

# Reduced Efficiency Roll-Off in Organic Light-Emitting Diodes by a Novel Short-Lived Organoeuropium Emitter

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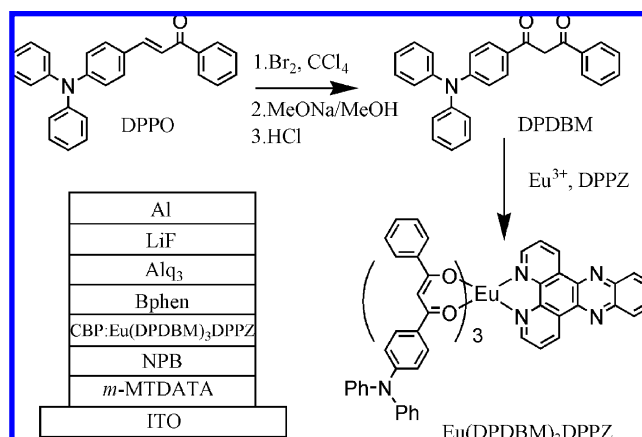
**ABSTRACT** In this paper, we report a novel organoeuropium complex [Eu(DPDBM)<sub>3</sub>DPPZ] based on a triphenylamine-derived  $\beta$ -diketone ligand for short-lived emitter exploration. The  $^5D_0 \rightarrow ^7F_2$  ( $\sim 610$  nm) luminescence lifetime of Eu(DPDBM)<sub>3</sub>DPPZ is only 30  $\mu$ s, which is 1 order of magnitude shorter than that of a typical Eu<sup>3+</sup> complex. The electroluminescence device using Eu(DPDBM)<sub>3</sub>DPPZ as the emitter achieves a maximum current efficiency of 3.0 cd/A, and the efficiency roll-off is largely reduced because of the emitter's short luminescence lifetime.

**KEYWORDS:** organoeuropium complex • OLED • electroluminescence •  $\beta$ -diketone ligand • short-lived • efficiency roll-off

## INTRODUCTION

Organoeuropium complexes, as a class of promising electroluminescence (EL) material for organic light-emitting diodes (OLEDs), have attracted much attention over the last 2 decades (1). Owing to the unique f-electron configuration, the physical properties of Eu<sup>3+</sup>-based emitters can be conveniently altered without compromising the extremely pure red emissions (2). Thanks to Jabbour's contribution to cathode development, device performances have been further improved (3). For example, the Eu<sup>3+</sup>-based EL device reported by Huang et al. reaches a maximum power efficiency of 2.7 lm/W (4). However, the device performance is still unsatisfactory when compared with that of EL devices containing pure organic and phosphorescent compounds as emitters. It is reported that the device efficiency drops rapidly with an increase in the current density in Eu<sup>3+</sup>-based OLEDs. Detailed research suggests that this efficiency roll-off is caused by the emitters' too long luminescence lifetimes, and two quenching mechanisms of triplet–triplet (T–T) and polaron–triplet (P–T) annihilation are believed to be responsible for the triplet exciton quenching (5–7). Thus, the most significant problem for Eu<sup>3+</sup>-based OLEDs is the exploration of short-lived emitters (5).

In this paper, a novel triphenylamine-derived  $\beta$ -diketone ligand, 1-[4-(diphenylamino)phenyl]-3-phenylpropane-1,3-



**FIGURE 1.** Molecular structures of DPDBM and Eu(DPDBM)<sub>3</sub>DPPZ, as well as the EL device structure.

dione (DPDBM), and another ligand, 4,5,9,14-tetraazabenzotriphenylene (DPPZ), are coordinated to the Eu<sup>3+</sup> center to form an organoeuropium complex of Eu(DPDBM)<sub>3</sub>DPPZ. The photoluminescence (PL) and EL properties are investigated.

## EXPERIMENTAL SECTION

The synthetic route to DPDBM is shown in Figure 1: a mixture of 10 mmol of 3-[4-(diphenylamino)phenyl]-1-phenylpropanone (DPPO), 3 mL of Br<sub>2</sub>, and 10 mL of CCl<sub>4</sub> was stirred at 0 °C for 30 min (8). The resulting solid was washed with EtOH and then added into a solution of 2.3 g of Na and 25 mL of MeOH. The mixture was stirred for 1 h at 80 °C. After cooling, the solution was neutralized with 10 mL of concentrated HCl and then stirred for 30 min at 100 °C. The crude product was purified by recrystallization from EtOH. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.22 (s, 1H), 7.99–7.97 (m, 2H), 7.93 (s, 1H), 7.87–7.84 (m, 2H), 7.79–7.58 (m, 4H), 7.50–7.35 (m, 5H), 7.10 (s, 1H), 6.97 (s, 1H), 6.67 (s, 1H), 6.52 (s, 1H), 3.26 (s, 1H). Anal. Calcd for C<sub>27</sub>H<sub>21</sub>NO: C, 86.37; H, 5.64; N, 3.73. Found: C, 86.21; H, 5.71; N, 3.56. A mixture of 0.1 mmol of EuCl<sub>3</sub>, 0.3 mmol of DPDBM, 0.1 mmol

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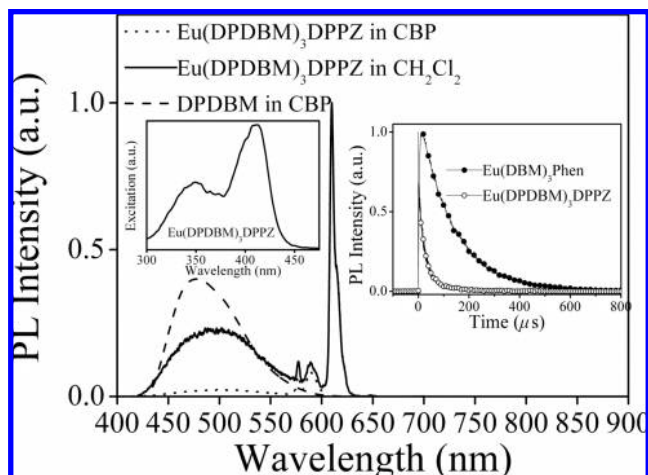


FIGURE 2. PL spectra of DPDBM (10 wt % in CBP) and  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  (10 wt % in CBP and  $1 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ) upon  $\lambda_{\text{ex}} = 410$  nm. Inset:  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  luminescence decay curve of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  and  $\text{Eu}(\text{DBM})_3\text{Phen}$  (10 wt % in CBP).

of DPPZ, and 10 mL of EtOH was neutralized to pH = 6.5 and then stirred at 80 °C for 4 h. The crude product was purified by vacuum sublimation to give a yellow solid. Anal. Calcd for  $\text{C}_{99}\text{H}_{70}\text{N}_7\text{O}_6\text{Eu}$ : C, 74.06; H, 4.39; N, 6.11. Found: C, 74.13; H, 4.28; N, 6.18.

The luminescence lifetimes were obtained with 355 nm light generated from a third-harmonic-generator pump, using a pulsed Nd:YAG laser as the excitation source. The Nd:YAG laser possesses a line width of  $1.0 \text{ cm}^{-1}$ , a pulse duration of 10 ns, and a repetition frequency of 10 Hz. A Rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. A picosecond lifetime spectrometer (Edinburgh Instruments Lifespec-Red) was used to measure the fluorescence lifetimes. A diode laser (operating at 372 nm, with a pulse duration of 69 ps) controlled by a picosecond light pulser (Hamamatsu PLP-10) was used as the excitation source. The triplet energy of DPDBM was measured by the low-temperature (77 K) phosphorescence of  $\text{Ga}(\text{DPDBM})_3 \cdot 2\text{H}_2\text{O}$  (see the Supporting Information for a detailed description). All PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured using an integrating sphere according to a literature method (9).  $^1\text{H}$  NMR spectra were obtained by use of a Varian INOVA 300 spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. EL devices were fabricated by sequentially depositing organic layers onto precleaned indium–tin oxide (ITO) glass substrates under high vacuum ( $\sim 3 \times 10^{-4}$  Pa). Current–voltage and luminance–voltage characteristics were measured with a computer-controlled Keithley 2400 Sourcemeter unit.

## RESULTS AND DISCUSSION

Figure 2 shows the PL characteristics of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  and free DPDBM measured from 4,4'-dicarbazolyl-1,1'-biphenyl (CBP) films (10 wt %) and  $\text{CH}_2\text{Cl}_2$  solutions ( $1 \times 10^{-5}$  mol/L). The excitation spectrum of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$ , peaking at 410 nm, covers a wide region, as shown by the inset of Figure 2 (see the Supporting Information for a detailed description). In solution,  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  emits not only the characteristic lines from the  $\text{Eu}^{3+}$  center with the main line at 610 nm but also a strong fluorescence from DPDBM peaking at  $\sim 500$  nm, indicating an incomplete energy-transfer process from DP-

DBM to the  $\text{Eu}^{3+}$  center. The fluorescence lifetime decreases largely from 6.83 ns for free DPDBM ( $1 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ) to 2.09 ns for  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  ( $1 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ). Because the singlet-state energy of DPDBM ( $20\,000 \text{ cm}^{-1}$ ) is proper for intramolecular energy transfer, it is thus expected that the dominant energy-transfer process happens between the DPDBM singlet state and the  $\text{Eu}^{3+}$  center (10), whereas in the CBP film, the  $\text{Eu}^{3+}$  characteristic lines dominate the PL spectrum, with the fluorescence weak enough to be neglected (4). The  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  luminescence (610 nm) of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  in the CBP film (10 wt %) demonstrates a short lifetime of 30  $\mu\text{s}$ , which is greatly shorter than that of a reference complex of  $\text{Eu}(\text{DBM})_3\text{Phen}$  (130  $\mu\text{s}$ , in 10 wt % CBP film), as shown in Figure 2, where DBM = 1,3-diphenyl-1,3-propanedione and Phen = 1,10-phenanthroline.

The luminescence lifetime ( $\tau$ ) is determined by the sum of radiative probability ( $k_r$ ) and nonradiative probability ( $k_{nr}$ ), as depicted by eq 1. Also, with the help of the quantum efficiency ( $\Phi$ ) defined by eq 2,  $k_r$  and  $k_{nr}$  of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  ( $\Phi = 0.36$ ) in the CBP film are calculated as  $1.20 \times 10^4$  and  $2.13 \times 10^4 \text{ s}^{-1}$ , respectively.

$$\frac{1}{\tau} = k_r + k_{nr} \quad (1)$$

$$\Phi = \frac{k_r}{k_r + k_{nr}} \quad (2)$$

The radiative and nonradiative probabilities of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  are 1 order of magnitude bigger than the corresponding ones of  $\text{Eu}(\text{DBM})_3\text{Phen}$  ( $\Phi = 0.70$ ,  $k_r = 5.4 \times 10^3 \text{ s}^{-1}$ , and  $k_{nr} = 2.3 \times 10^3 \text{ s}^{-1}$ ) and similar  $\text{Eu}^{3+}$  complexes, which is the direct cause of the short luminescence lifetime (11). As for  $k_r$ , the Judd–Ofelt theory suggests that the electric-dipole ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) radiative probability is proportional to the asymmetry of the coordination sphere around the  $\text{Eu}^{3+}$  center (12). The  $\Omega_2$  values of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  and  $\text{Eu}(\text{DBM})_3\text{Phen}$ , reflecting the asymmetries of local environments, are calculated as  $13.9 \times 10^{-20}$  and  $6.1 \times 10^{-20} \text{ cm}^2$ , respectively. The bigger  $\Omega_2$  value of  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$  suggests a more distorted coordination environment around the  $\text{Eu}^{3+}$  center in  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$ , which can be explained as follows. The strong steric hindrance of DPDBM may further distort the coordination geometry, resulting in the more asymmetric coordination environment around the  $\text{Eu}^{3+}$  center and, consequently, the increased  $k_r$ . As for  $k_{nr}$ , the triplet energy levels of DPDBM ( $18\,200 \text{ cm}^{-1}$ ; see the Supporting Information) and DPPZ ( $18\,500 \text{ cm}^{-1}$ ) make the energy return possible, which facilitates the nonradiative decay process of the excited  $\text{Eu}^{3+}$  center and, consequently, increases the  $k_{nr}$  (13, 14). However, this increased  $k_{nr}$  value is tolerable considering  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$ 's high quantum efficiency. Herein, an explanation of why the short luminescence lifetime is observed for  $\text{Eu}(\text{DPDBM})_3\text{DPPZ}$ , thanks to the presence of DPDBM and DPPZ, is clearly presented.

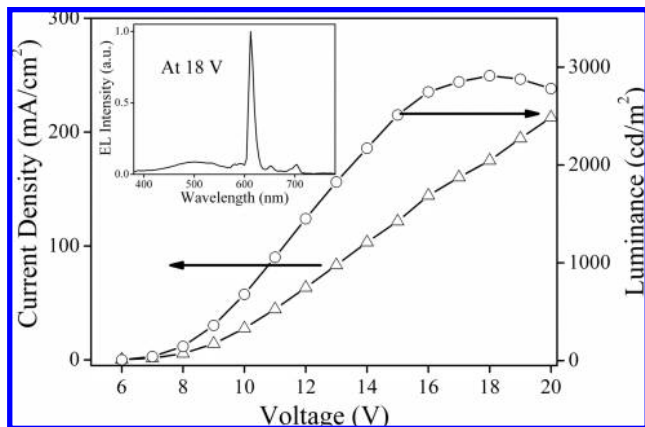


FIGURE 3. Luminance and current density vs voltage plots for a 13 wt %-doped EL device. Inset: EL spectrum for a 13 wt %-doped EL device at 18 V.

The EL devices are fabricated with a structure of ITO/*m*-MTDATA (30 nm)/NPB (20 nm)/CBP:Eu(DPDBM)<sub>3</sub>DPPZ (wt %) (35 nm)/Bphen (20 nm)/Alq<sub>3</sub> (20 nm)/LiF (0.8 nm)/Al, as shown in Figure 1 (see the Supporting Information for a detailed description). EL devices with various dopant concentrations are investigated to optimize the device structure, and the optimal dopant concentration is found to be 13 wt %, with a maximum current efficiency of 3.0 cd/A. Upon higher dopant concentrations, both the luminance and current efficiency tend to decrease. The characteristic emission from the Eu<sup>3+</sup> center (612 nm), as well as the weak fluorescence from DPDBM (500 nm), is observed, as shown in Figure 3. The ratio of Eu<sup>3+</sup> emission to DPDBM fluorescence is calculated as 2.1:1 by the area ratio of a typical EL spectrum at 18 V, which confirms that the EL emission is a red one. The current–voltage–luminance characteristics shown in Figure 3 suggest that both the current density and luminance increase dramatically with increasing voltage. It is observed that the maximum current density is nearly 2 times bigger than that of an EL device using Eu(DBM)<sub>3</sub>(N–N) as the dopant, where N–N stands for a diimine ligand (15, 16). This result reveals that the triphenylamine-derived ligand is effective in improving the charge-carrier transportation within the EL device. A maximum luminance of 2910 cd/m<sup>2</sup> is achieved at 18 V. Upon higher voltages, the high luminance remains, showing no decrease, which indicates that the EL device benefits from the short-lived emitter by suppressing the T–T and T–P annihilation (17, 18). In addition, the maxima of both the luminance and current efficiency are among the highest ones of Eu<sup>3+</sup>-based EL devices, suggesting that Eu(DPDBM)<sub>3</sub>DPPZ is a promising emitter for OLEDs.

The advantage of using Eu(DPDBM)<sub>3</sub>DPPZ as the emitter in EL devices is clearly established when we come to an efficiency roll-off comparison. The plots of current efficiency versus current density for the EL devices with four typical dopant concentrations from 5 to 13 wt % are shown in Figure 4. Unlike the literature in which sharp efficiency decreases are reported, the device efficiencies decrease slowly and smoothly with increasing current density (5–7, 19, 20). Particularly, the current efficiency of the 13 wt %-doped EL

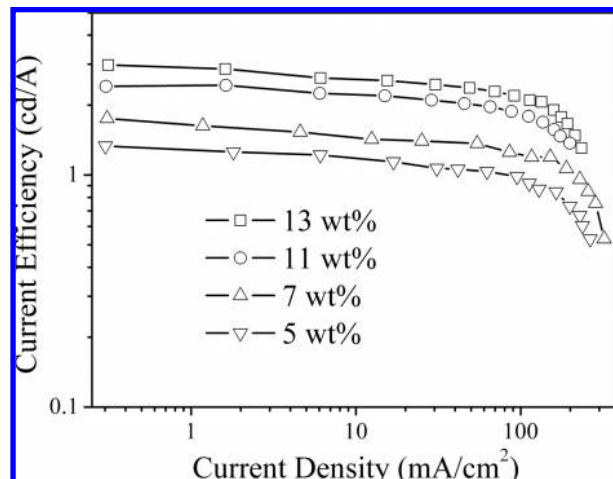


FIGURE 4. Device efficiency vs current density plots for 5–13 wt %-doped EL devices.

Table 1. Current Efficiencies upon Various Current Densities

| current density (mA/cm <sup>2</sup> ) | current efficiency (cd/A) |              |               |               |
|---------------------------------------|---------------------------|--------------|---------------|---------------|
|                                       | 5 wt %-doped              | 7 wt %-doped | 11 wt %-doped | 13 wt %-doped |
| 1                                     | 1.3                       | 1.7          | 2.4           | 2.9           |
| 10                                    | 1.2                       | 1.5          | 2.2           | 2.6           |
| 100                                   | 1.0                       | 1.2          | 1.8           | 2.1           |

device remains remarkably high even at a high current density of 100 mA/cm<sup>2</sup>, as shown in Table 1. This result indicates that the efficiency roll-off is largely reduced in Eu(DPDBM)<sub>3</sub>DPPZ-based devices, clearly because of the emitter's short luminescence lifetime.

## CONCLUSION

In summary, we report a novel organoeuropium complex for short-lived emitter exploration. The <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> luminescence lifetime is as short as 30 μs. The EL device using Eu(DPDBM)<sub>3</sub>DPPZ as the emitter achieves a maximum current efficiency of 3.0 cd/A, and the efficiency roll-off is largely reduced because of the emitter's short luminescence lifetime.

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**Supporting Information Available:** Absorption spectra of Eu(DPDBM)<sub>3</sub>DPPZ and DPDBM, low-temperature phosphorescence spectrum and characterization of Ga(DPDBM)<sub>3</sub>·2H<sub>2</sub>O, a detailed description of the device structure, and EL spectra at different voltages. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- (1) Kido, J.; Nagai, K.; Okamoto, Y. *Chem. Lett.* **1991**, 235, 1267.
- (2) Wang, J.; Wang, R.; Yang, J.; Zheng, Z.; Carducci, M. D.; Cayou, T.; Peyghambarian, N.; Jabbour, G. E. *J. Am. Chem. Soc.* **2001**, 123, 6179.
- (3) Jabbour, G. E.; Wang, J. F.; Kippelen, B.; Peyghambarian, N. *Jpn. J. Appl. Phys., Part 2* **1999**, 38, L1553.

- (4) Xin, H.; Li, F. Y.; Guan, M.; Huang, C. H.; Sun, M.; Wang, K. Z.; Zhang, Y. A.; Jin, L. P. *J. Appl. Phys.* **2003**, *94*, 4729.
- (5) Baldo, M. A.; Adachi, C.; Forrest, S. R. *Phys. Rev. B* **2000**, *62*, 10967.
- (6) Lamansky, S.; Kwong, R. C.; Nugent, M.; Djurovich, P. I.; Thompson, M. E. *Org. Electron.* **2001**, *2*, 53.
- (7) Reineke, S.; Walzer, K.; Leo, K. *Phys. Rev. B* **2007**, *75*, 125328.
- (8) Zhang, L.; Li, B.; Lei, B.; Hong, Z.; Li, W. *J. Lumin.* **2008**, *128*, 67.
- (9) Wrighton, M. S.; Ginley, D. S.; Morse, D. L. *J. Phys. Chem.* **1974**, *78*, 2229.
- (10) Buono-core, G. E.; Li, H. *Coord. Chem. Rev.* **1990**, *99*, 55.
- (11) Zhang, L.; Li, B.; Zhang, L.; Chen, P.; Liu, S. *J. Electrochem. Soc.* **2009**, *156*, H202.
- (12) Judd, B. R. *Phys. Rev.* **1962**, *127*, 750.
- (13) van der Tol, E. B.; van Ramesdonk, H. J.; Verhoeven, J. W.; Steemers, F. J.; Kerver, E. G.; Verboom, W.; Reinhoudt, D. N. *Chem.—Eur. J.* **1998**, *4*, 2315.
- (14) Xin, H.; Shi, M.; Gao, X. C.; Huang, Y. Y.; Gong, Z. L.; Nie, D. B.; Cao, H.; Bian, Z. Q.; Li, F. Y.; Huang, C. H. *J. Phys. Chem. B* **2004**, *108*, 10796.
- (15) Xin, Q.; Li, W. L.; Che, G. B.; Su, W. M.; Sun, X. Y.; Chu, B.; Li, B. *Appl. Phys. Lett.* **2006**, *89*, 223524.
- (16) Liang, C. J.; Zhao, D.; Hong, Z. R.; Zhao, D. X.; Liu, X. Y.; Li, W. L.; Peng, J. B.; Yu, J. Q.; Lee, C. S.; Lee, S. T. *Appl. Phys. Lett.* **2000**, *76*, 67.
- (17) Xin, H.; Guang, M.; Li, F. Y.; Bian, Z. Q.; Huang, C. H.; Ibrahim, K.; Liu, F. Q. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5895.
- (18) Xin, H.; Sun, M.; Wang, K. Z.; Zhang, Y. A.; Jin, L. P.; Huang, C. H. *Chem. Phys. Lett.* **2004**, *388*, 55.
- (19) Zhou, L.; Zhang, H.; Shi, W.; Deng, R.; Li, Z.; Yu, J.; Guo, Z. *J. Appl. Phys.* **2008**, *104*, 114507.
- (20) Sun, P. P.; Duan, J. P.; Shih, H. T.; Cheng, C. H. *Appl. Phys. Lett.* **2002**, *81*, 792.

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