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Highly Efficient Red-Emission Polymer Phosphorescent Light-Emitting Diodes Based on Two Novel Tris(1-phenylisoquinolinato-C2,N)iridium(III) Derivatives

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Organic light-emitting diodes (OLEDs) have often been considered one of the important candidates for the next generation of flat-panel displays, because of their emissive capability and fast response time. To enhance the efficiency, phosphorescent dyes have become an attractive research subject in OLEDs because of their ability to boost the internal quantum efficiency to 100%.^[1] Although polymer phosphorescent light-emitting diodes (P-PhoLEDs) have been making progress in achieving high efficiencies, polymeric LEDs (P-LEDs) are lagging behind in this category of technology. Unbalanced electron and hole currents are considered to be one of the main obstacles; these are mainly caused by a lack of fine engineering of the multiple layers by the solution process. Interfacial layers such as LiF between a metal cathode and polymer are commonly used to enhance electron injection, and hence to achieve a better balance between the electron and hole currents. However, the electron-injection enhancement caused by these interfacial materials cannot be precisely controlled, so in most cases the electron and hole currents are not perfectly balanced.

Intensive work has been devoted to high-efficiency green emitting P-PhoLEDs,^[2–6] in which poly(*N*-vinylcarbazole) (PVK) is chosen as the host material for its high triplet energy level, and *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) or tris(2-(4-tolyl)phenylpyridine) iridium (Ir(mppy)₃) is the dopant. By improving its electrical properties and device energy structure, the highest power efficiency of 67 lm W⁻¹ has been realized based on Ir(mppy)₃.^[6] However, there are far fewer reports about red-emission P-PhoLEDs for various reasons. In this manuscript, we report on very high efficiency solution-processed red P-PhoLEDs. Two novel red iridium-based phosphorescence dyes were used as dopants, and a polyfluorene derivative (PF) was used as the host material in this work. Pure-red emission from dopants was obtained at 4–6 wt %

dopant in the host polymer. An electron-injection/hole-blocking layer, Cs₂CO₃, was inserted between the light-emitting polymer (LEP) layer and the Al cathode through thermal deposition. By modulating the thickness of the Cs₂CO₃ layer, the electron injection could be precisely controlled to balance the hole injection. Direct trapping of charge by the dopants, which could be procured by changing the polymer thickness, helped to increase the efficiency of the device. By optimizing the parameters of the devices, peak efficiencies of 16.9 cd A⁻¹ and 17.6 lm W⁻¹ at 220 cd m⁻² were achieved for red-emission P-PhoLEDs. Even at a high brightness of 1000 cd m⁻², our best device still had a very high efficiency of 16 cd A⁻¹ and 13.4 lm W⁻¹. To the best of our knowledge, these are the highest reported efficiencies for red-emission P-PhoLEDs. Most importantly, this technique is universal for achieving high-efficiency P-LEDs, and has been successfully applied in other material systems.

Red-emissive homoleptic cyclometalated iridium complexes were found to have a high efficiency. A PhoLED with an external quantum efficiency of 10.3% and a power efficiency of 8.0 lm W⁻¹ at 100 cd m⁻² has been realized by adopting tris(1-phenylisoquinolinato-C2,N)iridium(III) (Ir(piq)₃) as the emission dopant.^[7] Originally, it was hoped that Ir(piq)₃ could be directly applied as dopant into the polymer host for red emission. Unfortunately it was found that Ir(piq)₃ did not dissolve in many common solvents such as *p*-xylene, chlorobenzene, and toluene. In order to use the cheap solution process for device fabrication, we used two materials, substituted with a long alkyl chain and fluorine, respectively. These substituents increased the solubility remarkably. Figure 1 shows the chemical structures of both compounds.^[8] The highest occupied molecular orbital (HOMO) of these materials was measured by using UV photoelectron spectroscopy (UPS) and the lowest unoccupied molecular orbital (LUMO) was calculated based on the UV-vis absorption spectrum edge and the HOMO. The HOMO/LUMO levels of Ir(C8piq)₃ were derived from other alkyl-substituted Ir complexes (Ir(*R*-piq)₃). All these data are outlined in Table 1. As expected, the electron-donating alkyl substituent decreased the HOMO/LUMO levels, and the HOMO/LUMO levels of the ligand, having the highly electron-withdrawing fluorine substituent, were increased compared to those of Ir(piq)₃. The relative HOMO/LUMO levels of PF and the dopants facilitate the energy transfer from PF to the dopants. Figure 1 shows the photoluminescence (PL) spectra of the two dopants

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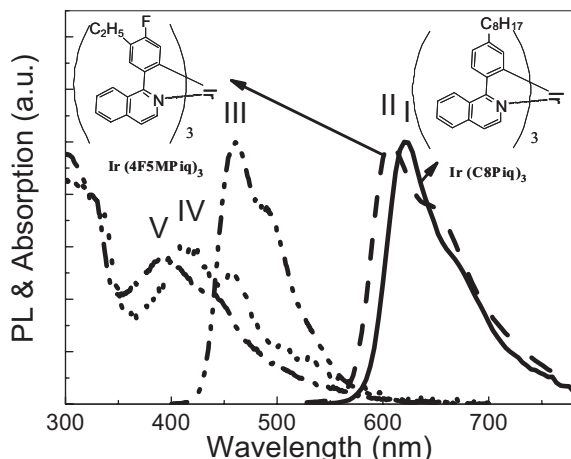


Figure 1 Photoluminescence (PL) spectra of Ir(C8piq)₃ (I), Ir(4F5Mpiq)₃ (II), PF (III), and absorption spectra of Ir(4F5Mpiq)₃ (IV) and Ir(C8piq)₃ (V); Chemical structures of Ir(C8piq)₃ and Ir(4F5Mpiq)₃ are shown in the figure (M = methyl).

Table 1 HOMO/LUMO levels of the dopants used and device performance using these dopants.

	HOMO [eV]	LUMO [eV]	CIE	Luminance efficiency [a] [cd A ⁻¹]	Power efficiency [a] [lm W ⁻¹]
Ir(piq) ₃	5.03	3.10	(0.68,0.32)	NA	10/4.5[b]
Ir(4F5mpiq) ₃	5.24	2.97	(0.65,0.35)	16.9/16	17.6/13.4
Ir(C8piq) ₃	4.9	2.8	(0.67,0.32)	11.2/8.6	11.2/5.4
PF	5.8	2.9			

[a] The former number is the maximum efficiency and the latter number is the efficiency measured at 1000 cd m⁻². [b] Data are obtained from the literature [7].

as well as that of PF. The dopant Ir(C8piq)₃ showed saturated red emission with the PL peak around 621 nm. The dopant with fluorine-substituted ligands, Ir(4F5Mpiq)₃, (M = methyl) still had the red emission but a blue-shifted PL peak around 608 nm, which can be ascribed to the participation of the fluorine, with high electron affinity, in conjugation.

In this work, two approaches were used to achieve high efficiencies: 1) the use of a polymer/dopant blend system as a LEP formed by a solution process, and 2) the balancing of electrons and holes achieved by using an interface modification layer (Cs₂CO₃). The red dopants in the polymer were separated from each other so that the intermolecular reaction (quenching) was diminished, and hence the photoluminescence quantum efficiency of the film was increased tremendously. Also, the red dopants acted as low-energy sites for efficient energy transfer, and moreover, the red dopants behaved as direct charge-trapping centers. When the polymer/dopant blend system was combined with the electron-injection layer (Cs₂CO₃), balanced electron and hole currents could be obtained by tuning the injection ability of the Cs₂CO₃ layer as well as by changing the thickness of the LEP layer. Details of the method can be found in the literature.^[9]

The devices had the following structure: ITO/PEDOT:PSS/LEP/Cs₂CO₃/Al (where ITO is indium tin oxide and PEDOT:PSS is poly(ethylene dioxythiophene):polystyrene sulfonate). In the LEP layer, PF was chosen as the host material, because PF is not only a good light-emission material, but also a good host material because of its large triplet-ground band gap, compatible with these two dopants. Furthermore, it shows good thin-film-forming ability and good electronic properties.^[9–12] Cs₂CO₃ is a good candidate as the interfacial layer between the LEP layer and the cathode, because it helps electron injection and blocks holes.^[9,13] The details of device fabrication can be found in the Experimental section. Two procedures were carried out for each dopant: first, determination of the dopant concentration; and second, optimization of the thickness of the LEP layer and Cs₂CO₃ electron-injection layer. These two procedures are discussed in detail below.

Optimizing the dopant concentration is an important step toward high device performance. If the dopant concentration is too low, the energy transfer from host to dopant is incomplete, and hence the color is not pure; on the other hand, if the dopant concentration is too high, the triplet-triplet annihilation (TTA) effect would reduce the quantum efficiency of the device. Also, high-density charge traps induced by a high dopant concentration would increase the device driving voltage, and hence reduce the power efficiency of devices. Energy transfer from host to dopant can occur via Förster and/or Dexter processes.^[14] In our devices, both processes worked simultaneously. As shown in Figure 1, the overlap between the absorption of the dopants and the emission spectrum of PF was significant, allowing efficient energy transfer from PF to dopants by Förster energy transfer. PL emission from PF could be eliminated at a high dopant concentration of 8–10 wt %, which means that at this concentration complete energy transfer from PF to Ir(C8piq)₃ was achieved. As this concentration of 8–10 wt % is relatively high, Dexter energy transfer is also believed to play an important role. We note that the concentration of dopant needed to eliminate the emission from PF is different in PL from that in electroluminescence (EL) spectra, as shown in Figure 2. EL emission from PF was eliminated at a lower concentration of 4–6 wt %. The direct charge-trapping effect induced by dopants accounts for this phenomenon, which occurs only in devices when injected charges transport through the LEP layer. Dopants can act directly as trapping sites for electrons and holes, and consequently form emission centers. To manifest the trapping effect of the dopants, we fabricated several devices that all have the same parameters except for the dopant concentration. A current density–voltage (*J*–*V*) plot of devices with an LEP of the PF:Ir(4F5Mpiq)₃ blend is shown in Figure 3a. One can see that the device current decreased with increased dopant concentration. However, it is not necessary that the device must have a lower efficiency at higher dopant concentration. The trapping effect from the dopant increased the driving voltage of the devices, and at the same time, increased the quantum efficiency of the devices because of more efficient energy transfer and direct-emission centers were formed

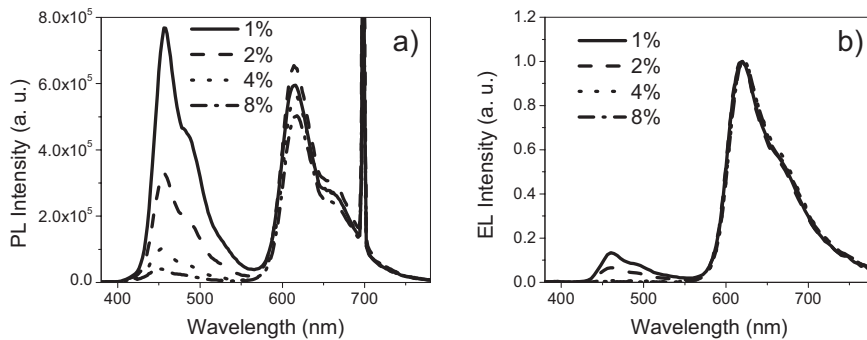


Figure 2 a) PL and b) EL spectra of the PF:Ir(C8piq)₃ blend with different dopant concentrations.

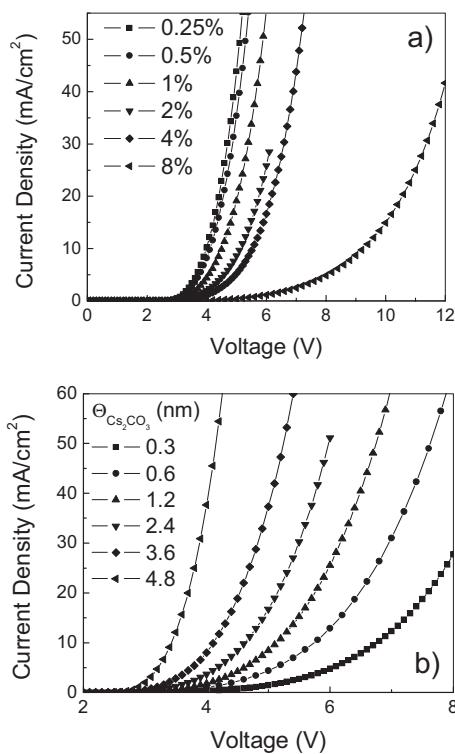


Figure 3 a) *J*–*V* plot for the PF:Ir(4F5Mpiq)₃ blend with different dopant concentrations; b) *J*–*V* plot of devices with different Cs₂CO₃ thicknesses (*θ*) with other conditions kept constant.

by the dopants. Fortunately, the increased driving voltage caused by the trapping effect can be partially compensated by supplying a sufficiently large electron current through efficient injection and transport,^[15] which is related to device-performance optimization.

In order to obtain high device performance, the electron and hole currents should be balanced. One main factor determining the electron current in P-LED devices is the electron-injection ability from the cathode. In this work, electron injection was modulated to increase gradually by controlling the thickness of the Cs₂CO₃ layer. Our X-ray photoelectron spectroscopy (XPS) and UPS studies showed that the work function of the Al cathode could be lowered gradually by increas-

ing the Cs₂CO₃ (thermally deposited) thickness. A very low work function of 2.2 eV was obtained when the thickness of Cs₂CO₃ approached 3–4 nm. A detailed study into this will be published elsewhere.^[13,16] The hole currents of the devices should not change much with the thickness of Cs₂CO₃, because the hole-injection barrier is unchanged. Therefore the perfect current balance point could be found by continuously increasing the electron current. Figure 3b illustrates how the electron currents in the devices could be modulated

continuously by varying the Cs₂CO₃ thicknesses. In these devices, all the parameters were kept the same except for the Cs₂CO₃ thickness. The currents in the devices increased monotonously with Cs₂CO₃ thickness. These increased currents were attributed to the enhanced electron injection from the cathode by Cs₂CO₃. Further evidence for the enhanced injection comes from the evaluation of the Cs₂CO₃/Al cathode by photovoltaic measurement. Similar to the electroabsorption measurement,^[17] photovoltaic measurements can provide information about the work-function shift of the electrode,^[10] particularly when the film is not a donor–acceptor-type composite. In this measurement, the P-LED devices were taken as the photovoltaic devices and the photocurrents were measured when the devices were subjected to simulated solar illumination. In order to exclude the effect of leakage current, the dark current was subtracted from the photocurrent to obtain the modified *J*–*V* curve. The open-circuit voltage (*V*_{oc}) was obtained from the modified *J*–*V* curve when the current was equal to zero. The *V*_{oc} from photovoltaic measurement reflects the built-in potential in P-LED devices. This is defined as the difference in the work function between anode and cathode in the absence of an interfacial dipole. As the parameters of our devices were the same except for the thickness of Cs₂CO₃, the dipole configuration at the interface, if one exists, was also the same for all devices. Hence the shift of *V*_{oc} must correspond to the change of the cathode work function. Figure 4 shows the relationship of measured *V*_{oc} to the thickness of the Cs₂CO₃ layer. As seen from Figure 4, *V*_{oc} increased as the thickness of the Cs₂CO₃ increased, until *V*_{oc} saturated with a rather thick Cs₂CO₃ layer. As mentioned above, the higher *V*_{oc} indicates essentially the lower work function of the Cs₂CO₃/Al cathode. The diagram is shown in the inset of Figure 4. This is direct evidence that evaporated Cs₂CO₃ can reduce the work function of Al and hence increase electron injection. The detailed study of the Cs₂CO₃/Al cathode mechanism will be published elsewhere.^[13]

As mentioned previously, direct trapping of charge on dopants plays an important role in increasing the efficiency of devices. The probability of charge being trapped by the dopant in the LEP layer is related to the thickness of this layer. In our experiment, the thickness of the LEP was varied from 90 to 150 nm by changing the spin rate of the polymer film. The

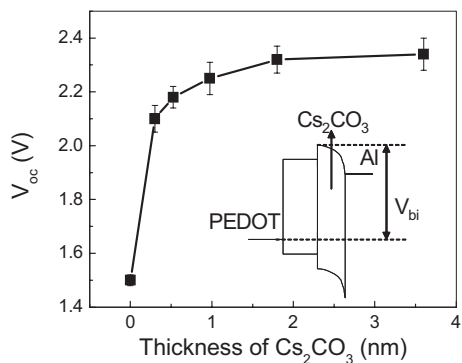


Figure 4 Open-circuit voltage of devices with different Cs_2CO_3 thicknesses with other conditions kept constant.

thickness of Cs_2CO_3 was varied gradually from 0.3 to 4.8 nm. These two parameters were changed independently to search for the optimized condition for each dopant, and also to determine the variation rules. Here the devices using dopants $\text{Ir}(4\text{F5Mpiq})_3$ were adopted for demonstration. Figure 5 shows the maximum luminance efficiency and power efficiency of devices using the dopant $\text{Ir}(4\text{F5Mpiq})_3$ with different LEP and Cs_2CO_3 thicknesses. The data can be understood if we keep in mind that the luminance efficiency is a characteristic of the extent of the balance between the electron and hole currents. As there is a large barrier for hole injection from PEDOT:PSS to PF (0.6–0.8 eV), the hole current in our devices was injection-limited. However, holes are still believed to be the majority carriers in devices with weak electron injection

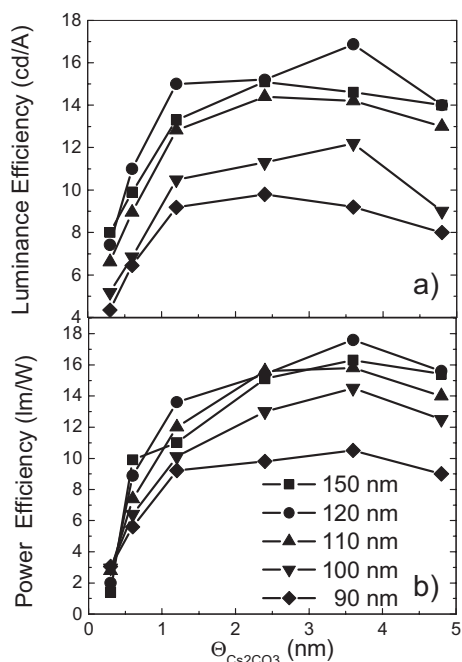


Figure 5 a) Maximum luminance efficiency and b) maximum power efficiency at different LEP and Cs_2CO_3 thicknesses.

tion because electrons sustain a severe trapping effect in PF.^[16,18] Cs_2CO_3 can facilitate the injection of electrons from the cathode to the LEP layer, and the injection ability kept increasing with increased Cs_2CO_3 thickness in the range of 0–4.8 nm (the driving voltages kept dropping with increased Cs_2CO_3 thickness).^[13] As observed from Figure 5, there were three stages for the change of luminance (power) efficiency with respect to thickness of Cs_2CO_3 : Firstly, when the thickness of Cs_2CO_3 was low (0.3–0.6 nm), the electron-injection ability was weak. Excess hole current results in the low luminance efficiency at this stage. The power efficiencies were quite low because of the high driving voltages and low luminance efficiencies. Secondly, when the thickness of Cs_2CO_3 was higher (1.2–3.6 nm), the electron-injection ability became much stronger. The best charge balance was achieved at this stage and luminance efficiencies reached their maximum. The maximum power efficiency predominately occurred when the Cs_2CO_3 thickness was 3.6 nm for all LEP thicknesses, because of the lower driving voltage at higher Cs_2CO_3 thickness; when the thickness of Cs_2CO_3 was increased (4.8 nm), both luminance efficiencies and power efficiencies dropped, because of excess electron injection. It should be mentioned that weak emission from PF appeared when the LEP was thin (80–100 nm), whereas it was completely eliminated from thick LEP devices. This can be explained by the trapping effect of the dopants: a thicker LEP layer provides more opportunity for the trapping of charge when charges are transported through this layer. Also the stronger trapping effect with a thicker LEP layer can explain the higher efficiency at higher LEP thickness.

Finally, Table 1 summarizes the best device performance using the two dopants. The highest efficiencies of 16.9 cd A^{-1} and 17.6 lm W^{-1} at 220 cd m^{-2} were obtained using the dopant $\text{Ir}(4\text{F5Mpiq})_3$ with red emission, and the highest efficiencies of 11.2 cd A^{-1} and 11.2 lm W^{-1} were obtained for saturated red emission using the dopant $\text{Ir}(\text{C8piq})_3$. It should be mentioned that the efficiencies of our devices dropped slowly with increasing brightness, and still have high efficiencies of 16.0 cd A^{-1} and 13.4 lm W^{-1} at a high brightness of 1000 cd m^{-2} , also shown in Table 1. To our knowledge, these are the highest reported efficiencies for red-emission P-Pho-LEDs.

The maximum external quantum efficiencies of our devices were calculated according to their spectra and luminance efficiencies, and we calculate 13.9% for $\text{Ir}(4\text{F5Mpiq})_3$ devices and 11% for the $\text{Ir}(\text{C8piq})_3$ based devices. As the perfect balanced current was achieved in our experiment by gradually adjusting the electron-injection current, we do not expect a further increase in the internal quantum efficiency of these devices based on the same device configuration and the same material impurity grade. However we do believe the power efficiency can be further improved by reducing the driving voltage of the devices through inserting a proper hole-injection/electron-blocking layer between the PEDOT:PSS and the LEP. From the data above we know that the power efficiency of the device begins to drop at high Cs_2CO_3 thicknesses be-

cause of the excess electron injection, despite the reduced driving voltage, as there is still a large hole injection barrier. So the hole-injection/electron-blocking layer could not only increase the hole injection, but also block the excess electrons, while further increasing the Cs_2CO_3 thickness. Further investigation is currently being carried out.

Experimental

For the device fabrication, the ITO substrates first underwent a routine cleaning procedure, which included sonication in detergent followed by repeated rinsing in deionized water, acetone, and isopropyl alcohol, and finally treatment with UV ozone. PEDOT:PSS (Barron-P 4083) was first spun-cast onto an ITO/glass substrate at a spin speed of 4000 rpm, which corresponds to a thickness of 25 nm, and baked at 150 °C for 20 min before spin-casting the polymer film. For the polymer:dopant mixture solution preparation, PF, and the dopants were first dissolved in p-xylene separately, and then mixed together by ratio. The thickness of the LEP, measured by using an Alphastep profilometer, was changed by varying the spinning rate. The spin-coated films were baked at 70 °C for 30 min before being transferred into the evaporation chamber. All these processes after PEDOT:PSS spin-coating were carried out in glove-boxes. The cathode of the polymer LED was formed by the thermal evaporation of Cs_2CO_3 and Al from tungsten boats at a pressure of around 3×10^{-6} torr (1 torr = 133.322 Pa). The diode area was 12 mm².

For the device and film characterization, PL spectra were obtained from a Jobin Yvon Spex Fluorolog-3 double-grating spectrofluorometer. EL and the Commission International de L'Eclairage (CIE) coordinators were obtained from Spectra-scan PR 650. All devices were tested under a nitrogen environment.

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