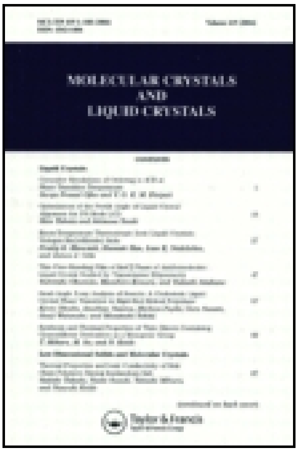

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# Properties of Blue Polymer Light Emitting Diodes According to the Doping Concentrations of FIrpic Phosphorescence

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# Properties of Blue Polymer Light Emitting Diodes According to the Doping Concentrations of FIrpic Phosphorescence

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*PFO [poly(9,9-dioctylfluorene-2-7-diyl) end capped with N,N-Bis(4-methylphenyl)-4-aniline] based blue polymer light emitting diodes (PLEDs) that use a FIrpic [iridium(III) bis[4,6-(difluorophenyl) pyridinato-N,C20 picolinate] phosphorescent dopant as an emission layer were fabricated using a host-dopant system in order to achieve high luminance and efficiency properties. To find the optimum doping concentration, the FIrpic was doped at various concentrations, ranging from 1 to 4 wt%, into the PFO host. Blue phosphorescence PLEDs with the structure of ITO/PEDOT:PSS/PFO:FIrpic/TPBI/LiF/Al were prepared. The electrical and optical properties were investigated and compared in the prepared PLED devices with and without the FIrpic dopant. The luminance and the current efficiency were improved by introducing the FIrpic dopant. For the PLED device with a 2 wt% FIrpic concentration, the maximum luminance and current efficiency was found to be 4128 cd/m$^2$ and 0.92 cd/A, respectively. The CIE color coordinates was (x, y = 0.19, 0.28), exhibiting a sky-blue color.*

**Keywords** Polymer light emitting diode (PLED); energy transfer; host-dopant system; high luminance; blue color

## Introduction

The organic and polymer light emitting diodes (OLED/PLED) have attracted considerable attention for next generation displays and solid-state lighting because of their many advantages, such as a low power consumption, a wide color gamut, and a good viewing angle due to their self-emittance, as well as in thin film and flexible devices. The PLEDs have a great deal of advantages in low cost manufacturing, due to their simple structure and easily soluble processes, such as spin coating [1], ink-jet printing [2], screen printing [3], and the roll-to-roll process [4], compared to the thermal deposited OLED. One of the most important requirements of an OLED/PLED that is needed for displays and lighting is a high luminance and efficiency. The OLED has a demonstrated high efficiency that reaches nearly

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100% of internal quantum efficiency when doped with phosphorescent dopants [5–7]. However the PLED has a problem in overcoming its low luminance and efficiency. Therefore, many researches have been carried out on the PLED in order to achieve higher luminance and efficiencies by using a host-dopant energy transfer system, introducing phosphorescent dopants, such as Ir and Pt heavy metal complexes [8–13]. An energy transfer can occur from the host to the dopant material, and the combined effect of this result in higher electrical and optical properties in the PLED. Generally, the admitted internal quantum efficiency (QE) of the fluorescent and phosphorescent materials was limited to 25% and 75%, respectively, which leads to singlet ($S_1$) and triplet ($T_1$) excited states. As a consequence, the host-dopant energy transfer system using fluorescent and phosphorescent materials leads to a 100% external QE maximum value.

In this work, we fabricated PFO [poly(9,9-dioctylfluorene-2–7-diyl) end capped with N,N-Bis(4-methylphenyl)-4-aniline] based blue PLEDs including a FIrpic [iridium(III) bis[4,6-(difluorophenyl) pyridinato-N,C20 picolinate] phosphorescent dopant with an ITO (150 nm)/PEDOT:PSS[poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)](50 nm)/ PFO:FIrpic(60 nm)/TPBI[2,2′,2′′-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimida-zole)] (30 nm)/LiF(1 nm)/Al (120 nm) structure. The PFO [11,12,14–16] and the FIrpic [11,12,17,18] as a host and dopant for the emission layer (EML) are well known as a blue fluorescence polymer and a blue phosphorescence Ir complex. Therefore, we expected higher electrical and optical properties in PFO based blue PLED devices with the FIrpic dopant using the host-dopant energy transfer system. The electrical and optical properties of PLED devices with and without a FIrpic dopant at various FIrpic concentrations were investigated and compared in order to find the optimum doping concentration.

## Experimental

### *The Fabrication of the Blue PLED*

ITO/glass substrates were cleaned using an ultrasonic precision cleaning process with acetone, methanol, isopropyl alcohol (I.P.A) and de-ionized water. The ITO anode film with an emitting area of 2 mm × 2 mm was patterned by a photolithography method, and the SC-1 process (volume ratio of $H_2O_2$-$NH_2OH$-$H_2O$ = 1:1:5) was carried out in order to remove the organic particles. The plasma treatment done before the coating of the polymer layer films was expected to reduce the energy barrier for an effective hole injection and to improve the adhesion between the ITO and the polymer layer. The $O_2$ plasma treatment on the ITO anode film was at a RF power of 100 watts under an $O_2$ gas pressure of 40 mtorr for 30 seconds. The PEDOT:PSS [Baytron P AI4083] was coated for the hole injection layer (HIL). The PFO fluorescence polymer [ADS 329BE] and the FIrpic phosphorescence [CU BD550] were used as the host and dopant materials in the EML, respectively. The PFO host and the FIrpic dopant were dissolved in toluene and chlorobenzene solvents with a concentration of 1.0 wt%, respectively. The PFO host and FIrpic dopant were then mixed with different concentrations of PFO:FIrpic = 100:1, 100:2, 100:3, and 100:4 wt%. These precursor solutions were coated onto the PEDOT:PSS/ITO/glass substrate using the spin-coating method. The TPBI [LT E302] was deposited onto the EML by thermal evaporation as an electron transport layer (ETL) and a hole blocking layer (HBL). The LiF and aluminum as the electron injection layer (EIL) and the cathode were deposited by the thermal evaporation method in a vacuum chamber with a base pressure of $5 \times 10^{-7}$ torr.

Figure 1 shows (a) the energy band diagram of the prepared PLED devices and (b) the chemical structures of the materials.

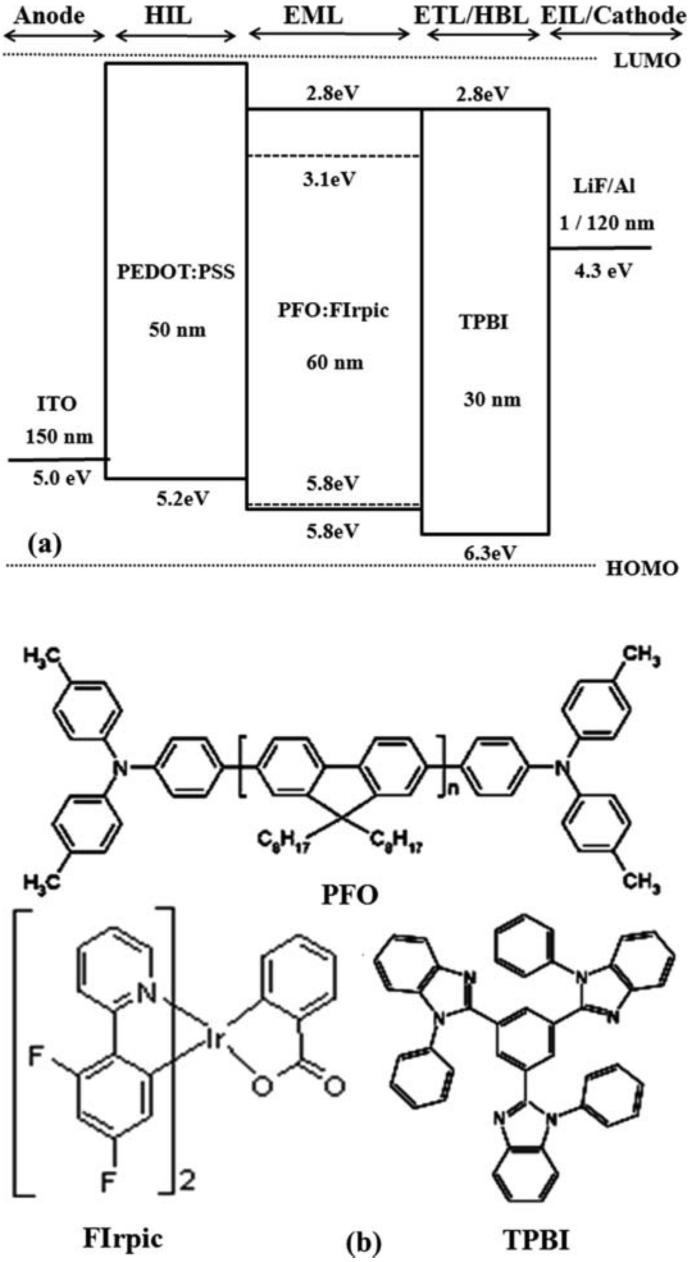

**Figure 1.** (a) The energy band diagram of the prepared PLEDs, and (b) the chemical structures of the materials.

### *The Measurements*

The absorbance and emission spectra of the host and dopant materials were measured by UV-vis and a photoluminescence (PL) spectrometer. The electrical and optical properties were investigated using a POLARONIX M6100 I-L-V measurement system. The emission spectrum and CIE color coordinates were evaluated using a CS-1000 spectro-radiometer (MINOLTA) in a dark room.

## Results and Discussions

In order to improve the electrical and optical properties of blue PLEDs, the host-dopant energy transfer system was introduced into the EML of the PLEDs.

Figure 2 shows the energy transfer mechanism [19] from the PFO host to the FIrpic dopant. The energy transfer from the PFO host to the FIrpic dopant is explained by the Förster and Dexter energy transfer theory. The Förster energy transfer mechanism is accomplished through a dipole-dipole interaction between the transition dipole moments of the host and dopant, and Dexter energy transfer mechanism exchange of electrons from the host to the dopant. The PFO host emitted blue fluorescence by the energy transition from the $S_1$ exited state to the $S_0$ ground state. The FIrpic dopant emitted blue phosphorescence by the energy transition from the $T_1$ exited state to the $S_0$ ground state. The energy transfers from PFO host to FIrpic dopant were as the follows: (i) the singlet($S_1$)-singlet($S_1$) energy transfer from PFO host to FIrpic dopant by Förster and Dexter energy transfer mechanism. (ii) the triplet($T_1$)-triplet($T_1$) energy transfer from PFO host to FIrpic dopant by Dexter energy transfer mechanism.

In order to bring an effective energy transfer, the conditions suggested in the Förster (1) [20] and the Dexter (2) [21] equations must be satisfied. The energy transfer speed coefficient, $k_{H^*\text{->}G}$ can be expressed by (1) and (2).

$$k_{H^*\to G} = \frac{9000K^2 \ln 10}{128\pi^5 n^4 N\tau_0 R^6} \int \frac{f'_H(v)\varepsilon_G(v)dv}{v^4} \tag{1}$$

$$k_{H^*\to G} = \left(\frac{2\pi}{h}\right) K^2 \exp\left(-\frac{2R}{L}\right) \int f'_H(v)\varepsilon_G(v)dv \tag{2}$$

where, $f'_H(v)$ = the PL emission spectrum of the host, $\varepsilon_G(v)$ = the absorption spectrum of the dopant, N = Avogadro's number, n = the refraction index, $\tau_o$ = the radiation lifetime of the host, K = the orientation factor, R = the intermolecular distance between the host and the dopant, and L = effective Bohr radius and is equal to the sum of the van der Waal′s radii of the host and dopant molecules. As a consequence, in order to improve the energy transfer, it is desirable to increase the spectral overlap between the PL emission of the host

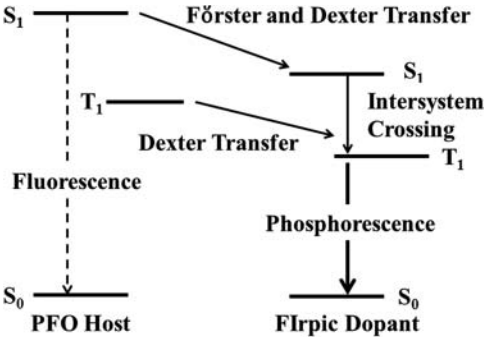

**Figure 2.** The energy transfer mechanism of the PFO host and the FIrpic dopant.

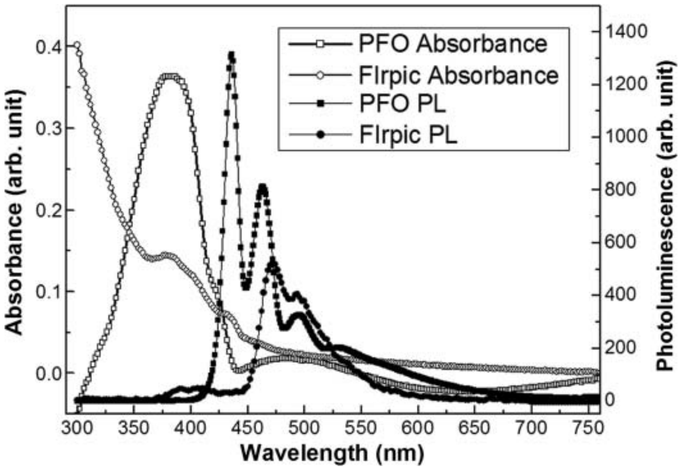

**Figure 3.** The UV-vis absorbance and PL emission spectra of the PFO host and the FIrpic dopant films.

($f_H$ ($v$)) and the absorption of the dopant ($\varepsilon_G(v)$)), as well as to reduce the intermolecular distance (R) between the host and the dopant.

Figure 3 shows the UV-vis absorption and the PL emission spectra of the PFO host and the FIrpic dopant films. The wide spectral overlap between the PL emission of the PFO host and the UV absorption of the FIrpic dopant were clearly observed at a wavelength of around 470 nm, suggesting an effective energy transfer from the host to the dopant. Therefore, we posit that the luminance and efficiency of the blue PLED device with the host and dopant system can be increased by an effective energy transfer, that is, by increased values of $k_{H^* - > G}$ from (1) and (2).

Figure 4 shows (a) the current density and luminance *versus* the voltages (J-V-L) and (b) the correlation of the J-V properties of the blue PLEDs at various FIrpic concentrations. The J-V (open graphs) and L-V (closed graphs) properties of the PLEDs with the FIrpic dopant were higher than the one without the FIrpic dopant. The turn-on voltage ($V_T$, at 10 cd/m$^2$) of the PLED without the FIrpic dopant was measured at 5.2 V and slightly decreased to about 5.0 V in the doped PLEDs. The maximum luminance of PLED without the FIrpic dopant (close squares) was found to be 1274 cd/m$^2$ and increased greatly by introducing the FIrpic dopant into the PFO host. The maximum PLED luminance with the FIrpic dopant was obtained 4128 cd/m$^2$ at 2 wt% concentrations (closed triangle). However, at a 3 wt% concentration of the FIrpic (closed diamond) the luminance started to decrease slightly. At the FIrpic concentration of 4 wt% (closed inverted-triangle), the luminance was greatly decreased to 2218 cd/m$^2$, which is likely attributable to the quenching effect between the host and the dopant molecules at higher doping concentrations [22,23]. From the J-V correlation graph (Fig. 4(b)), the luminance increased more sharply, compared to the ones without the FIrpic dopant, with the increase of the current density up to 480 mA/cm$^2$.

Figure 5 shows the current efficiency as a function of the current density of the blue PLEDs at various FIrpic doping concentrations. The maximum current efficiency was found in the sample with the 2 wt% FIrpic concentration, indicating a 0.92 cd/A. In the case of the sample without the FIrpic dopant, the current efficiency was only 0.29 cd/A. In conclusion, the current efficiency of the PLEDs having a FIrpic dopant was improved

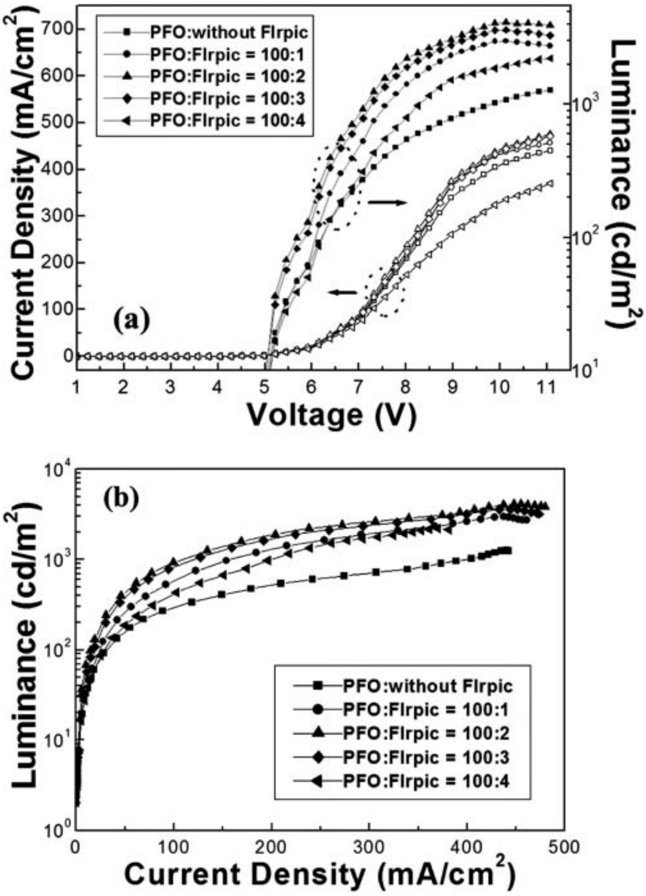

**Figure 4.** (a) The J-L-V properties and (b) the correlation of the J-V properties of the blue PLEDs at various FIrpic doping concentrations.

over 3 times compared with the one without the Firpic dopant. Furthermore, the current efficiency values of the PLEDs with the 2 and 3 wt% of Firpic concentration were almost constant regardless of their current densities, which ranged from 50 to 300 mA/cm$^2$. On the contrary, in the case of the PLEDs without the FIrpic dopant, the current efficiency lineally decreased with the increasing current densities. This result suggests that the PLEDs with the FIrpic phosphorescent dopant have more stability compared to the ones without the FIrpic dopant.

Figure 6 shows the electroluminescence (EL) spectra of the blue PLEDs as a function of wavelength at the various FIrpic concentrations. The EL emission peaks of the PFO host were the 433, 462 and 493 nm wavelengths, and the peaks of the FIrpic dopant were 490 and 518 nm. In all of the prepared blue PLEDs, the main EL peak of the PFO host was found to be 433 nm with the same EL intensity. However, the EL peaks of the PLEDs were changed by introducing the FIrpic dopants into the PFO host, showing higher intensities of the EL peaks at 490 and 518 nm. The EL intensities of the the FIrpic tended to increase as the FIrpic concentration increased, indicating that the maximum intensity occurred for the sample having a 2 wt% FIrpic concentration. These results show that the PLEDs without

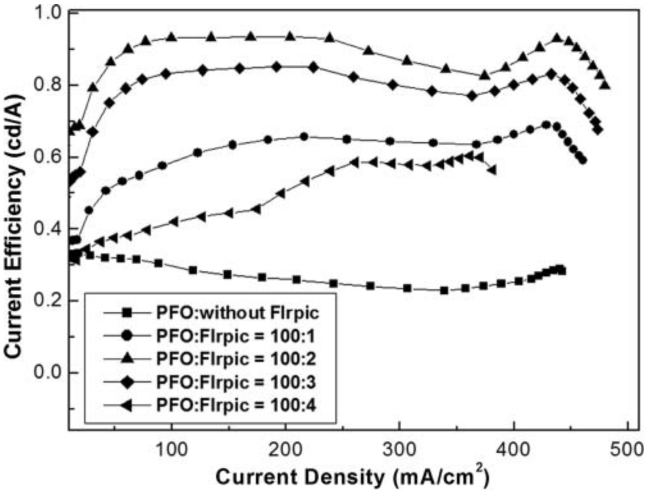

**Figure 5.** The current efficiency *versus* the current density property of the blue PLEDs at various FIrpic doping concentrations.

Firpic dopant had a deep blue color and shifted to a sky blue color when PFO doped by the FIrpic. From the CIE color coordinate chart, we found that the CIE value of the PLED without the FIrpic was (x, y = 0.17, 0.08) and changed to (x, y = 0.19, 0.28) for the sample with the 2 wt% FIrpic concentration. As discussed in reference to Fig. 4, the lowest EL intensity of the PFO host and the FIrpic dopant for the PLED with the 4 wt% FIrpic concentration may be related to the quenching effect at high doping concentrations. Considering these results, it may be concluded that an improvement of luminance and the current efficiency is accomplished by introducing the FIrpic phosphorescent dopant into

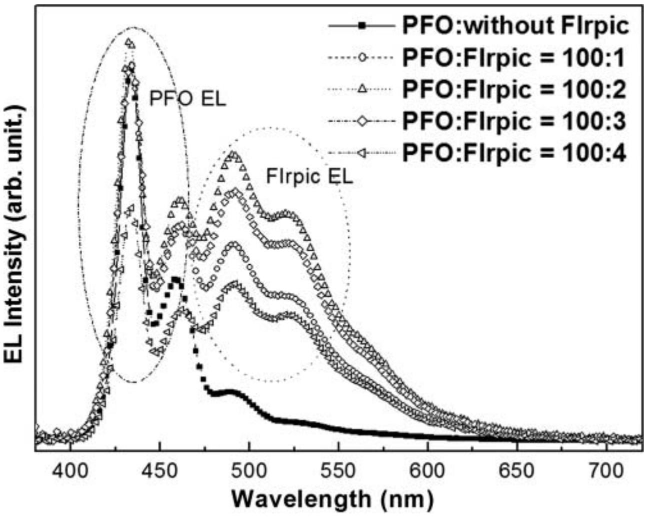

**Figure 6.** The electroluminescence (EL) spectra of the blue PLEDs at various FIrpic doping concentrations.

**Table 1.** The electrical and optical properties of the blue PLEDs at various FIrpic concentrations.

| PFO:Firpic concentrations (wt%) | Max. Luminance at Voltage (cd/m$^2$) | Power Efficiency at Max. Lumi. (lm/W) | Current Efficiency at Max. Lumi. (cd/A) | Turn-on Voltage at 10 cd/m$^2$ (V) | CIE coordinate (x,y) |
|---|---|---|---|---|---|
| Without | 1274 at 11 V | 0.08 | 0.29 | 5.2 | 0.17,0.08 |
| 100:1 | 2992 at 10 V | 0.21 | 0.68 | 5.1 | 0.19,0.23 |
| 100:2 | 4128 at 10 V | 0.29 | 0.92 | 5.0 | 0.19,0.28 |
| 100:3 | 3624 at 10 V | 0.25 | 0.82 | 5.0 | 0.19,0.27 |
| 100:4 | 2218 at 11 V | 0.17 | 0.60 | 5.2 | 0.20,0.28 |

the PFO fluorescent host with an optimal doping concentration. These improved electrical and optical properties must come from an effective energy transfer from host to dopant, and have a large energy transfer speed coefficient ($K_{H^* -> G}$).

The electrical and optical properties of the blue PLEDs at various FIrpic concentrations are summarized in Table 1.

## Conclusions

We fabricated blue polymer light emitting diodes (PLEDs) with a ITO/PEDOT:PSS/PFO:FIrpic/TPBI/LiF/Al structure by using a host-dopant energy transfer system in the emission layer (EML). The PFO fluorescent polymer and the FIrpic phosphorescent iridium complex were used as a host and dopant material, respectively. The blue PLEDs with the FIrpic dopant had better electrical and optical properties compared to the ones without the FIrpic dopant. The maximum luminance and current efficiency of the PLED device with a 2 wt% FIrpic concentration were found to be 4128 cd/m$^2$ and 0.92 cd/A, respectively, which may be ascribed to the energy transfer from the PFO host to the FIrpic dopant. The electroluminescent (EL) peaks of the PLEDs were changed by the introduction of the FIrpic dopants. The EL intensities of the FIrpic dopant (490 and 518 nm) tended to increase with an increase of the doping concentration, and showed the highest EL intensities with the 2 wt% FIrpic concentration, with a color shift from deep blue to sky blue. The improvement of luminance and current efficiency of the PLEDs with the FIrpic phosphorescence may have originated from the effective energy transfer from the host to the dopant, as discussed in the Förster and Dexter equations of the energy transfer speed coefficient. However, at higher FIrpic doping concentrations into the PFO host, all of the EL intensities decreased due to the concentration quenching effect of the FIrpic dopant.

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