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Polymer light-emitting devices based on europium(III) complex with 11-bromo-dipyrido[3,2-*a*:2′,3′-*c*]phenazine

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Polymer light-emitting diodes (PLEDs) containing Eu(DBM)3(BrDPPz) (DBM is dibenzoylmethane, and BrDPPz is 11-bromo-dipyrido[3,2-*a*:2′,3′-*c*]phenazine) doped in a blend of poly(9,9-dioctylfluorene) (PFO) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) as the host matrix are reported. Eu(DBM)3(BrDPPz) exhibited high thermal stability and intense UV-Vis absorption. Narrow-bandwidth red emission at 612 nm with a full width at half-maximum (FWHM) of 14.0 nm was observed from $Eu(DBM)_3(BrDPPz)$ in these double-layered PLEDs at dopant concentrations from 1 wt% to 8 wt%. For the PLED containing 1 wt% $Eu(DBM)_3(BrDPPz)$, a maximum luminance of 829 cd/m^2 at 153.5 mA/cm^2, highest external quantum efficiency of 1.70% at 2.1 mA/cm^2 and maximum luminance of 0.74 cd/A at 4.31 mA/cm^2 were obtained.

europium(III) complexes, electroluminescence, optophysical properties, polymer light-emitting diodes

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1 Introduction

Europium(III) complexes have been considered promising red-emitting materials for use in full-color displays since Kido *et al*. [1,2] initially reported the applications of europium(III) complexes. Compared to the high efficiency of red-emitting iridium(III) and platinum(II) complexes [3–7], europium(III) complexes exhibit considerable advantages because of their extremely narrow emission spectral bandwidth. Recently, spin-casting techniques have been used to fabricate europium(III) complex-doped polymer light-emitting diodes (PLEDs) containing conjugated polymers as the host matrix [8–20]. PLEDs formed by this method can be simply fabricated by solution processing, and luminescence quenching by concentration effects is prevented. For instance, Zhang *et al*. [8] reported a high-efficiency PLED based on the europium(III) complex $Eu(FTA)_3Phen$ (FTA=4,4,4-trifluoro-1-phenyl-1,3-butanedione, Phen=1,10-phenanthroline) with an external quantum efficiency (EQE) of 4.3%. Recently, we reported high-efficiency PLEDs based on the europium(III) complex $Eu(DBM)_3$(DTPA-Phen) (DBM=dibenzoylmethane, DTPA-phen=3,8-bis[4-(diphenylamino)phenyl]-1,10-phenanthroline) with a maximum brightness of 1333 cd/m^2 and maximum EQE of 1.8%, and another PLED based on $Eu(DBM)_3(DPPz)$ (DPPz is dipyrido[3,2-*a*:2′,3′-*c*]phenazine) with a maximum brightness of 1783 cd/m^2 and maximum EQE of 2.5% [9,11]. However, devices formed by this method exhibited low luminous efficiency and brightness compared with those of devices formed by vacuum deposition [21–35]. For example, Liu *et al.* [21] made an organic light-emitting device (OLED) using $Eu(DBM)_3(BPhen)$ (Bphen=4,7-biphenyl-1,10-phenanthroline) doped into triphenyldiamine with a high EQE of 7.5%±0.5% at 0.02 mA/cm^2 and Ma *et al.* [22] used tris-(thenoyltrifluoroacetone)(3,4,7,8-tetramethyl-1,10-phenant-

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hroline)europium(III) as a dopant and (dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran as a host to fabricate OLEDs with a high brightness of 3000 cd/m^2 at 190 mA/cm^2 and high luminance efficiency of 14.5 cd/A at 0.08 mA/cm^2.

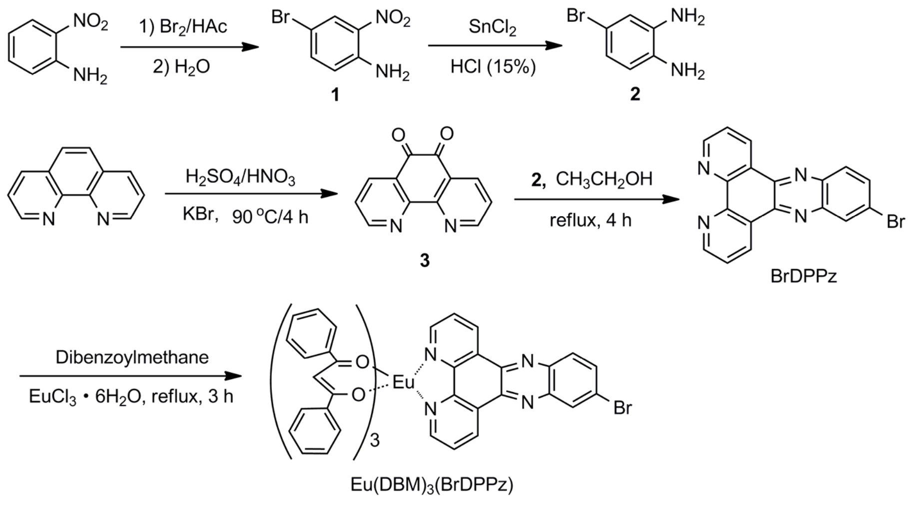
To acquire europium(III) complexes that produce good device performance and charge transport characteristics, a variety of functional europium(III) complexes have been developed. Recently, the improved electroluminescence (EL) performance of OLEDs containing fluorine- and chlorine-functionalized europium(III) complexes has been reported [27–32]. In contrast, PLEDs using bromine-functionalized europium(III) complexes as emitters have seldom been investigated [17].

In this paper, we report the bromine-functionalized europium(III) complex Eu(DBM)$_3$(BrDPPz) (BrDPPz=11-bromodipyrido[3,2-*a*:2′,3′-*c*]phenazine), the molecular structure of which is shown in Scheme 1. In this europium(III) complex, BrDPPz is used instead of 3,8-dibromo-1,10-phenanthroline (DBrPhen) [11] as the second ligand. This is expected to improve the performance of devices because the extended conjugation, heavy atom and steric bulk of BrDPPz should help to control concentration quenching [17,27–31]. DBM was chosen as the first ligand because of its relatively high photoluminescence (PL) efficiency in europium(III) complexes. The PL, electrochemical and photophysical properties of devices fabricated containing this europium(III) complex as a dopant at various concentrations from 1 wt% to 8 wt% in a blend of poly(9,9-dioctylfluorene) (PFO) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) (30 wt%) as a host matrix are also investigated. Highly efficient monochromic red emission at 612 nm with a maximum luminance of 829 cd/m^2 at 153.5 mA/cm^2 and maximum EQE of 1.70% at 2.1 mA/cm^2 are achieved for the device containing 1 wt% Eu(DBM)$_3$ (BrDPPz).

2 Experimental

2.1 Reagents and physical measurements

Commercially available reagents and starting materials were used to synthesize Eu(DBM)$_3$(BrDPPz). All reactions and manipulations were carried out under an inert gas atmosphere. ^{1}H NMR spectra were measured in CDCl$_3$ solution on a Bruker DPX (400 MHz) NMR spectrometer using tetramethylsilane (TMS) as the internal standard. MALDI-TOF mass spectrometric measurements were performed on a Bruker Biflex III MALDI-TOF spectrometer (Switzerland). Elemental analyses (C, H, N) were performed with a Perkin-Elmer 240 instrument (USA). Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10 °C/min using a Perkin-Elmer TGA-7 thermal analyzer (USA). UV-Vis absorption spectra were recorded with a Shimadzu UV-265 spectrometer (Japan) at room temperature. PL spectra were recorded on an RF-5301 PC spectrometer (Perkin Elmer, USA) under excitation with a He:Cd laser at 325 nm. PL quantum yields (Φ_{PL}) were determined using $EuCl_3\cdot6H_2O$ as a reference in solution [36]. Cyclic voltammetry was performed on a CHI660A electrochemical workstation with a scan rate of 50 mV/s at room temperature under argon. A Pt disk, Pt plate, and Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively, in n-Bu_4NPF_6 (0.1 mol/L) in acetonitrile. For calibration, the redox potential of the ferrocene/ferrocenium (Fc/Fc$^+$) couple was measured under the same conditions. Optical band gaps were estimated based on absorption edges. Reduction potentials were calculated from the corresponding optical band gap and oxidation potential. On the basis of the energy level of ferrocene (4.74 eV under vacuum), and the oxidation and reduction potentials, the highest occupied molecular orbital (HOMO) and lowest



Scheme 1 Synthesis of the bromine-functionalized europium(III) complex Eu(DBM)$_3$(BrDPPz).

molecular orbital (LUMO) energy levels of the complex were calculated according to an empirical formula [27,34]. PLEDs were fabricated as we reported previously [11]. The devices had the following structure: indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT:PSS, 50 nm)/poly(*N*-vinylcarbazole) (PVK, 40 nm)/ Eu(DBM)$_3$(BrDPPZ) in PFO-PBD (80 nm)/Ba (4 nm)/Al (150 nm). ITO was used as the anode, PEDOT:PSS as a hole-injection layer and Ba/Al as a cathode. The weight ratio of PBD in the PFO-PBD blend was 30 wt%. The doping concentration of Eu(DBM)$_3$(BrDPPZ) in the active layer ranged from 1 wt% to 8 wt%.

2.2 Synthesis of intermediates and target complex

Intermediates **1**, **2**, **3** and BrDPPz were synthesized according to our previous work [37]. Eu(DBM)$_3$(BrDPPz) was synthesized by reacting europium trichloride hydrate with DBM and BrDPPz according to a conventional procedure [28]. The structures of the intermediates were confirmed by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. Eu(DBM)$_3$(BrDPPz) was characterized by elemental analysis and MALDI-TOF mass spectrometry.

2.2.1 Synthesis of BrDPPz

11-Bromo-dipyrido[3,2-*a*:2',3'-*c*]phenazine (BrDPPz) was synthesized according to a reported method [37]. Yield: 72%. m.p.: 249.0–251.0 °C, ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 9.47 (t, J=13.6 Hz, 2H); 9.26 (d, J=4.0 Hz, 2H); 8.43 (s, 1H); 8.11 (d, J=8.8 Hz, 1H); 7.94 (dd, J=8.8 Hz, 1H); 7.76–7.73 (m, 2H). MALDI-TOF MS (*m/z*): 361.7 for [M$^+$].

2.2.2 Synthesis of Eu(DBM)$_3$(BrDPPz)

Eu(DBM)$_3$(BrDPPz) was synthesized according to a reported procedure [31]. Yield: 53.0%. m.p.: 251.0–253.0 °C. Anal. calcd for $EuC_{63}H_{42}BrN_4O_6$: C, 63.97; H, 3.58; N, 4.74; Found: C, 63.63; H, 3.45; N, 4.58. MALDI-TOF MS (*m/z*): 1284.2 for [M$^+$].

3 Results and discussion

3.1 Thermal stability

The thermal properties of Eu(DBM)$_3$(BrDPPZ) were studied by TGA under nitrogen atmosphere, and the results are presented in Figure 1. Eu(DBM)$_3$(BrDPPZ) exhibits high thermal stability, with a decomposition temperature (T_d) at 5% weight loss of about 363.5 °C, which is favorable for use in PLEDs.

3.2 Photophysical properties

Figure 2 shows the normalized UV-Vis absorption and PL spectra of Eu(DBM)$_3$(BrDPPz) in dilute CHCl$_3$ solution (about 1×10^{-6} mol/L) and a thin film of the PFO-PBD (30 wt%) blend at 298 K. The UV-Vis absorption spectrum contains two major absorption peaks at 274 and 369 nm, in which the former is attributed to a ligand-centered π-π* electron transition of BrDPPz and the latter is assigned to a ligand-centered π-π* electron transition of DBM [31]. The PL spectrum of the film contains a sharp peak at 613 nm with a full width at half-maximum (FWHM) of 8 nm as well as four weak peaks at 580, 596, 654 and 700 nm, which correspond to the $^5D_0\to{}^7F_j$ (j=2, 0, 1, 3, 4) electronic transitions of the Eu^{3+} ion under photoexcitation, respectively. No emission from the BrDPPz ligand was observed. This indicates that complete energy transfer from BrDPPz to the Eu^{3+} ion occurs in this europium(III) complex, and modifying the DPPz ligand with a heavy atom (bromine) has no effect on the PL spectrum of its europium(III) complex [14,15]. The absorption spectrum of Eu(DBM)$_3$ (BrDPPz) (Figure 2) overlaps well with the PL spectrum of the PFO-PBD host. As a result, efficient energy transfer from the PFO-PBD to Eu(DBM)$_3$(BrDPPz) can be expected to occur via Förster energy transfer [15]. Φ_{PL} of Eu(DBM)$_3$

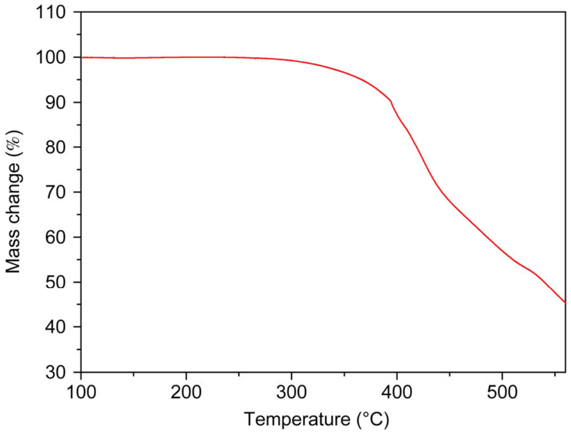


Figure 1 TGA curve of Eu(DBM)$_3$(BrDPPz) at a heating rate of 10 °C/min under nitrogen atmosphere.

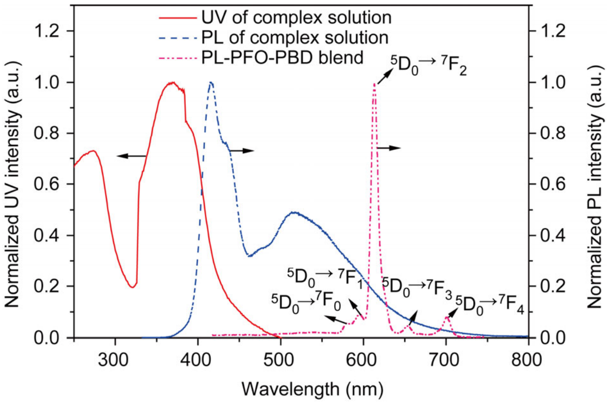


Figure 2 Normalized UV-Vis absorption spectrum and PL spectrum (λ_{ex}=349 nm) of Eu(DBM)$_3$(BrDPPZ) in dilute CHCl$_3$ solution and PL spectra in solution and a thin film of the PFO-PBD blend.

(BrDPPz) in CH_2Cl_2 was measured using $EuCl_3 \cdot 6H_2O$ (Φ_f=0.73% in water) as a reference [36]. Φ_{PL} of Eu (DBM)$_3$ (BrDPPz) is 28.3%, which is higher than that of Eu(DBM)$_3$ (DPPz) (27.1%) [9]. This exceedingly high PL efficiency can be ascribed to the heavy atom effect of bromine, which increases luminescent efficiency [27–29].

To investigate the efficiency of Förster energy transfer between the host matrix and emissive dopant, PFO-PBD films with various concentrations of Eu(DBM)$_3$(BrDPPz) were prepared and excited by a He-Cd laser (325 nm). Figure 3 shows the PL spectra of the films of Eu(DBM)$_3$ (BrDPPz) (1 wt%–8 wt%) in PFO:PBD (30 wt%). Two intense emission peaks at 417 and 519 nm are observed for these Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD blend films, which are assigned to PFO-PBD emission. Furthermore, a series of weak emission peaks from the Eu^{3+} ion at 612 nm were observed in the doped films at doping concentrations from 4 wt% to 8 wt%. The intensities of the peaks at around 417 and 519 nm originating from PFO-PBD emission decreased with the increasing intensity of Eu(DBM)$_3$(BrDPPz) emission at 612 nm with increasing concentration of Eu(DBM)$_3$(BrDPPz). This indicates that Förster energy transfer occurred from the PFO-PBD host to the Eu(DBM)$_3$ (BrDPPz) guest [9,17]. Similar energy transfer from host to guest has been observed in some other host-guest systems of conjugated polymers and europium(III) complexes [19,20].

3.3 EL properties

The EL spectra and Commission Internationale de L'Eclairage (CIE) chromaticity diagrams of the Eu(DBM)$_3$ (BrDPPz)-doped PFO-PBD PLEDs with different dopant concentrations are presented in Figure 4. Similar EL spectra are observed for these doped devices, which are different from the PL profiles of the Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD films. An EL emission maximum at 612 nm with a FWHM of 14 nm and three weak peaks at 574, 648 and 702 nm are observed in these EL profiles [14,15]. The weak emission peaks at 400 to 550 nm also appear in the EL spectra, and obviously decrease in intensity with increasing dopant concentration. These minor high-energy emissions probably correspond to exciplex/electroplex emission and fluorenone emission from the PFO-PBD blend [12]. This suggests that EL emission from the Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD devices is mostly dominated by the dopant rather than the PFO-PBD host at dopant concentrations from 1 wt% to 8 wt% [8,12], which is the dominant mechanism in OLEDs [12,35]. A dramatic difference was observed between PL and EL spectra for iridium complex-doped PLEDs, which was attributed to different emission mechanisms [35]. The CIE coordinates of the PLEDs at near-saturated red emission change slightly from (0.591, 0.347) to (0.607, 0.332) with increasing dopant concentration from 1 wt% to 8 wt%.

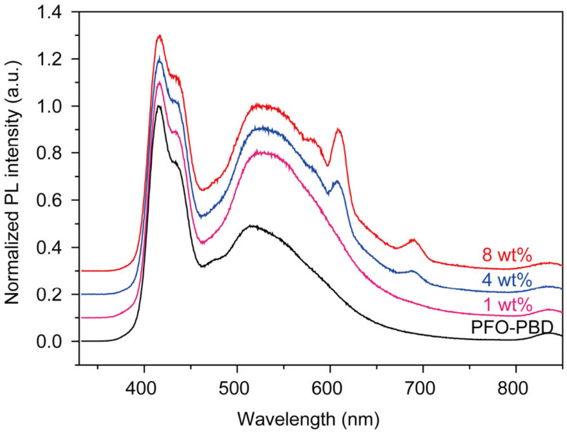


Figure 3 Normalized PL spectra of a PFO-PBD blend and Eu(DBM)$_3$ (BrDPPz)-doped PFO-PBD blend films with different dopant concentrations from 1 wt% to 8 wt%.

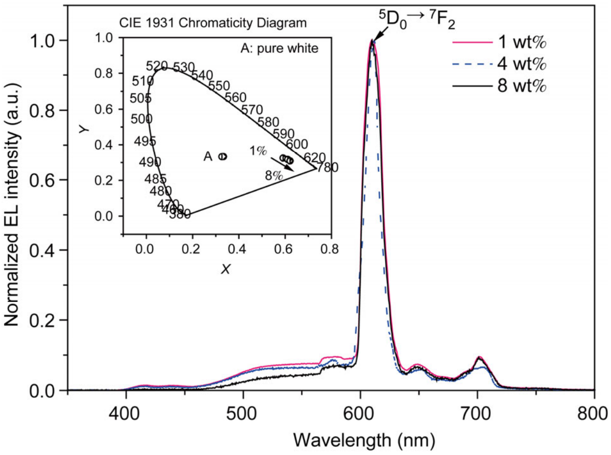


Figure 4 Normalized EL spectra of Eu(DBM)$_3$(BrDPPz)-doped PLEDs at different dopant concentrations from 1 wt% to 8 wt%. The inset is CIE 1931 chromaticity diagrams.

The EQE-current density (J) and brightness (B)-current density (J) curves of these devices with different doping concentrations are shown in Figure 5. The performance of these Eu(DBM)$_3$(BrDPPZ)-based devices with different dopant concentrations is listed in Table 1. The turn-on voltages of the devices increase from 11.2 to 16.8 V with increasing doping level from 1 wt% to 8 wt%. This further indicates that the devices mainly operate by the carrier-trapping mechanism rather than the energy-transfer mechanism [17,38]. A maximum brightness of 829 cd/m^2 at 153.5 mA/cm^2 and maximum EQE of 1.7% at 2.1 mA/cm^2 were obtained for the device with 1 wt% Eu(DBM)$_3$ (BrDPPz). The present results indicate that introduction of a large π-conjugated system is responsible for the improved device performance [31]. However, when the doping concentration was increased to 8 wt%, the EQE and brightness decreased to 0.94% and 344 cd/m^2, which is caused by triplet-triplet annihilation [25]. Figure 6 presents the dependence of luminance efficiency (η_L) and power efficiency (η_p) on current

Table 1 Performance of Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD devices with different dopant concentrations from 1 wt% to 8 wt%

Doping ratio (wt%)	Turn on voltage (V)	Maximum EQE		Maximum B		J=100 mA/cm^2		CIE	η_L [a] (cd/A),	η_p [a] (lm/W),
		J (mA/cm^2)	EQE (%)	J (mA/cm^2)	B (cd/m^2)	EQE (%)	B (cd/m^2)	(X, Y)	J (mA/cm^2)	J (mA/cm^2)
1	11.2	2.1	1.70	153.5	829	0.76	742	(0.591, 0.325)	0.74, 4.31	0.18, 4.31
4	16.2	3.2	1.14	111.2	439	0.72	435	(0.613, 0.317)	0.39, 7.67	0.06, 7.67
8	16.8	7.0	0.94	92.2	344	0.29	332	(0.621, 0.309)	0.22, 30.59	0.04, 30.59

a) Maximum values of each device, η_L=luminance efficiency, η_p=power efficiency.

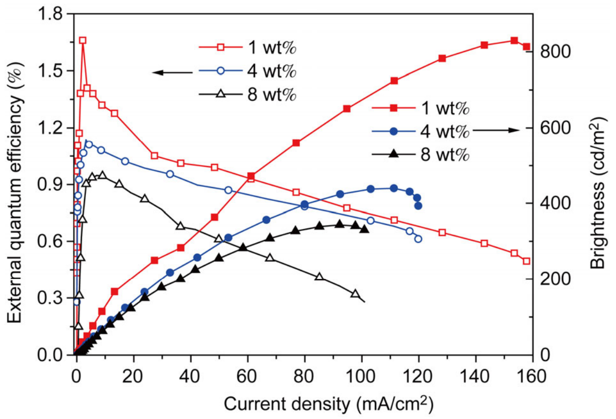


Figure 5 External quantum efficiency-current density (EQE-J) and brightness-current density (B-J) curves for the Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD devices with different dopant concentrations from 1 wt% to 8 wt%.

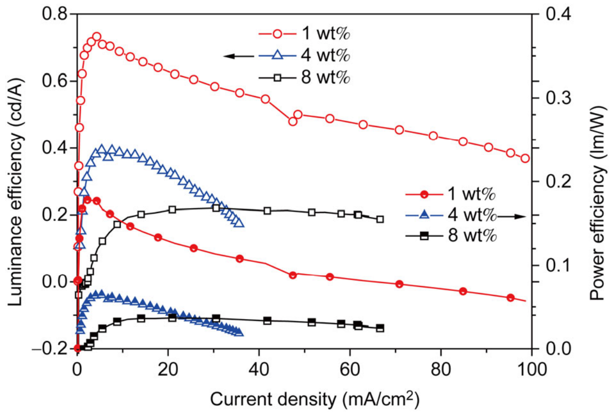


Figure 6 Luminance efficiency-current density-power efficiency characteristics of the Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD devices with different dopant concentrations.

density (J) for Eu(DBM)$_3$(BrDPPZ) devices with several doping concentrations, and the data is listed in Table 1. The highest η_L of 0.74 cd/A with a maximum η_p of 0.18 lm/W at 4.31 mA/cm^2 were obtained for the device with 1 wt% Eu(DBM)$_3$(BrDPPz). With increasing doping concentration from 1 wt% to 8 wt%, the maximum η_L and η_p gradually decreased at high current density. This implies that efficiency roll-off in the Eu(DBM)$_3$(BrDPPZ)-based devices is suppressed with increasing dopant concentration and current density.

3.4 Dispersibility

To evaluate its dispersibility in a polymer matrix, a film of 8 wt% Eu(DBM)$_3$(BrDPPZ) doped in a blend of PFO-PBD was prepared. The surface morphology of the film was examined by atomic force microscopy (AFM), and the resulting image is shown in Figure 7. An average surface roughness R_a of 1.463 nm is observed for the Eu(DBM)$_3$(BrDPPZ)-doped PFO-PBD blend film. Compared to our reported complex Eu(DBM)$_3$(DPPz) [11], Eu(DBM)$_3$(BrDPPZ) exhibits poor dispersibility in the same matrix. Therefore, appropriate domain size and phase separation strongly influences the performance of the PLEDs [39].

3.5 Electrochemical properties

The electrochemical properties of Eu(DBM)$_3$(BrDPPz) were examined by cyclic voltammetry. The measured reversible onset oxidation/reduction potentials (E_{ox}/E_{red}) for Eu(DBM)$_3$(BrDPPz) were 0.80/–2.08 V, respectively. According to an empirical formula [34], the LUMO and HOMO energy levels for Eu(DBM)$_3$(BrDPPz) were calculated to be −2.65 and −5.54 eV, respectively. Compared to those of Eu(DBM)$_3$(DBrPhen) [17], Eu(DBM)$_3$(BrDPPz) displayed a minor increase in HOMO level, which could improve its hole-transporting properties [40]. Compared to Eu(DBM)$_3$(DBrPhen), Eu(DBM)$_3$(BrDPPz) as a dopant can trap carriers from PFO more efficiently, which results in efficient EL in the corresponding devices [17,41]. However,

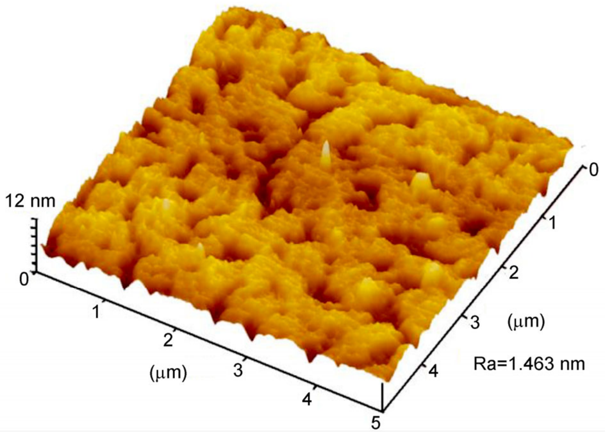


Figure 7 Atomic force microscope (AFM) image of an Eu(DBM)$_3$-(BrDPPz)-doped PFO-PBD film containing 8 wt% dopant.

compared with Eu(DBM)$_3$(DPPz) [11], Eu(DBM)$_3$(BrDPPz) possesses a higher LUMO energy level by 0.05 eV [42]. This implies that Eu(DBM)$_3$(BrDPPz) is poorer at trapping electrons than Eu(DBM)$_3$(DPPz), which would decrease the EL efficiency of the Eu(DBM)$_3$(BrDPPz)-doped PFO-PBD devices [12,43]. Therefore, to obtain the better device performance, further studies on the EL properties of Eu(DBM)$_3$ (BrDPPz) to optimize polymeric host and device configuration should be performed.

4 Conclusions

In conclusion, we fabricated high-efficiency europium complex-based PLEDs by doping Eu(DBM)$_3$(BrDPPz) into a PFO-PBD blend. These devices exhibited a sharp emission at 612 nm, with a FWHM of 14 nm even at low dopant concentration. A maximum EQE of 1.7% at 2.1 mA/cm^2, $L_{\max}$ of 829 cd/m^2 at 153.5 mA/cm^2 and maximum η_L of 0.74 cd/A at 4.31 mA/cm^2 were obtained from a PLED containing 1 wt% Eu(DBM)$_3$(BrDPPz). This initial study indicates that incorporation of a large π-conjugated system into europium(III) complexes results in an efficient red-emitting material for use in optoelectronic devices.

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