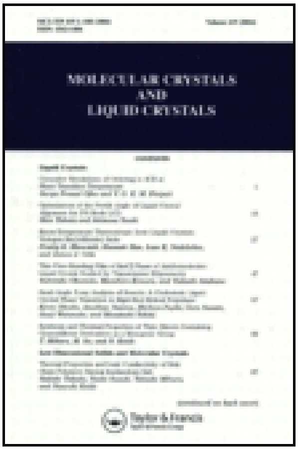

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Phosphorescent PLEDs Using Donor-Acceptor Liquid-Crystalline Polymers Containing Oxadiazole and Carbazole

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Phosphorescent PLEDs Using Donor-Acceptor Liquid-Crystalline Polymers Containing Oxadiazole and Carbazole

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Blue-emitting polymers based on a donor-acceptor architecture composed of oxadiazole and carbazole moieties containing various substituted groups in the same side chain were used as a host polymer in phosphorescent polymer light-emitting diodes (PhPLEDs). The polymer containing N-methylcarbazole showed a liquid-crystalline (LC) phase above its glass transition temperature but the other polymer containing N-ethylhexylcarbazole exhibited an amorphous phase. The single-layer PLEDs using these polymers exhibited blue emission with peaks from 430 to 440 nm. To examine the LC polymer (LCP) and the amorphous polymer as host materials, we fabricated simple devices using Ir(ppy)$_3$ and (btp)$_2$lr(acac) as phosphorescent dopants at various doping concentrations. The device composed of lTO/PEDOT-PSS/2 wt% of (btp)$_2$Ir(acac) doped into LCP/MgAg showed intense red light (0.67, 0.32) with the luminance efficiency of 4.7 cd/A. The luminance efficiency of the PhPLEDs using the LCP was higher than that of the PhPLEDs using the amorphous polymer.

Keywords: donor-acceptor; electroluminescence; liquid-crystalline polymer; phosphor; phosphorescent polymer light-emitting diodes

INTRODUCTION

Polymer light-emitting diodes (PLEDs), fabricated by solution processes with active materials, provide much less expensive manufacturing processes than those of LEDs which are prepared with small molecules by high vacuum deposition [1,2]. For commercialization, PLEDs are typically required to show a high emitting efficiency. The efficiency of PLEDs can be improved by introduction of a phosphorescent dye into

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a polymer as an emissive layer, because the so-called phosphorescent PLEDs (PhPLEDs) may use both singlet and triplet excitons [3,4]. These efficient PhPLEDs, however, necessitate the development of suitable polymers that enable an efficient energy transfer (*via* Förster/Dexter mechanism), the efficiency of which is proportional to the overlap between an emission spectrum of a host polymer and an absorption spectrum of a phosphorescent guest [5].

In the previous works, we have focused on the synthesis of bipolar polymers based on a donor-acceptor architecture possessing liquid-crystalline (LC) properties and already observed polarized blue emission from PLEDs using the LC polymers (LCPs) [6,7]. Likewise, with a goal of balancing the charge injection and transport, a modulation of the polymer structure so as to contain both electron- and hole-transporting units is a reasonable approach to achieve a high performance in PhPLEDs [8]. We synthesized a class of bipolar polymers containing oxadiazole (OXD) as an electron-transporter and carbazole (Cz) as a hole-transporter and modified chemical structures of the polymers so as to show intense blue emission, bipolar charge-transporting property and good film formation to achieve high performance in PLEDs [9].

Herein, we fabricated simple devices using the bipolar polymers doped with Ir complexes as an emitting layer to examine the bipolar polymers as host materials in PhPLEDs. Particularly we used a LCP as an efficient host material doped with the Ir complex as an emitting layer with the aid of energy transfer from the LCP to the Ir complex in phosphorescent PhPLEDs.

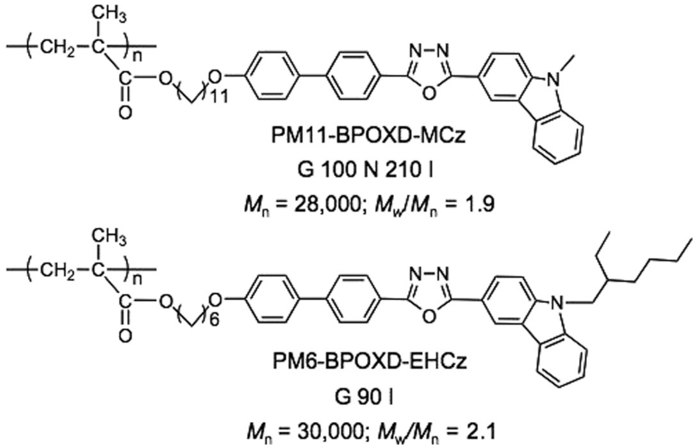
EXPERIMENTAL

Material

Scheme 1 shows the chemical structures of two donor-acceptor polymers used as host emitters in this study. The polymers were prepared as reported previously and identified by means of ^{1}H NMR spectroscopy, elemental analysis and mass spectroscopy [10]. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC; JASCO model DG-980-50; columns, Shodex K802 + K804 + K805; eluent, chloroform) calibrated with polystyrene standards.

Characterization

Absorption and photoluminescence (PL) spectra were measured at room temperature with a UV-vis spectrometer (JASCO, V-550) and a fluorescence spectrophotometer (Hitachi, F-7010), respectively.



SCHEME 1 Chemical structures of the donor-acceptor polymers used in this study.

Single-layer PLEDs were fabricated using blends of the polymers and Ir complexes at various concentrations as an emitting layer. The polymer solutions were spin-coated onto ITO glass substrates and annealed at 160°C. In PhPLEDs, PEDOT-PSS films were built up onto ITO glass substrates, and then polymer solutions in 1,1,2,2-tetrachloroethane (1.5 wt%) containing Ir complexes at various concentrations were spin-coated onto mechanically rubbed PEDOT-PSS films to give thin films of less than 100 nm. On a top of the polymer film, a thin layer of magnesium and silver (Mg : Ag = 10 : 1) as a cathode was deposited by thermal vacuum evaporation at a vacuum pressure less than 10^{-5} torr. Thickness of each film was measured with a Dektak surface profiler. Electroluminescence (EL) spectra were measured with the fluorescence spectrophotometer at room temperature. Current density and luminance characteristics of the devices were measured with a power supply (Advantest, R6243) and a luminance meter (Minolta, LS-500). The emitting area was 2 × 3 mm^2. All measurements were performed under an ambient atmosphere.

RESULTS AND DISCUSSION

Optical Properties

Two donor-acceptor polymers showed blue emission in thin films. As indicated in Figure 1, the PL spectrum of the LCP and the absorption spectra of $Ir(ppy)_3$ and $(btp)_2Ir(acac)$ were overlapped in the region of

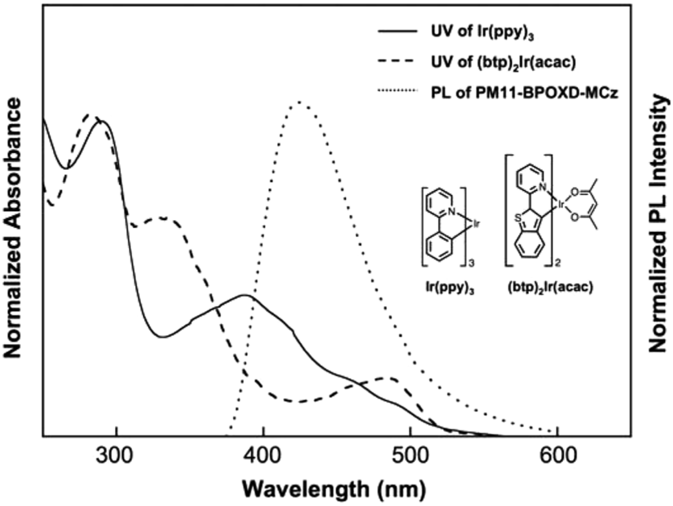


FIGURE 1 Absorption spectra of $Ir(ppy)_3$ and $(btp)_2lr(acac)$ and PL spectrum of PMll-BPOXD-MCz (LCP) in a film.

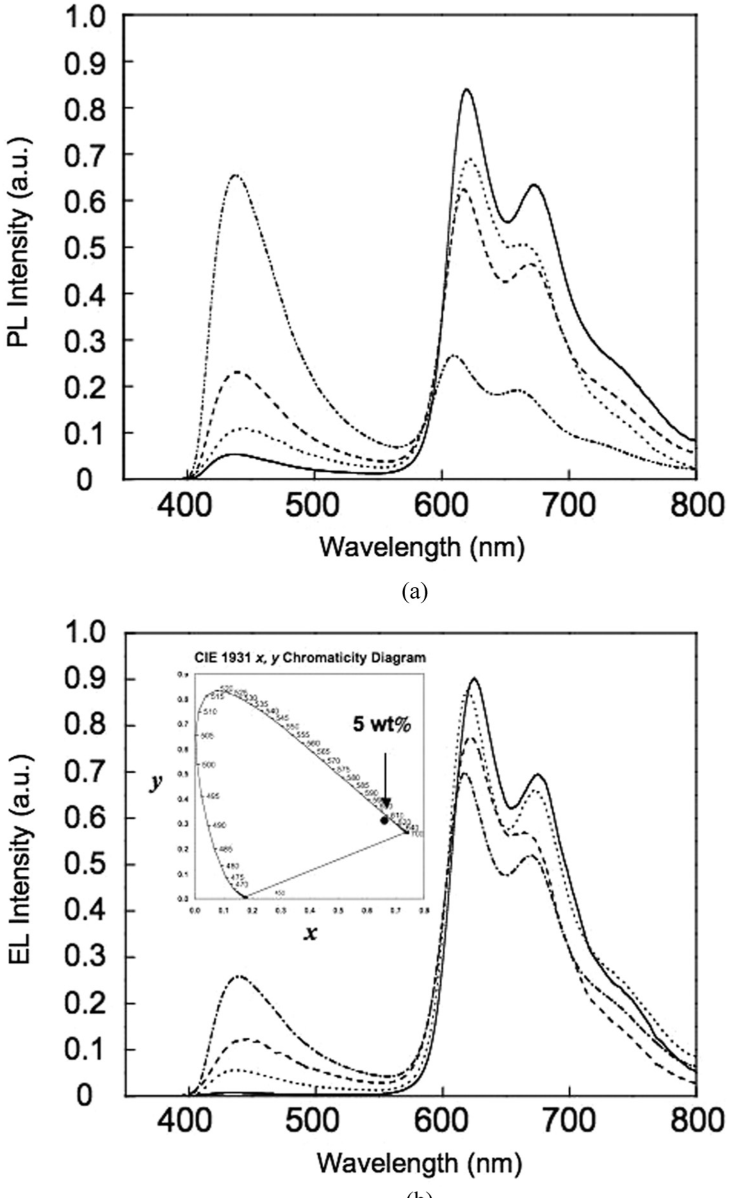
350–550 nm. These spectral overlaps could induce an energy transfer from the singlet-excited state of the host to the metal-to-ligand charge transfer (MLCT) state of the guest, followed by fast intersystem crossing to the triplet state of the dopants, which causes emission from the triplet state [11].

Phosphorescent Polymer Light-Emitting Diodes

We evaluated the potential of the LCP for applications as an efficient host material in PLEDs with a configuration of ITO/rubbed PEDOT-PSS/Ir-doped PMll-BPOXD-MCz/MgAg.

The PL and EL spectra shown in Figure 2 demonstrate that energy transfer occurs between the host polymer and $(btp)_2Ir(acac)$ at doping concentrations from 0.5 to 5 wt%. The PL spectra showed two broad peaks at 440 nm originated from PMll-BPOXD-MCz and 620 ran corresponding to the triplet emission of $(btp)_2Ir(acac)$ upon photoexcitation of the host polymer ($\lambda_{ex} = 330$ nm). The emission at 440 nm was significantly reduced as the doping concentration of the Ir complex increased. At the doping concentration of 5 wt%, the PL spectrum was dominated by the triplet emission at 620 nm.

In Figure 2(b), the devices with the LCP doped with $(btp)_2Ir(acac)$ showed very weak peaks at 440 nm derived from the host polymer



(a)

(b)

FIGURE 2 PL spectra of the (btp)$_2$Ir(acac)-doped PMll-BPOXD-MCz films (a) and EL spectra of the (btp)$_2$lr(acac)-doped devices (b) at various doping concentrations of (btp)$_2$Ir(acac).

and intense emission peaks at 620 nm originated from the emission of $(btp)_2Ir(acac)$. The emission from PMll-BPOXD-MCz at 440 nm was quenched at the doping concentration of $(btp)_2Ir(acac)$ at 5 wt%. The difference between the PL and EL spectra may indicate that both Forster energy transfer and direct charge trapping on the Ir complex contribute mainly to the observed EL spectra [12].

The CIE color coordinates of the EL emission from the device with 5 wt% of $(btp)_2Ir(acac)$ are shown in the inset of Figure 2(b). The color-matching function converted from the EL spectrum was red (0.67, 0.32), which is very close to the pure red (0.67, 0.33) required by the National Television Committee (NTSC) (Table 1).

Figure 3 presents the device performance of the PLEDs using the Ir-doped LCP at various doping concentrations. Table 1 summarizes the performance of the $(btp)_2Ir(acac)$-doped PLEDs. The device based on the 0.5 wt% blend (D2) showed an external quantum efficiency of 6.5% at 200 cd/m^2. The device (D3) with 1 wt% of $(btp)_2lr(acac)$ turned on at 5 V and reached a maximum brightness of 1450 cd/m^2. A maximum brightness of the 2 wt% $(btp)_2Ir(acac)$-doped device (D4) was 1910 cd/m^2 and a luminance efficiency of 4.7 cd/A was obtained at 200 cd/m^2. The device (D5) with the highest doping concentration of 5 wt% showed slightly decreased external quantum efficiency and luminance efficiency at high driving voltage, which might be caused by concentration quenching and triplet-triplet annihilation of $(btp)_2Ir(acac)$ [12]. We observed no significant difference in the spectral characteristics when raising the applied voltage to 30 V. Furthermore, we investigated PM6-BPOXD-EHCz (non LCP) as a host material in PhPLEDs with the $(btp)_2Ir(acac)$-doped polymer film (0.5 wt%) as an emitting layer.

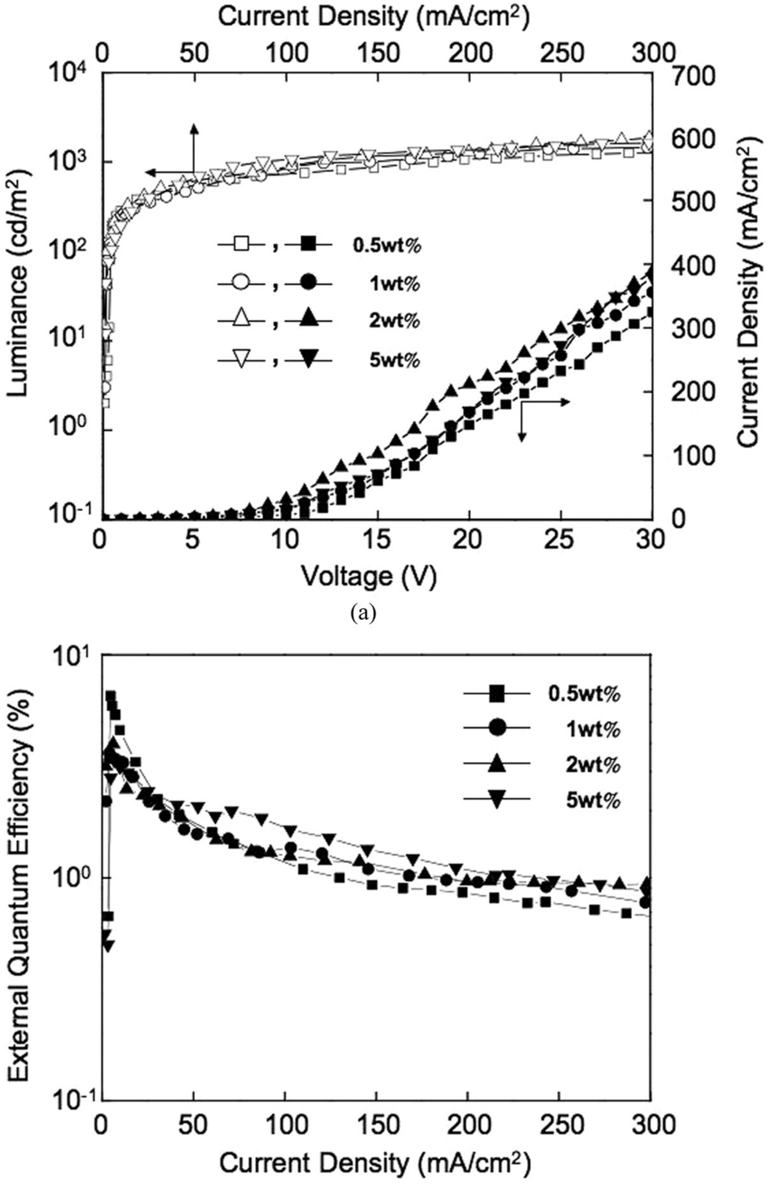
The luminance efficiency of the device using PMll-BPOXD-MCz (LCP) was higher than that with PM6-BPOXD-EHCz at the same doping concentration of $(btp)_2lr(acac)$ as shown in Figure 4. The improved efficiency might be caused by an increased recombination probability and the well-aligned structure of the LCP.

Figure 5 shows the EL spectra of the devices using the LCP doped with two Ir complexes. We observed green and red emission from the devices with 5 wt% of $Ir(ppy)_3$ and $(btp)_2Ir(acac)$, respectively. We also explored PLEDs with the LCP as a host emitter to obtain white emission. The fabricated device using the LCP doped with 2 wt% of $Ir(ppy)_3$ exhibited an emission spectrum with CIE coordinates of $(x, y) = (0.21, 0.26)$. By doping two Ir complexes, the devices using the blue-emitting LCP as a host emitter and a small amount of green and red Ir complexes as guest emitters exhibited white light (0.38, 0.28) as shown in Figure 6.

TABLE 1 EL Characteristics of PhPLEDs

device[a]	(btp)2Ir(acac) wt%	turn-on voltage[b], V	brightness[c] cd/m^2	R_{EL}[d]	λ_{max}[e] nm	external quantum efficiency[f], %	luminance efficiency[g] cd/A	CIE[h] (x, y)
Dl	–	–	–	5.1	440	–	–	0.17, 0.04
D2	0.5	6	1300 (550)	–	440, 620	6.5 (6.1)	4.1 (3.8)	0.45, 0.25
D3	1	5	1450 (500)	–	440, 620	3.3 (3.4)	2.3 (2.1)	0.54, 0.29
D4	2	4	1.910 (610)	–	440, 620	3.8 (3.9)	4,7 (3.4)	0.61, 0.30
D5	5	4	1730 (650)	–	620	3.1 (3.4)	2.1 (2.0)	0.67, 0.32

[a] Fabrication of PhLEDs: Dl – D5 consist of ITO/rubbed PEDOT-PSS/(btp)2Ir(acac)-doped LCP/MgAg at Ir-doping concentrations of 0, 0.5, 1, 2 and 5 wt%, respectively. [b] Recorded at 1 cd/m^2. [c] The maximum brightness (brightness at 50 mA/cm^2). [d] Dichroic ratio of polarized EL. [e] The peak wavelengths of the EL spectrum. [f] The maximum external quantum efficiency of the phosphorescent PLE D (external quantum efficiency at 200 cd/m^2). [g] The maximum luminance efficiency (luminance efficiency at 200 cd/m^2). [h] CIE coordinates, x and y, evaluated with the EL spectrum recorded at 15 V.



(a)

(b)

FIGURE 3 Luminance *vs* applied voltage (a) current density *vs* applied voltage (b) and external quantum efficiency *vs* current density (c) of the devices, ITO/ruubed PEDOT-PS5/$(btp)_2Ir(acac)$-doped PMll-BPOXD-MCz (LCP)/MgAg, at various doping concentrations of $(btp)_2Ir(acac)$.

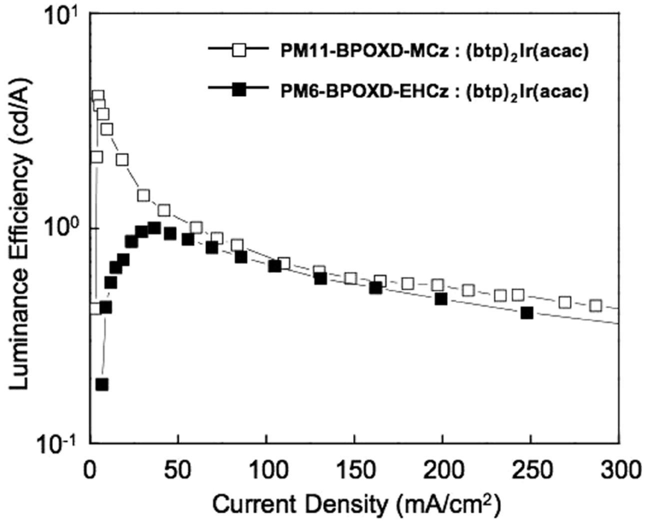


FIGURE 4 Luminance efficiencies *vs* current density of the devices using the 0.5 wt% of (btp)$_2$Ir(acac)-doped polymers.

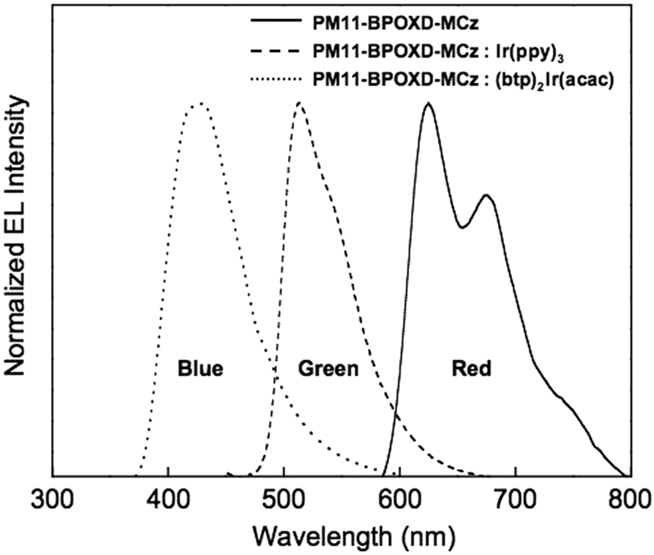


FIGURE 5 EL spectra of the devices; ITO/rubbed PEDOT-PSS/PMll-BPOXD-MCz/MgAg (dotted line), ITO/rubbed PEDOT-PSS/PMll-BPOXD-MCz: Ir(ppy)$_3$ (95: 5 wt%)/MgAg (dashed line) and ITO/rubbed PEDOT-PSS/PMll-BPOXD-MCz: (btp)$_2$Ir(acac) (95 : 5 wt%)/MgAg (solid line).

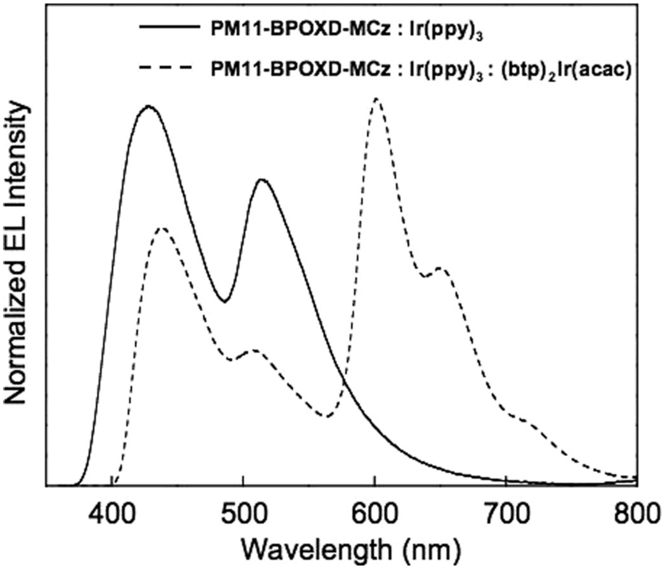


FIGURE 6 EL spectra of the devices: ITO/rubbed PEDOT-PSS/PMll-BPOXD-MCz: Ir(ppy)$_3$(98: 2 wt%)/MgAg (solid line) and ITO/rubbed PEDOT-PSS/PMll-BPOXD-MCz: Ir(ppy)$_3$: (btp)$_2$Ir(acac) (98.5 : 0.5 :1 wt%)/MgAg (dashed line).

CONCLUSIONS

In this study, we evaluated the potential of the LCP for applications as an efficient host material in PLEDs with a configuration of ITO/rubbed PEDOT-PSS/Ir-doped PMll-BPOXD-MCz/MgAg. By doping 5 wt% of (btp)$_2$Ir(acac) into the LCP, the resultant PLEDs showed red emission (0.67, 0.32) due to the efficient energy transfer from the LCP to the Ir complex. The luminance efficiency and external quantum efficiency increased to 4.7 cd/A and 3.9%, respectively. By doping two Ir complexes into the LCP, we observed white emission from the PhPLEDs.

This bipolar blue-emitting LCP could be a good candidate for the host material with the aid of energy transfer between the LCP and a phosphorescent dye for application in PhPLEDs.

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