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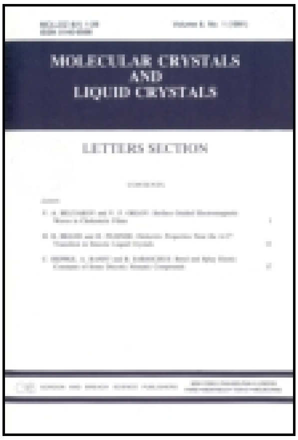

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Fabrication and Characterization of White Phosphorescent Polymer Light Emitting Diodes Using PVK:FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$

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White phosphorescent polymer light emitting diodes (WPhPLEDs) with a glass/ITO/PEDOT:PSS/PVK:FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$/TPBI/LiF/Al structure were fabricated to investigate the effects of the doping concentration of Ir(piq)$_3$ emission materials. The PVK, FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$ organic materials as the host and guest emission materials were spin coated at various concentrations of Ir(piq)$_3$ ranging from 0.1 to 0.4 wt%. With increasing the concentration of Ir(piq)$_3$ from 0.1 to 0.3 wt%, the luminance was increased clearly. However, the luminance was decreased by 6400 cd/m^2 when the Ir(piq)$_3$ doping concentration reached 0.4 wt%. The drop in luminance is caused by the quenching effect at a high doping concentration. The maximum luminance and current efficiency were 9486 cd/m^2 and 2.23 cd/A, respectively for WPhPLED with 0.3 wt% of Ir(piq)$_3$. The average CIE color coordinates for the WPhPLED with 0.2 wt% of Ir(piq)$_3$ were about (x=0.32, y=0.33) at 12V, showing a good white emission color.

Keywords CIE color coordinate; FCNIrpic; Ir(mppy)$_3$; Ir(piq)$_3$; phosphorescent; white polymer light emitting diode

Introduction

Organic light emitting materials and processing techniques have much attention for developing high efficient organic light emitting diodes (OLEDs) because of their promising applications in the next-generation displays and lighting sources. Recently, white polymer LEDs (WPLEDs) have been considered to be the next generation large and flexible lighting sources since they have advantages of inexpensive solution processes, such as spin coating, ink-jet printing, spray coating and roll to roll process [1–4]. However, WPLEDs have some drawbacks for the commercial applications due to a low light efficiency of the device. In addition, WPLEDs have usually exhibited lower efficiencies compared with multilayer white OLEDs with low molecular organic materials. Generally, the admitted internal quantum efficiency (QE) of the fluorescent and phosphorescent materials was limited to 25% and 75%, respectively, which leads to singlet (S1) and triplet (T1) excited stats. As a consequence, the host-dopant energy transfer system using phosphorescent materials can get a 100% in external QE theoretically. Therefore, this experimental was attempted to improve

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*Address correspondence to Prof. Ho Jung Chang, Department of Electronics Engineering, Dankook University, San 29, Anseo-dong, Dongnam-gu, Cheonan-si, Chungnam 330-714, Korea (ROK). Tel.: (+82)41-550-3569; Fax: (+82)41-550-3589. E-mail: hjchang@dankook.ac.kr the light efficiency of white phosphorescent PLEDs (WPhPLEDs) using phosphorescent organic materials. The single host blended system in WPLEDs shows lower efficiency and brightness compared with the host and guest compound system [5]. The performance of a WPLED is controlled mainly by the optimization of the organic materials and the device structure as well as by the surface modification of the film layers. The white light emissions can be basically realized by a sequential deposition in order to form a multi-layer device, in which each layer gives a single color emission of red, green and blue light. In the previous work, we reported the white PLEDs with an emission layer containing of orange-blue polymer materials [6]. In this work, we focused on the single white emission layer using red-green-blue blending phosphorescent iridium complexes within host. In spite of their simple structure and straightforward solution process, the prepared devices showed good color purity and improved current efficiency considerably.

For this, we prepared phosphorescent blended single layer WPhPLEDs with glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/poly(N-vinylcarbazole) (PVK):bis((3,5-difluoro-4-cyanophenyl)pyridine)iridium picolinate (FCNIrpic):Tris(2-(p-tolyl)pyridine) iridium(III) (Ir(mppy)$_3$):Tris(1-phenylisoquinoline) iridium(III) (Ir(piq)$_3$)/(1,3,5-tris(2-N-phenylbenzimida zolyl) benzene) (TPBI)/lithium fluoride (LiF)/aluminum (Al) structures. The optical and electrical properties of the devices at various concentrations of the Ir(piq)$_3$ in the PVK:FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$ emission layer were investigated.

Experimental

Patterned ITO/glass substrates of the size 1 × 1 inch square were used as substrates to prepare WPhPLEDs with glass/ITO/PEDOT:PSS/PVK:FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$/TPBI/LiF/Al structure. The substrates were cleaned with acetone, isopropyl alcohol (IPA), and deionized water in the ultrasonic bath. The remaining solvent was removed by soft baking for 10 min at 100°C. The PEDOT:PSS was used for the hole transport layer [7]. The PVK [8, 9] as the host material and FCNIrpic [10], Ir(mppy)$_3$ [11, 12], Ir(piq)$_3$ [13, 14] phosphorescent materials as the guest materials were introduced into the white emission layer. The emission layer of the WPhPLED was fabricated by blending various concentrations of Ir(piq)$_3$ into the PVK host and FCNIrpic, Ir(mppy)$_3$ guest materials with fixed concentrations of PVK:FCNIrpic:Ir(mppy)$_3$ = 100:1.5:0.1 wt%. The starting PVK, FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$ organic materials were dissolved with 1.0 wt% with monochlorobenzene, separately for the precursor solutions. Following this, the prepared solution of PVK, FCNIrpic and Ir(mppy)$_3$ was mixed with the Ir(piq)$_3$ guest materials in different concentrations ranging from 0.1 to 0.4 wt%. The PVK, FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$ mixed solution was spin coated onto the PEDOT:PSS/ITO/glass substrate at a rotation speed of 5000 rpm for 30 sec. To improve the quantum efficiency through effective hole blocking from the emission layer, the TPBI was thermally evaporated onto the emission film layer. The LiF and aluminum cathode electrode (LiF/Al) were deposited by thermal evaporation in a vacuum chamber with a base pressure of 5×10^{-7} Torr.

Figure 1 shows (a) the energy band diagram and (b) the chemical structures of consisting organic materials for the WPhPLEDs. The electrical properties of the devices were investigated using a POLARONIX M6100 I-L-V test system. The absorption spectra of the host and guest materials were measured by ultra violet (UV)-visible and a photoluminescence (PL) spectrometer. The morphology and roughness of the emission film layers were analyzed by atomic force microscopy (AFM). The measurements of the optical properties, such as luminance, emission spectrum, and Commission Internationale de I'Eclairage

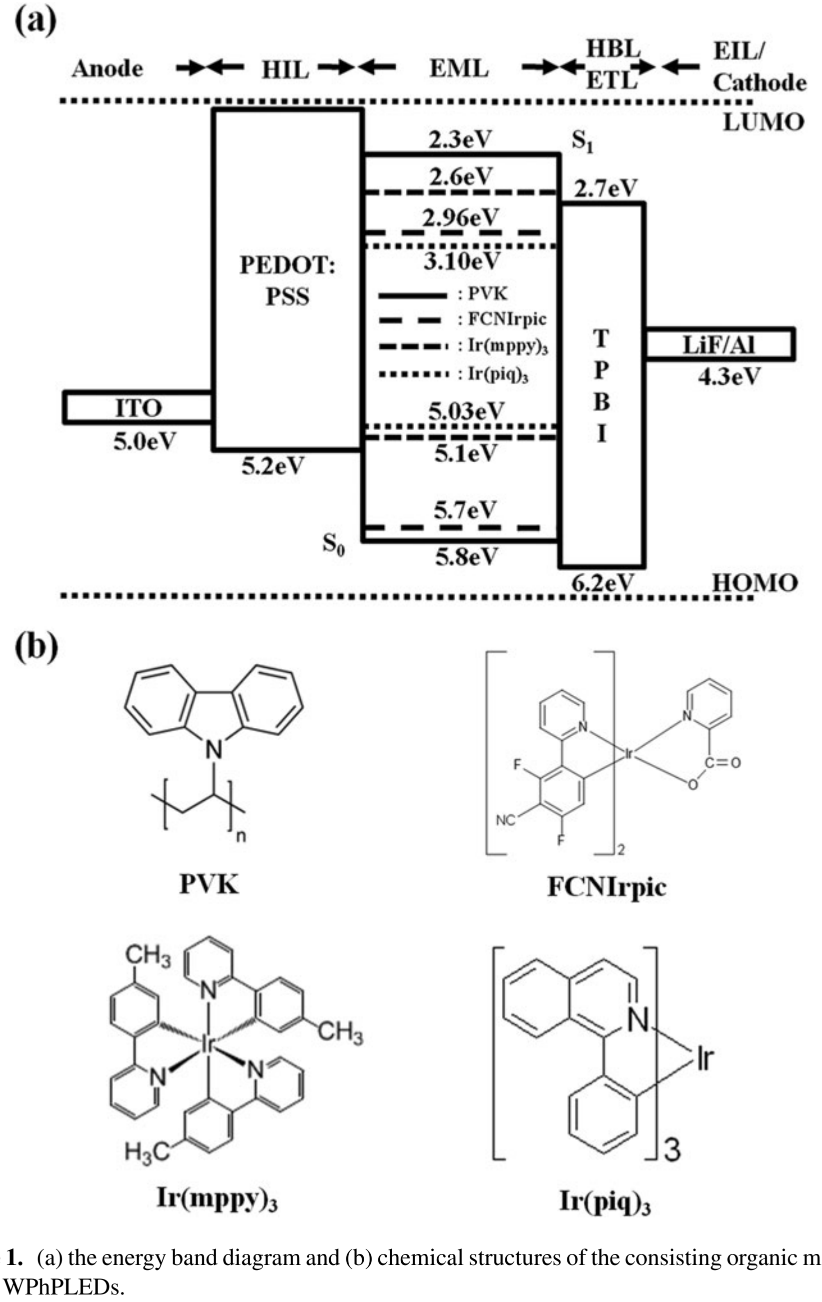

Figure 1. (a) the energy band diagram and (b) chemical structures of the consisting organic materials for the WPhPLEDs.

(CIE) color coordinates were measured and evaluated using a CS-1000 spectro-radiometer in a dark room.

Results and Discussion

As shown in the energy band diagram of Fig. 1(a), the energy band gap (S1 and S0 energy states) in PVK host is larger than those of FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$ phosphorescent

Table 1. Energy levels of the phosphorescent light emission materials.

Host or Guest materials	HOMO [eV]	LUMO [eV]	E_T* [eV]	Ref.
PVK	5.8	2.3	3.0	8, 9
FCNIrpic	5.7	2.96	2.74	10
$Ir(mppy)_3$	5.1	2.6	2.4	11, 12
$Ir(piq)_3$	5.03	3.10	2.0	13, 14

*E_T : triplet energy level

guests, which emit red, green and blue colors, respectively, by means of the energy transition from the PVK host to the guest materials. To improve the efficiency of the energy transfer, it is desirable to broaden the spectra overlap between the host and guest materials in the UV-visible and PL spectrum measurement. Therefore, in order to investigate the spectral overlap between the host and the guest materials, the absorption and emission spectra of the consisting materials such as PVK, FCNIrpic, $Ir(mppy)_3$ and $Ir(piq)_3$ were measured [15]. Triplet energy levels of PVK, FCNIrpic, $Ir(mppy)_3$ and $Ir(piq)_3$ are 3.0 eV, 2.74 eV, 2.4 eV, and 2.0 eV, respectively, as shown in Table 1. Generally, the host should have higher triplet energy than the guest materials. The PVK has higher triplet energy than FCNIrpic, $Ir(mppy)_3$ and $Ir(piq)_3$ guest materials so that the triplet energy can be effectively transferred from the host to the guest material.

Figure 2 shows the normalized PL spectrum of PVK host, and the absorption spectra of the FCNIrpic, $Ir(mppy)_3$ and $Ir(piq)_3$ guest materials. The absorption spectrum of FCNIrpic showed relatively good overlap with the emission PL of PVK host at a wavelength of around 390 nm. In the same way, the absorption spectrum of $Ir(mppy)_3$ and $Ir(piq)_3$ showed also

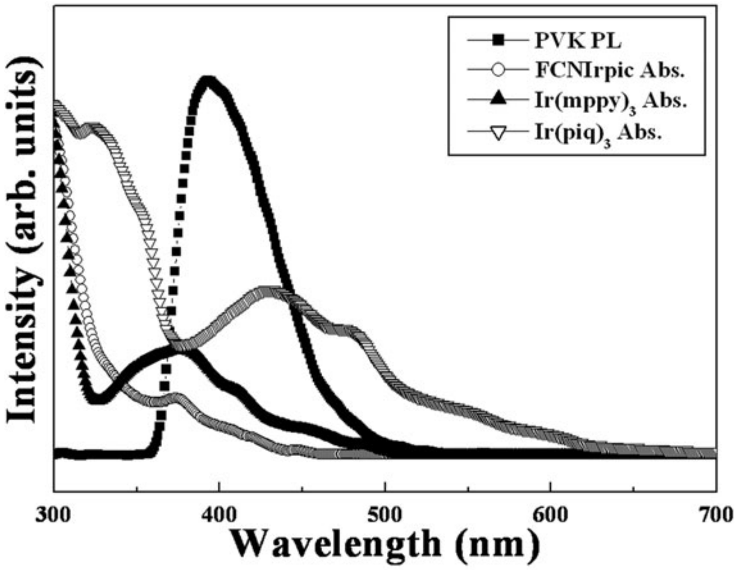

Figure 2. Photoluminescence spectra of the PVK host and UV-visible absorption of the FCNIrpic, $Ir(mppy)_3$ and $Ir(piq)_3$ guest materials.

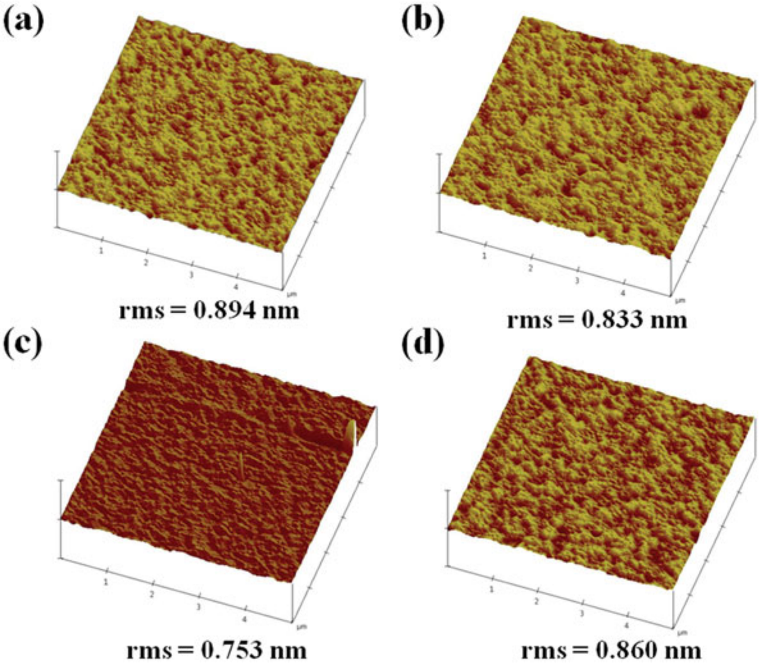

Figure 3. AFM surface images of the PVK:FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$ emission film layer at various Ir(piq)$_3$ concentrations: (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4 wt%.

excellent overlap with the emission PL of PVK, suggesting highly effective energy transfer from the PVK host to the FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$ guest materials. Considering the results of each PL spectrum of the emission materials, it may be concluded that the WPhPLEDs with the single emission layer using PVK, FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$

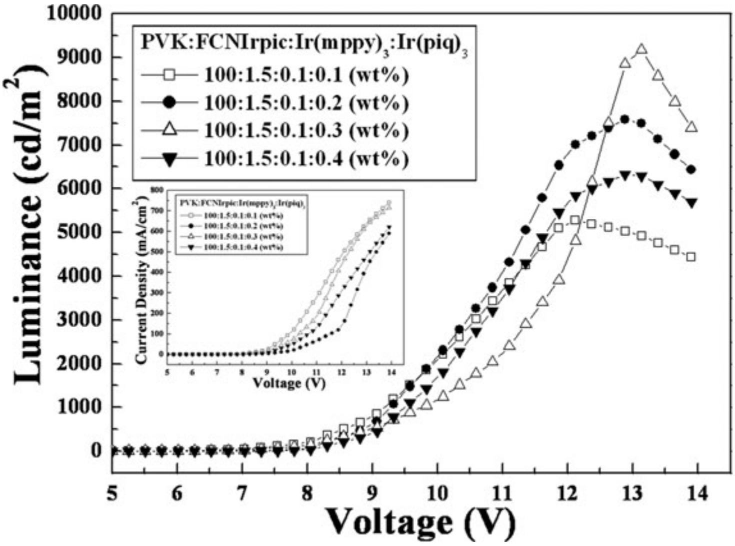

Figure 4. Luminance *versus* voltage (L-V) curves for the WPhPLEDs at various Ir(piq)$_3$ doping concentrations.

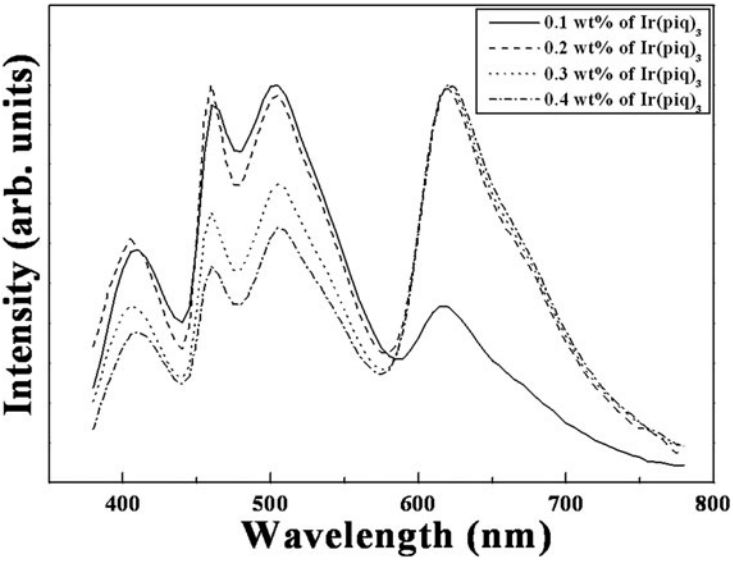

Figure 5. Electroluminescence spectra of the WPhPLEDs at different Ir(piq)$_3$ doping concentrations.

phosphorescent materials can lead an effective energy transfer in the emission layer which contribute to improve the light efficiency. It is generally explained that the light efficiency can be improved by the increments of the energy transfer speed coefficient, $k_{H^{*}\text{->}G}$ from the Dexter energy transfer equation [16].

Figure 3 shows the surface morphologies and the root-mean-square (rms) values of the PVK: FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$ film layer at various Ir(piq)$_3$ concentrations. The

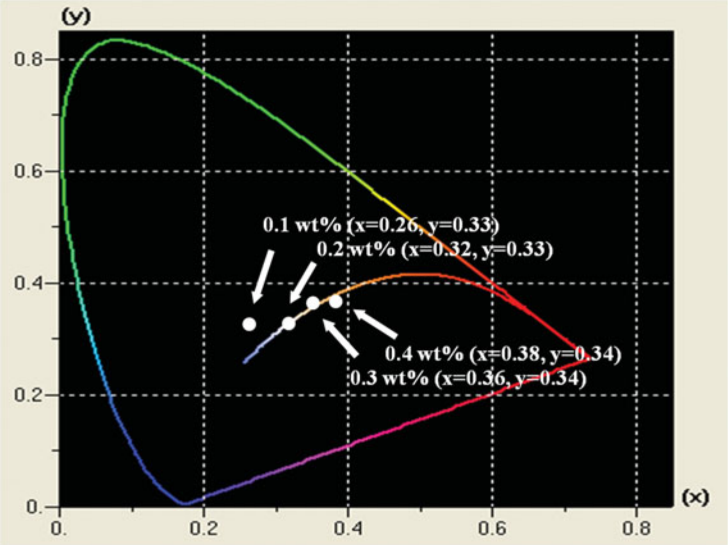

Figure 6. CIE color chart of the WPhPLED devices using PVK:FCNIrpic:Ir(mppy)$_3$:Ir(piq)$_3$ emission film layer.

Table 2. The characteristics of the WPhPLEDs at various Ir(piq)$_3$ concentrations.

Ir(piq)$_3$ Concentration (wt%)	Max. Luminance at Voltage (cd/m^2)	Current Density at Max. Lumi. (mA/cm^2)	Current Efficiency at Max. Lumi. (cd/A)	Power Efficiency at Max. Lumi. (lm/W)	CIE Color Coordinator (x, y)
0.1	5314 at 12V	424	1.25	0.32	0.26, 0.33
0.2	7674 at 13V	429	1.78	0.43	0.32, 0.33
0.3	9486 at 13V	425	2.23	0.53	0.36, 0.34
0.4	6400 at 13V	443	1.44	0.34	0.38, 0.34

rms value decreased from 0.894 to 0.753 nm with increasing the Ir(piq)$_3$ concentrations from 0.1 to 0.3 wt%, suggesting that the film layer showed a smooth film surface when the solution of the emission materials was spin coated at higher doping concentrations. It would be expected that a smooth roughness of the emission layer may result in an increase of the luminance of the devices.

Figure 4 shows the luminance values as a function of input voltages (L-V) for the WPhPLEDs at different Ir(piq)$_3$ concentrations. It was observed clearly that the luminance was increased from 5314 to 9486 cd/m^2 as the Ir(piq)$_3$ concentration increased from 0.1 to 0.3 wt%. The increased luminance at high guest concentration may be related to an intermolecular distance between PVK, FCNIrpic, Ir(mppy)$_3$ and Ir(piq)$_3$ molecules as reported in the Dexter equation [16]. In addition, the smooth roughness of the emission layer may also lead to an increased luminance, as shown in AFM measurements. However, the luminance was decreased by 6400 cd/m^2 when the Ir(piq)$_3$ doping concentration reached 0.4 wt%. The drop in the luminance is caused by the accelerated self quenching effect at higher doping concentration of guest material, which leads to decay the carrier recombination, as reported by Lamansky, S. *et al.* [17].

Figure 5 shows the electroluminescence (EL) spectra of the WPhPLEDs as a function of wavelength at different Ir(piq)$_3$ concentrations. Four intense peaks of WPhPLEDs were observed at the wavelength of around 410 nm, 460 nm, 505 nm, and 620 nm, respectively, showing a good white emission color. The maximum intensity of EL spectrum was shown for the prepared WPhPLED sample with the concentration of 0.2 wt% Ir(piq)$_3$.

Figure 6 shows the CIE color coordinators of the prepared WPhPLEDs at various Ir(piq)$_3$ concentrations. The CIE color coordinates for the WPhPLEDs with 0.2 wt% of Ir(piq)$_3$ was found to be (x=0.32, y=0.33) at 12V, showing a good white emission color. In addition, the emission colors of prepared devices are close to the ideal CIE color coordinate of a pure white color.

The maximum luminance, current density, current efficiency, power efficiency and CIE color coordinates as a function of Ir(piq)$_3$ concentrations for the WPhPLEDs are summarized in Table 2.

Conclusions

The PVK, FCNIrpic, Ir(mppy)$_3$, and Ir(piq)$_3$ as the host and guest emission materials were spin coated onto PEDOT:PSS/ITO/glass substrates for the fabrication of white phosphorescent polymer light emitting diodes (WPhPLEDs). We investigated the dependence of Ir(piq)$_3$ doping concentrations on the optical and electrical properties of the WPhPLEDs. The Ir(piq)$_3$ phosphorescent guest material was doped with ranging from 0.1 to 0.4 wt% into a fixed host and guest materials with the concentration of PVK:FCNIrpic:Ir(mppy)$_3$ = 100:1.5:0.1 wt%. The maximum luminance and current efficiency were 9486 cd/m^2 and 2.23 cd/A, respectively for WPhPLED with 0.3 wt% of Ir(piq)$_3$. From AFM measurement, the rms value decreased as the Ir(piq)$_3$ concentration increased from 0.1 to 0.3 wt%, indicating a smooth film surface at the higher doping concentrations. However, the luminance was decreased sharply when the Ir(piq)$_3$ doping concentration reached 0.4 wt%. The drop in the luminance may be caused by the self quenching and a rough film surface at highest doping concentration. The CIE color coordinates for the WPhPLED with 0.2 wt% of Ir(piq)$_3$ was about (x=0.32, y=0.33) at 12V, showing a good white color.

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