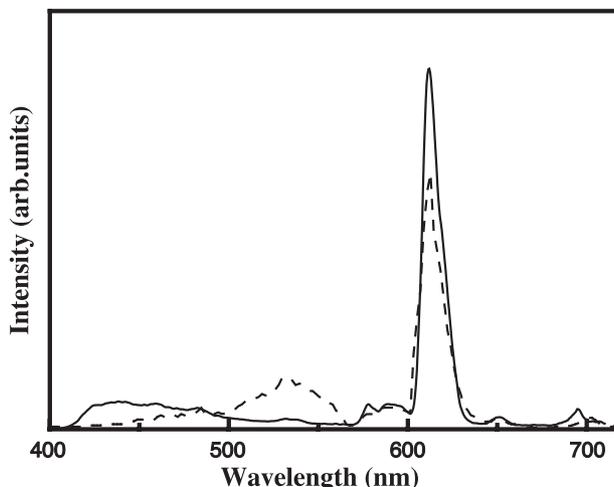


Fig. 3. The normalized EL spectra of complex Eu(DBM)₃(OMe-Spiro-DF) (dot line) and Eu(DBM)₃(OXD-Spiro-DF) (solid line) at 17 V.

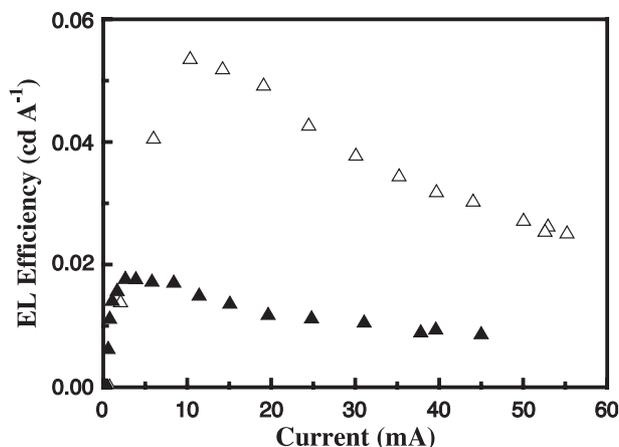


Fig. 4. The EL efficiency characteristics of the devices based on complex $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ (▲) and $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ (△).

current as well as bias voltage in both devices. The red light originating from $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ with a maximum luminance of 154 cd/m^2 was observed at 17 V and 56 mA, which is about a factor of 4 brighter than that of the $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ -based device with a value of 40 cd/m^2 at 22 V. Fig. 3 shows the EL spectra of $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ and $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ at 17 V. It can be seen that the EL spectra show a red emission at 612 nm in both devices. However, the significant difference is that only emission peaks of europium (III) ion can be observed at lower bias voltage in the double-layer device with $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ as emitting layer, with the increasing of the bias voltage, the others emission appear around 520 nm. It makes the emitting color become orange-red. This can be attributed to the emission from exciplex at the interface of $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ and TPD layer [22]. Compared to EL spectrum of $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$, no exciplex emission was observed between hole-transporting layer and $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ at high voltage 17 V in the double-layer device. This characteristic demonstrates that the $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ layer acts both as an emitting and electron-transporting layer facilitating more balanced carrier injection from the anode and cathode. Therefore, the excitons can be generated directly on the $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ by direct recombination of holes and electrons trapped on the ligand, which could decrease the turn-on voltage and quench the formation of exciplex. The $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ -based device also shows a higher EL efficiency of 0.055 cd/A , as shown in Fig. 4. Compared to a maximum EL efficiency of 0.016 cd/A for the $\text{Eu}(\text{DBM})_3(\text{OMe-Spiro-DF})$ -based device, the EL efficiency device based on $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ has been enhanced by a factor of more than three times. It is worth mentioning that these results were fabricated using double-layer device architecture. It is believed that a much better EL performance can be achieved by fabricating multilayer device. Also, we also found that the EL and PL spectra of $\text{Eu}(\text{DBM})_3(\text{OXD-Spiro-DF})$ exhibit a broad

trace emission line at 430 nm, the possible explanation may be contributed to incomplete Förster energy transfer from oxadiazole segment to europium (III) complex. This work will be studied in the future.

4. Conclusions

In conclusion, a novel europium (III) complex containing oxadiazole-functionalized second ligand was synthesized. A bright red light with the maximum luminance of 154 cd/m^2 was observed from the double-layered EL device without any additional electron transport layer. The result demonstrates that to incorporate oxadiazole unit into the ligand is a useful strategy for balancing injection, transport, and recombination of charge carriers in europium (III) complex. The further efforts on the device optimizing will be discussed in the near future and reported elsewhere.

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