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# Properties of Phosphorescence Polymer Light Emitting Diodes with PVK: Ir(ppy)$_3$: PFO:Ir(pq)$_2$acac Emission Layer

HAK MIN LEE,[1] SU CHOEL GONG,[1] JIN EUN CHOI,[1] SEUNG JUN BAEK,[1] YOUNG CHUL CHANG,[2] AND HO JUNG CHANG[1]

[1]Department of Electronics Engineering, Dankook University, Chungnam, Korea
[2]School of Mechatronics Engineering, Korea University of Technology and Education, Chungnam, Korea

*Phosphorescence polymer LEDs (PhPLEDs) with the structure of ITO/PEDOT:PSS/PVK:Ir(ppy)$_3$:PFO:Ir(pq)$_2$acac/TPBI/LiF/Al were fabricated to investigate the effects of the doping concentration of Ir(pq)$_2$acac on the electrical and optical properties of the devices. PVK(poly-vinylcarbazole) and Ir(ppy)$_3$ [tris(2-phenylpyridine)iridium(III)] polymers were used as the host and guest materials, respectively. PFO[poly(9,9-dioctylfluorene)] and Ir(pq)$_2$(acac)[bis(2-phenyl-1-quinoline)iridiumacetyl acetonate] were also introduced as blue and red component guest materials for the white emission. The concentration ratio of PVK:Ir(ppy)$_3$:PFO was fixed at 100:2.0:1.0 vol%. The Ir(pq)$_2$acac concentration in the emission layer was varied from 1.0 to 5.0 vol%. White PhPLEDs were obtained for the samples with 5.0 vol% of Ir(pq)$_2$acac, for which the luminance and current density were about 2530 cd/m$^2$ and 720 mA/cm$^2$ at 8 V, respectively. The CIE color coordinates were x, y = 0.33, 0.33, showing a pure white color.*

**Keywords** CIE color coordinates; Ir(ppy)$_3$; Ir(pq)$_2$acac; luminance; phosphorescence; polymer light emitting diode; PVK; white emission

## Introduction

Organic light-emitting diodes (OLEDs) have drawn much attention owing to their promising applications in next-generation displays [1]. Generally, OLEDs can be classified into small molecule LEDs and polymer LEDs (PLEDs) according to the emission materials introduced into the devices. Recently, PLEDs have attracted much attention for use in large and flexible displays, because of their relatively simple device architecture and soluble processes involving the use of the spin coating, ink-jet printing and spray coating methods [2–4]. To improve their light quantum efficiency and reliability, it is important to optimize the electron and hole

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Address correspondence to Dr. Ho Jung Chang, Department of Electronics Engineering, Dankook University, San 29, Anseo-dong, Cheonan, Chungnam 330-714, Korea (ROK). Tel.: (+82)41-550-3569; Fax: (+82)41-550-3589; E-mail: hjchang@dankook.ac.kr

recombination process by introducing an optimum hole blocking layer (HBL) as well as phosphorescence materials into the emission layer (EML) [5]. The phosphorescence materials emit light from both singlet and triplet excitons, so that the internal quantum efficiency can theoretically reach 100%. One can anticipate a four-fold luminance increase in phosphorescence polymer LEDs (PhPLEDs) in comparison with fluorescence PLEDs which emit light only from singlet excitons [6,7]. The PLED is a current operational device which emits light through the recombination of excitons (electron-hole pairs) injected from the anode and cathode electrodes. The single host blended system in PLEDs shows lower efficiency and brightness compared with the host and guest (dopant) system [8]. The light emission and energy transfer in the latter system can occur from both the host and guest materials, the combined effect of which results in a high light efficiency and brightness.

In this study, the PhPLEDs with the multi-layer structure of ITO/PEDOT:PSS/PVK:Ir(ppy)$_3$:PFO:Ir(pq)$_2$acac/TPBI/LiF/Al were fabricated. The emission layer consists of fluorescent (PVK and PFO) and phosphorescent (Ir(ppy)$_3$ and Ir(pq)$_2$acac) blended organic materials for white emission. The effects of the Ir(pq)$_2$acac concentration and the introduction of the HBL (TPBI and balq) between the EML and LiF/Al film layer on the electrical and optical properties of the PhPLEDs were investigated.

## Experimental

### *Fabrication of PhPLEDs*

The ITO coated glass substrate (ITO/glass) with a resistivity of 10 Ω/□ was cleaned by an ultrasonic precision cleaning process with acetone, methanol and isopropyl alcohol (IPA) [9]. The ITO transparent anode film with an emitting area of 2 mm × 2 mm was patterned using the conventional photo lithographic process [10]. In order to remove the organic particles, the patterned ITO/glass substrates were cleaned using the SC-1 process (volume ratio of $H_2O_2$-$NH_2OH$-$H_2O$ = 1:1:5) [11], followed by an ultrasonic precision cleaning process with acetone, IPA and de-ionized water. The remaining solvent was removed by soft baking for 10 minutes at 100°C in a vacuum oven. The plasma treatment of the ITO/glass substrate was carried out at an RF power of 150 Watts for 2 minutes under an $O_2$ gas pressure of 8 mTorr. The plasma treatment before the deposition of the organic layer is expected to reduce the energy barrier for effective hole injection from the anode and to improve the adhesion between the ITO and organic layer [12]. PEDOT:PSS [poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate] was used as the hole transport layer [13]. PVK(poly-vinylcarbazole) was used as the host material in the EML. PFO[poly(9,9-dioctylfluorene)], Ir(ppy)$_3$ [tris(2-phenylpyridine)iridium(III)] and Ir(pq)$_2$acac[bis(2-phenyl-1-quinoline)iridium-acetyl acetonate] conjugated polymers were also used as guest materials for the white emission. Based on a previous experiment [14], the concentrations of PVK, Ir(ppy)$_3$ and PFO were optimized and fixed at 100, 2.0 and 1.0 vol%, respectively, and Ir(pq)$_2$acac was introduced at various concentrations ranging from 1.0 to 5.0 vol%. Before the mixing with various host and guest materials, the starting polymer materials were dissolved with 0.5 wt% chlorobenzene for the precursor solutions.

Following this, the prepared solutions were mixed again with a concentration ratio of PVK:Ir(ppy)$_3$:PFO:Ir(pq)$_2$acac = 100:2.0:1.0:1.0∼5.0 vol%. The prepared solution for the EML was spin-coated onto the PEDOT:PSS/ITO/glass substrate at successive rotation speeds of 4000 and 5000 rpm for 20 sec each. The balq[Bis

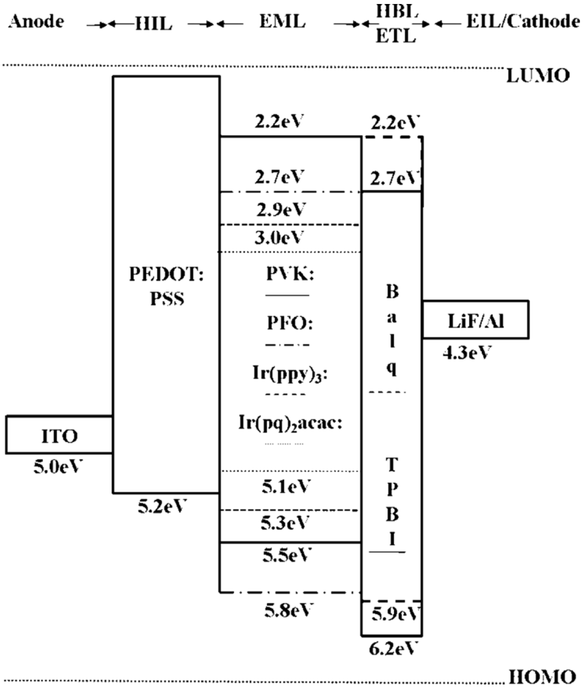

**Figure 1.** Energy band diagram of the phosphorescence polymer LEDs (PhPLEDs).

(2-methyl-8-quinolinolato-N1,O8)-(1,1′-Biphenyl-4-olato)aluminum] and TPBI[2,2′, 2″-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)] materials used as the HBL were introduced to improve the internal quantum efficiency. The LiF and aluminum cathode electrode were deposited by the thermal evaporation method in a vacuum chamber with a base pressure of $5 \times 10^{-8}$ Torr. Finally, PhPLEDs with the structure of ITO/PEDOT:PSS/PVK:Ir(ppy)$_3$:PFO:Ir(pq)$_2$acac/TPBI/LiF/Al were fabricated to investigate their electrical and optical properties at various concentrations of Ir(pq)$_2$acac.

These processes were carried out in a glove box under an $N_2$ gas atmosphere to protect the devices from moisture and oxygen.

The energy band diagram of the PhPLEDs is shown in Figure 1.

## Measurements

The electrical properties were investigated using a POLARONIX M6100 I-L-V test system. The measurement of the luminance, emission spectrum and CIE (Commission International de I'Eclairage) color coordinates was performed using a CS-1000(Minolta) spectro-radiometer in a dark room.

## Results and Discussion

### *Introducing the Hole Blocking Layer Between the Emission and LiF/Al Cathode Films*

The hole blocking layer (HBL) with TPBI and balq organic materials was introduced to improve the performance of the device.

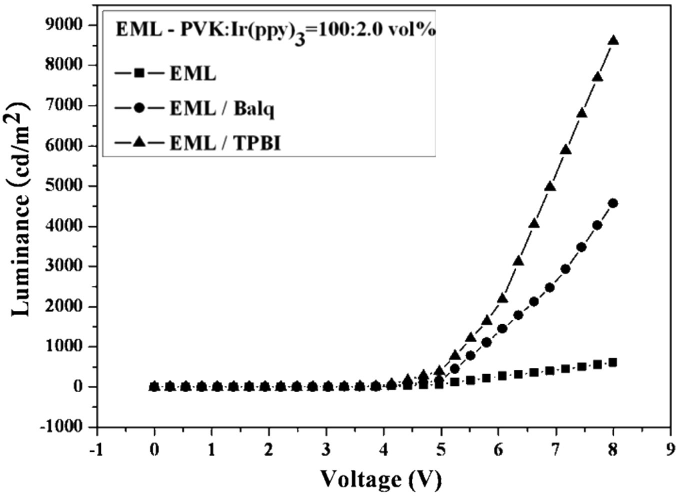

**Figure 2.** Luminance *versus* voltage (L-V) curves for the PhPLEDs with and without a hole blocking layer (HBL).

Figure 2 shows the luminance *versus* voltage curves of the PhPLEDs with and without the HBL. The luminance was found to be about 610 cd/m$^2$ at 8 V for the PhPLED without the HBL. In contrast, the luminance increased greatly up to 4570 cd/m$^2$ and 8530 cd/m$^2$ at 8 V for the device with balq and TPBI materials, respectively. This result suggests that the HBL plays a key role in the effective recombination of the excitons in the EML, by blocking the diffusion of holes into cathode layer, which results in an improvement of the light quantum efficiency. In addition, the luminance for the PhPLED with the TPBI layer was about 1.8 times higher than that with the balq layer. This originated from the energy level difference between the TPBI and balq layers, that is, TPBI has a higher energy level in the lowest unoccupied molecule orbit (LUMO) and highest occupied molecule orbit (HOMO), suggesting that the transportation of electrons is more effective in the device with the TPBI layer. The relatively low luminance of the PhPLED without the HBL may be caused by non-radiative recombination due to the diffusion of excitons into the cathode film layer.

Figure 3 shows the current densities as a function of input voltages for the PhPLEDs with and without the HBL. The current density of the device without the HBL was 289 mA/cm$^2$ at 8 V, whereas those of the PhPLEDs with the Balq and TPBI layers were 686 mA/cm$^2$ and 544 mA/cm$^2$, respectively. Thus, it is important to introduce the optimum HBL materials, having energy levels with higher LUMO and HOMO situated between EML and cathode film layers. In this experiment, the maximum luminance and current density were observed for the device with the TPBI layer (ITO/PEDOT:PSS/PVK:Ir(ppy)$_3$/TPBI/LiF/Al structure). These green emitting devices were used for the white emitting PhPLEDs by doping them with blue and red component organic materials, as discussed in following section.

### *The Effect of the PFO and Ir(pq)$_2$acac Concentrations on the Electrical and Optical Properties of the White PhPLEDs*

PFO and Ir(pq)$_2$acac were introduced into the EML as guest materials to obtain a white emission from the devices. First, PFO with various concentrations ranging

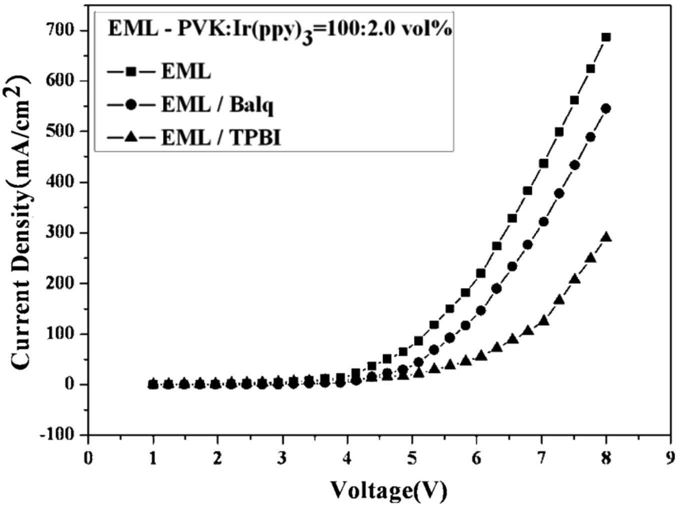

**Figure 3.** Current densities as a function of input voltage for the PhPLEDs with and without a hole blocking layer (HBL).

from 1.0 to 5.0 vol% was mixed with the previously prepared PVK and $Ir(ppy)_3$ ($PVK:Ir(ppy)_3 = 100:2.0$ vol%), and the effect of the PFO concentration on the optical properties of the devices was investigated.

Figure 4 shows the relative emission peak intensity between the blue spectrum peak (420 nm) and green spectrum peak (510 nm) of the devices at various PFO concentrations. The maximum relative emission intensity was observed for the device with a PFO concentration of 1.0 vol%, indicating that it exhibited a stronger blue

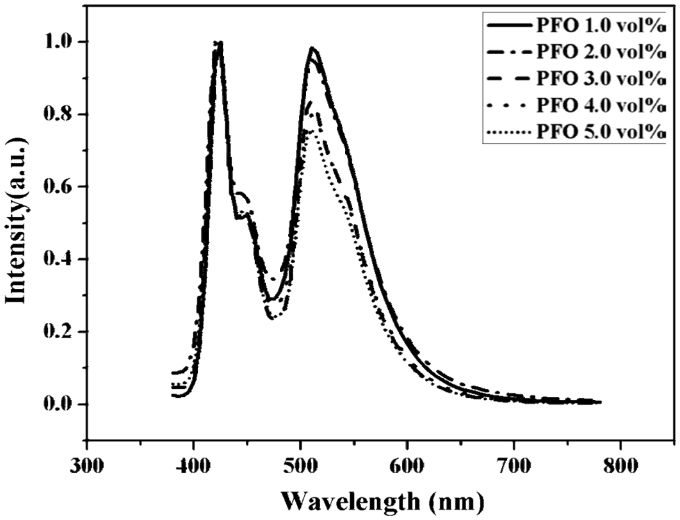

**Figure 4.** Relative emission peak intensities of the PhPLEDs at various PFO guest material concentrations.

range emission peak compared with the other samples. The relatively small green spectrum peak of $Ir(ppy)_3$ may be related to the fact that the energy transfer in PFO occurred before the energy was transferred from PVK to $Ir(ppy)_3$. Therefore, we decided to fix the concentration ratio of PVK, $Ir(ppy)_3$ and PFO in the EML at 100:2.0:1.0 vol%. Then, white PhPLEDs were fabricated using $Ir(pq)_2acac$ red phosphorescence dopant with concentrations ranging from 1.0 to 5.0 vol%. The electrical and optical properties of the prepared devices with the structure of ITO/PEDOT:PSS/PVK:$Ir(ppy)_3$:PFO:$Ir(pq)_2acac$/ TPBI/LiF/Al were investigated.

The color coordinate chart of the PhPLEDs with various $Ir(pq)_2acac$ concentration is shown in Figure 5. White PhPLEDs were obtained for the sample with 5.0 vol% $Ir(pq)_2acac$ at an applied voltage of 8 V, for which the CIE color coordinates were x, y = 0.33, 0.33 (pure white color). In contrast, the CIE color coordinates of the PhPLEDs with 1.0 vol% $Ir(pq)_2acac$ were x, y = 0.25, 0.37 (bluish green color). From the CIE color measurement, it was found that the emission color became more reddish (was shifted to longer wavelengths) as the $Ir(pq)_2acac$ concentration increased from 0.1 to 5.0 vol%.

Figure 6 shows (a) the luminance *versus* voltage and (b) the current density *versus* voltage characteristics for the PhPLEDs with various concentrations of $Ir(pq)_2acac$. The luminance decreased from 3990 to 2530 cd/m$^2$ as the $Ir(pq)_2acac$ concentration increased from 1.0 to 5.0 vol%. This result may be due to the lower emission energy of $Ir(pq)_2acac$ compared with the other guest materials, viz. PFO and $Ir(ppy)_3$. The luminance and current density of the white PhPLED with 5.0 vol% $Ir(pq)_2acac$ were about 2530 cd/m$^2$ and 720 mA/cm$^2$, respectively.

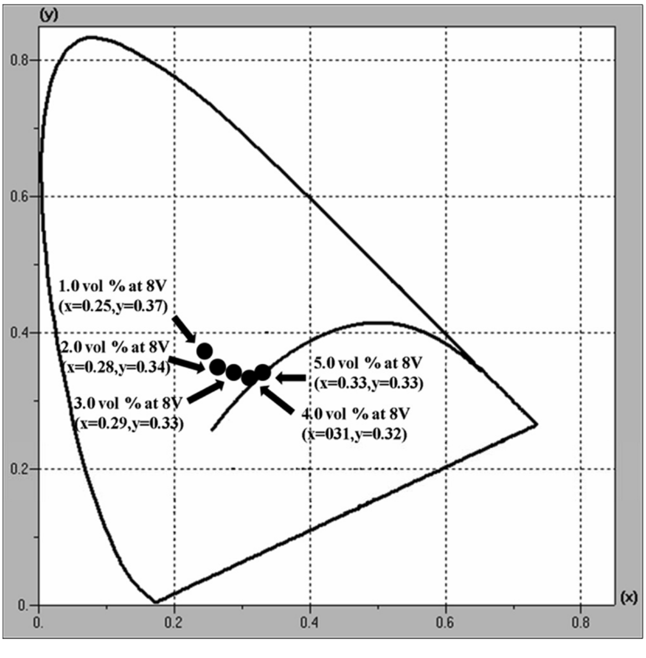

**Figure 5.** The color coordinate chart of the PhPLEDs at various $Ir(pq)_2acac$ concentrations in the emission layer.

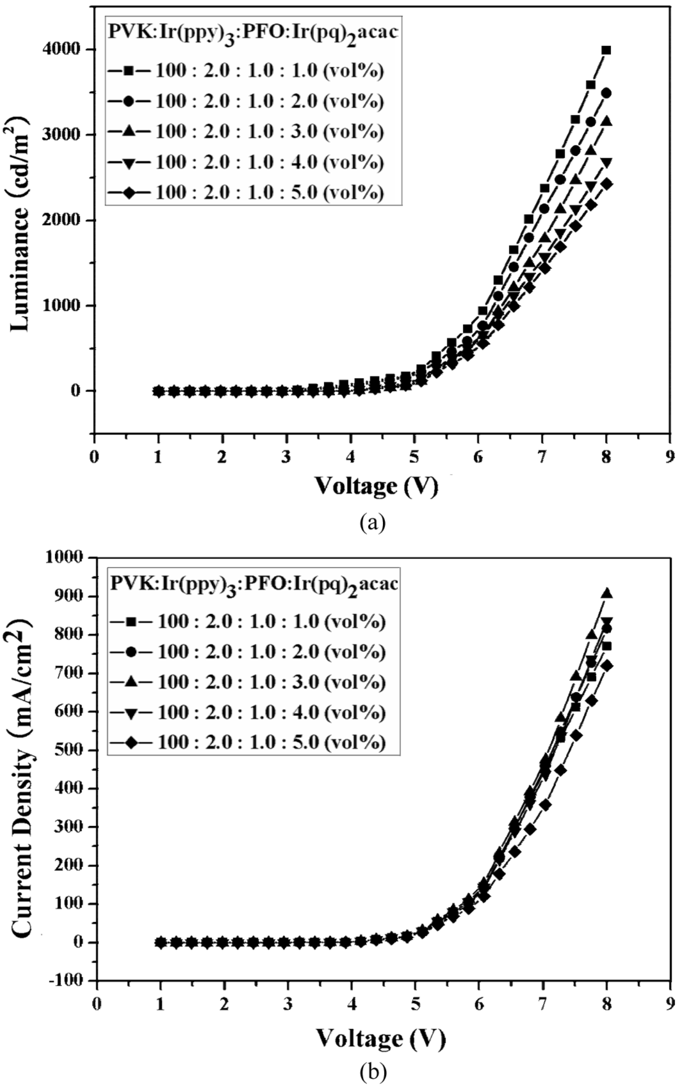

**Figure 6.** (a) The luminance *versus* voltages (L-V) and (b) the current density *versus* voltage (J-V) curves for the PhPLEDs at various Ir(pq)$_2$acac concentrations in the emission layer.

Figure 7 shows (a) the emission spectra and (b) CIE color coordinates as a function of the input voltage for the white PhPLEDs with an Ir(pq)$_2$acac concentration of 5.0 vol%. The concentration ratio of PVK:Ir(ppy)$_3$:PFO: Ir(pq)$_2$acac was fixed at 100:2.0:1.0:5.0 vol%.

The emission spectra and color coordinates varied with the input voltage, which may be ascribed to the phase separation of the mixed host and guest materials at different input voltages [15]. The emission color changed from yellowish white (x,y = 0.39, 0.38) to bluish white (x,y = 0.28, 0.31) as the input voltage was increased from 5 to 9 V.

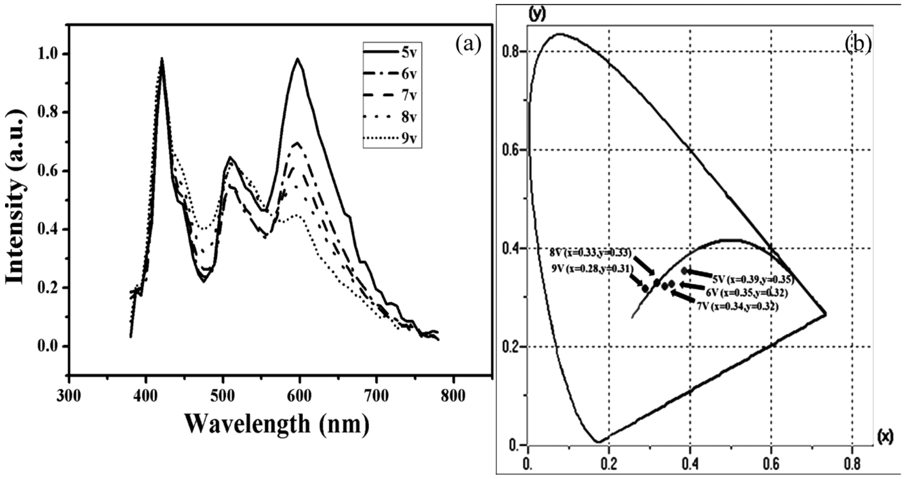

**Figure 7.** (a) The emission spectrum and (b) the CIE color chart of the PhPLEDs with 5.0 vol% $Ir(pq)_2acac$ as a function of the input voltage.

### *Conclusions*

Phosphorescence polymer light emitting diodes (PhPLED) with the structure of ITO/PEDOT:PSS/PVK:$Ir(ppy)_3$:PFO:$Ir(pq)_2acac$/TPBI/LiF/Al were fabricated and the effects of the concentration of $Ir(pq)_2acac$ red phosphorescent dopant and the introduction of a hole blocking layer (HBL) on the optical and electrical properties of the device were investigated. The luminance of the PhPLED was increased by about 13 times (from 610 to 8530 cd/m$^2$) by introducing the TPBI layer between the emission and LiF/Al cathode films. This may be related to the more effective exciton formation in the emission layer (EML) afforded by blocking the diffusion of holes into the cathode film layer. PFO and $Ir(pq)_2acac$ were introduced into the EML as blue and red guest materials for the white emission, respectively. White PhPLEDs with the structure of ITO/PEDOT:PSS/PVK:$Ir(ppy)_3$:PFO:$Ir(pq)_2acac$/LiF/Al were fabricated. The luminance and current density of the white PhPLEDs with an $Ir(pq)_2acac$ concentration of 5.0 vol% were about 2530 cd/m$^2$ and 720 mA/cm$^2$ at 8 V, respectively. Their CIE color coordinates were found to be x, y = 0.33, 0.33, showing a pure white color. The color varied according to the input voltage, which may be due to the phase separation of the mixed host and guest emitting materials.

## Acknowledgments

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