



## Highly efficient solution-processed red organic light-emitting diodes with long-side-chained triplet emitter

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### ARTICLE INFO

#### Article history:

Received 30 August 2010

Received in revised form 2 November 2010

Accepted 11 November 2010

Available online 13 December 2010

#### Keywords:

Polymer light-emitting diodes  
Ir complexes

### ABSTRACT

Newly synthesized red Ir complexes tris[2-(4-n-hexyl-phenyl)quinoline]iridium(III) and tris[(4-n-hexylphenyl)isoquinoline]iridium(III) with long alkyl side chains are utilized to demonstrate the high efficiency multi-layer solution-processed red organic light-emitting diodes. Solubilities of these triplet emitters are high which enable them to be uniformly dispersed in the polymer host. Blade coating method is utilized to prepare organic multi-layers without mutual dissolution between different layers. 17 cd/A current efficiency, 10 lm/W power efficiency, and 8.8% external quantum efficiency can be achieved for the device with CsF/Al cathode. 10,000 cd/m<sup>2</sup> is reached at 10 V. Similar quantum efficiency is also achieved with an electron-transport layer and LiF/Al cathode.

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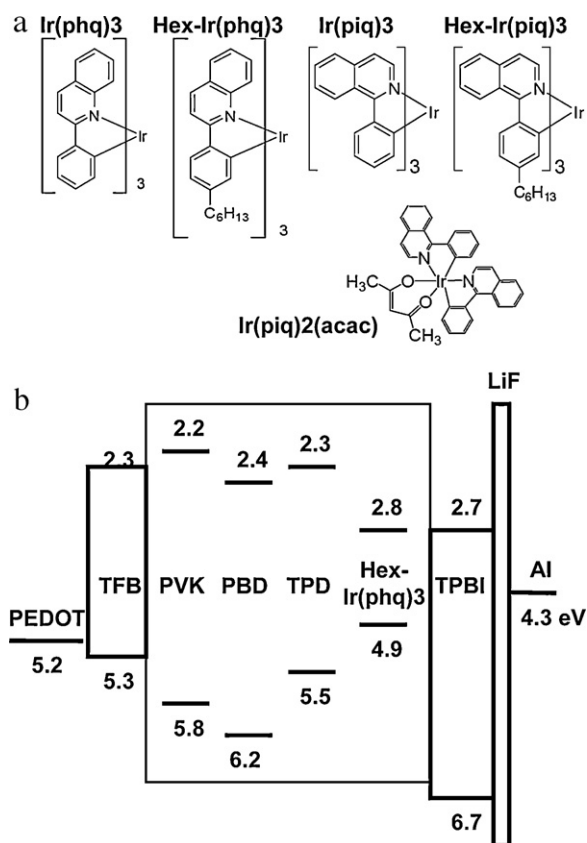
Organic light-emitting diode (OLED) is an emerging technology for lighting and display. There are two processing paradigms for the organic semiconductors: vacuum deposition and solution deposition. So far vacuum deposition gives superior efficiency and dominate the initial industrial applications. Among the three primary colors, the gap between the performances of vacuum-processed and solution-processed OLED is the greatest for red emission. High-efficiency OLED is mostly based on phosphorescence with a metal-organic complex as the triplet emitter in a organic host. For vacuum-processed OLED 10% of external quantum efficiency (EQE) was achieved for Ir complex [1,2]. Recently it was raised to 15% by increasing the emitter concentration in the host [3]. The high efficiency vacuum process has intrinsically high cost and is considered impractical for large-area lighting applications. Solution-processing for high-performance red OLED is therefore highly desired. There are reports on the combined paradigm with solution-processed emissive layer and vacuum processed electron-transport layer. The polymer poly(vinylcarbazole) (PVK) blended with the electron-transport small molecule 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) were used as the host for the triplet emitter while the small molecule 1,3,5-tris(N-phenylbenzimidazol-2-yl) benzene (TPBI) was vacuum deposited as the electron transport layer [4–6]. External quantum efficiency

up to 8% was reached. Devices with Ir complex as both the host and the guest were also reported [7]. For such combined strategy the process cost is still limited by the vacuum deposition of the electron transport layer. Several approaches for all-solution processed red OLED were reported. Ir complex is grafted into a polymer chain and resulted in EQE of 3% [8]. Multi-layer solution-processed OLED using cross-linked hole-transport layer gives EQE of 7.4% [9]. The driving voltage was however high, resulting in poor power efficiency of 2.5 lm/W at the standard luminance of 1000 cd/m<sup>2</sup> for lighting. 3.8% EQE at 1000 cd/m<sup>2</sup> was reported for single-layer solution-processed red OLED with PVK:PBD host [10]. The emitter tris(1-phenylisoquinoline) iridium (Ir(piq)<sub>3</sub>) is however known to have poor solubility and there are concerns on the processing stability. The origins of the inferior performance of solution-processed OLED are the difficulty of uniform dispersion of the triplet emitters in the polymer host and the lack of general fabrication method for multi-layer structures required for electron-hole current balance.

In this work we use newly synthesized red Ir complexes with long alkyl side chains attached to the ligand to enhance the solubility and the uniform dispersion in the polymer host. Multi-layer OLED is fabricated by a recently developed blade coating method without dissolution problem [11–13]. Electron-transport small molecules are successfully deposited on top of the emissive layer composed of a blend of polymer and small molecules. The solubility of the side-chained red Ir complex is over 3 wt% in chlorobenzene in sharp contrast to solubility of 0.25 wt% for the similar Ir complex without side chain. Uniform dispersion is evidenced by the absence

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**Fig. 1.** (a) Chemical structures of the triplet emitters Ir(phq)<sub>3</sub>, Hex-Ir(phq)<sub>3</sub>, Ir(piq)<sub>3</sub>, Hex-Ir(piq)<sub>3</sub>, and Ir(piq)<sub>2</sub>(acac). (b) Schematic energy level diagram of the device. Electron affinity and ionization potential of materials used in this work are also shown. Numbers are given in eV.

of emissive of (TPD<sup>+</sup>PBD<sup>-</sup>)<sup>\*</sup> exciplexes in the devices. 17 cd/A corresponding to 8.8% EQE is achieved for CsF/Al cathode. High power efficiency of 10 lm/W is achieved at 5 V, and 1000 cd/m<sup>2</sup> is reached at 8 V. Similar quantum efficiency is achieved with an electron-transport layer and LiF/Al cathode. The overall performance of such all-solution processed red OLED is approaching the best results for vacuum deposited devices. The necessity of the side chain is further supported by the fact that OLED with similar Ir complexes without side chain in otherwise the same device structure all show poor efficiencies.

Tris[2-(4-n-hexyl-phenyl)quinoline]iridium(III) (Hex-Ir(phq)<sub>3</sub>) and tris[(4-n-hexylphenyl)isoquinoline]iridium(III) (Hex-Ir(piq)<sub>3</sub>) are newly synthesized red Ir complexes with long alkyl side chains attached to the ligand to enhance the solubility. The molecular structures of Hex-Ir(phq)<sub>3</sub> and Hex-Ir(piq)<sub>3</sub> are shown in Fig. 1(a). Nuclear magnetic resonance (NMR) spectra of Hex-Ir(phq)<sub>3</sub> and Hex-Ir(piq)<sub>3</sub> are shown in Fig. 2. Hex-Ir(phq)<sub>3</sub> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.81 0.85 (m, 9H), δ 1.17 1.29 (m, 24H), δ 2.17 2.25 (m, 6H), δ 6.27 (s, 3H), δ 6.60 6.53 (m, 6H), δ 7.10 7.13 (m, 3H), δ 7.58 7.60 (m, 6H), δ 7.95 8.00 (m, 9H). Hex-Ir(piq)<sub>3</sub> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.79 0.82 (m, 9H), δ 1.17 1.29 (m, 24H), δ 2.33 2.38 (m, 6H), δ 6.74 6.76 (dd, *J* = 8 Hz, 2 Hz, 3H), δ 6.80 (s, 3H), δ 7.01 7.02 (d, *J* = 6 Hz, 3H), δ 7.22 7.23 (d, *J* = 6 Hz, 3H), δ 7.57 7.59 (m, 6H), δ 7.66 7.68 (m, 3H), δ 8.04 8.05 (d, *J* = 8 Hz, 3H), δ 8.91 8.93 (m, 3H). Tris(2-phenylquinoline)iridium(III) (Ir(phq)<sub>3</sub>), Tris(1-phenylisoquinoline)iridium(III) (Ir(piq)<sub>3</sub>), and bis(1-phenyl)isoquinoline iridium (III) acetylacetonate (Ir(piq)<sub>2</sub>(acac)) are three similar Ir complexes without long side chain used to demonstrate the necessity of the side chain. Molecular structures of Ir(piq)<sub>2</sub>(acac), Ir(phq)<sub>3</sub>, and Ir(piq)<sub>3</sub> are also shown in Fig. 1(a).

Devices are fabricated on patterned and cleaned indium tin oxide (ITO) glass substrate. The electronic energy profiles for these devices as well as the electron affinity (EA) and ionization potential (IP) of the polymers are shown in Fig. 1(b). A layer of 500 Å poly-(3,4-ethylenedioxythiophene)doped with poly-(styrenesulfonate) (PEDOT:PSS, CLEVIOSTM P CH8000) is spin coated and annealed at 100 °C for 40 min in vacuum. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-*s*-butylphenyl))diphenylamine)] (TFB) is coated on the substrate by blade and spin coating as the hole-transport layer, as well as the electron blocking layer. The gap of the blade coater is 60 μm, and the TFB (*M*<sub>w</sub> = 197,000, American Dye Source) toluene solution is 1 wt%. The substrate is spined at 4000 rpm immediately after bladeing TFB. The TFB layer is annealed at 180 °C for 40 min in vacuum to remove the solvent, and spin rinsed to remove the still soluble part. The thickness of the TFB remain on the substrate is about 500 Å. The emission layer (EML) is coated on TFB by blade and spin coating. The EML is a blend of various materials. The red Ir complex is doped into PVK (Sigma–Aldrich, *M*<sub>w</sub> = 1,100,000) host blended with PBD and N,N'-diphenyl-N,N'-(bis(3-methylphenyl)-[1,1-biphenyl]-4,4'-diamine) (TPD). PBD and TPD (purchased from Luminescence Technology Corporation) are functional materials to enhance carrier transporting ability. Chlorobenzene is used as solvent. The weight blending ratios of Hex-Ir(phq)<sub>3</sub> are PVK:PBD:TPD:Hex-Ir(phq)<sub>3</sub> = 61:24:9:6, 57:24:9:10, 53:24:9:14, and 49:24:9:18. The weight blending ratios of Hex-Ir(piq)<sub>3</sub> is PVK:PBD:TPD:Hex-Ir(piq)<sub>3</sub> = 61:24:9:6. The weight blending ratios of similar Ir complexes without side chain are PVK:PBD:TPD:Ir(piq)<sub>2</sub>(acac) = 61:28:9:6, PVK:PBD:TPD:Ir(phq)<sub>3</sub> = 61:24:9:6, and PVK:PBD:TPD:Ir(piq)<sub>3</sub> = 61:24:9:6. The emission layer is annealed at 80 °C for 30 min in vacuum. For devices with CsF(2 nm)/Al(100 nm) cathode, no small molecular electron-transport layer (ETL) is deposited on the EML. For devices with LiF(1 nm)/Al(100 nm) cathode, another layer of 20 nm TPBI serving as ETL is formed by blade and spin coating on emission layer without annealing. The TPBI solution is dissolved in methanol (0.5 wt%). All the devices are packaged in the glove box. The film thickness is measured by the Kosaka ET4000 Surface Profiler. The EL efficiency is measured by the Photo Research PR650 spectrophotometer integrated with Keithley 2400 multimeter.

Fig. 3 shows the characteristics of the devices with the Hex-Ir(phq)<sub>3</sub> as the triplet emitter. Tri-layer devices with TFB/EML/TPBI/LiF/Al structure are compared with bi-layer devices with TFB/EML/CsF/Al. As shown in Fig. 3(a), the current density and the luminance of the bi-layer devices are higher than the tri-layer devices which may results from that CsF/Al cathode is a better cathode having a good electron injection property without electron-transport layer. The peak luminance of 9579 cd/m<sup>2</sup> (at 14 V) and 1398 cd/m<sup>2</sup> (at 14 V) was achieved for bi-layer device and tri-layer device, respectively. In Fig. 3(b), it is shown that these two structures have similar device performances. The maximum current efficiency of 17 cd/A (at 7 V) and 16.6 cd/A (at 5.5 V) are obtained for bi-layer device and tri-layer device, respectively. The maximum EQE of 8.8% (at 7 V) and 9% (at 5.5 V) are obtained for bi-layer device and tri-layer device, respectively. Although TPBI/LiF/Al may not provide as efficient electron injection as CsF/Al does, but the TPBI in the tri-layer also have hole-blocking effect and hence the device efficiency of tri-layer device can be as high as bi-layer device. The blade-coated ETL has a similar effect as with the equivalent vacuum deposited layers. No dissolution of the EML can be observed while blade-coating the ETL.

The influence of the host-to-emitter weight ratio on the characteristics of Hex-Ir(phq)<sub>3</sub> device with CsF/Al cathode are shown in Fig. 4(a) and (b). The weight ratios of the electron-transporting PBD and hole-transporting TPD are fixed at 24% and 9% respectively. The ratio of the emitter increases from 6% to 18% with the corresponding decrease of the PVK host polymer ratio. Below 10 V, both the

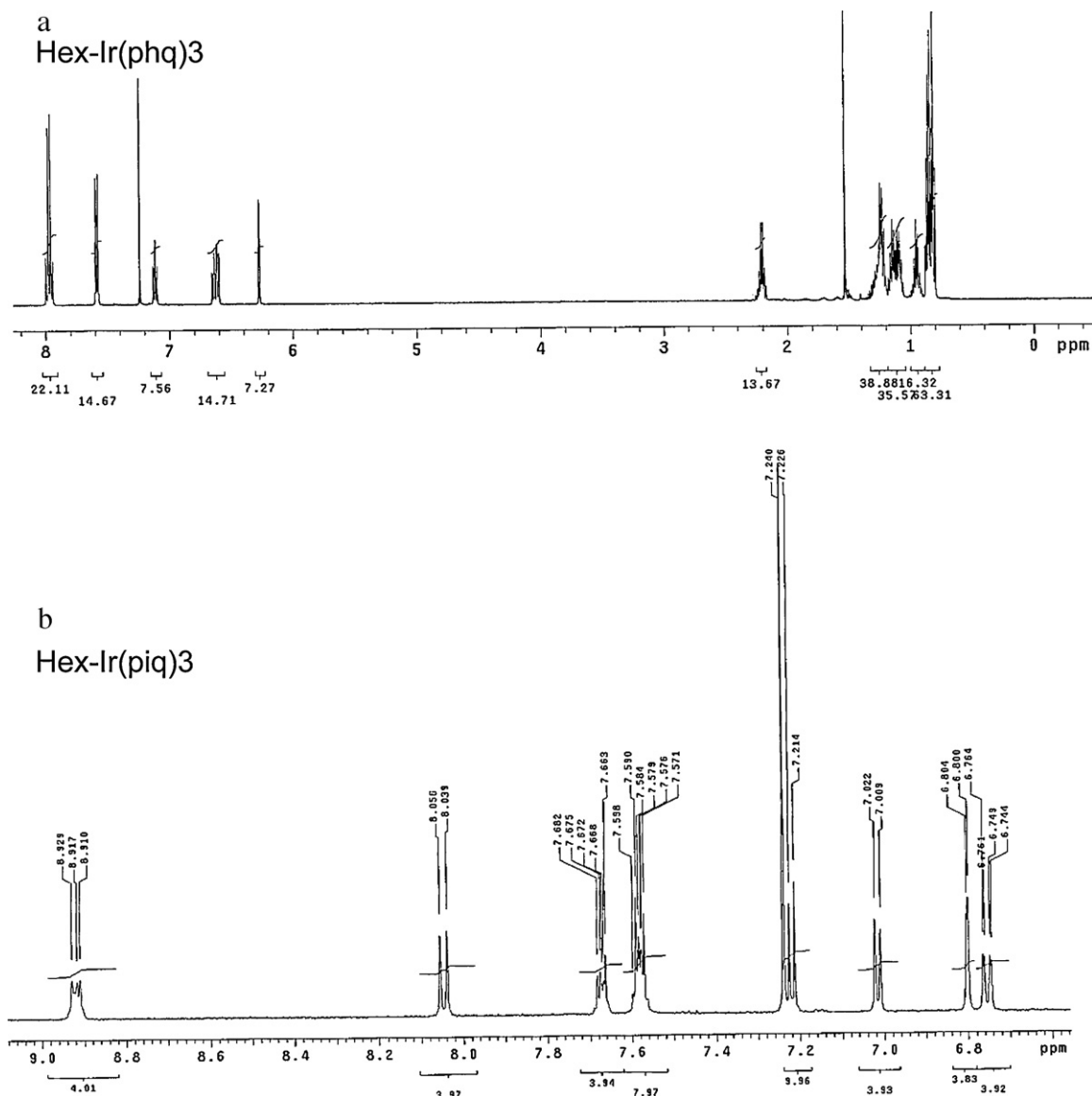
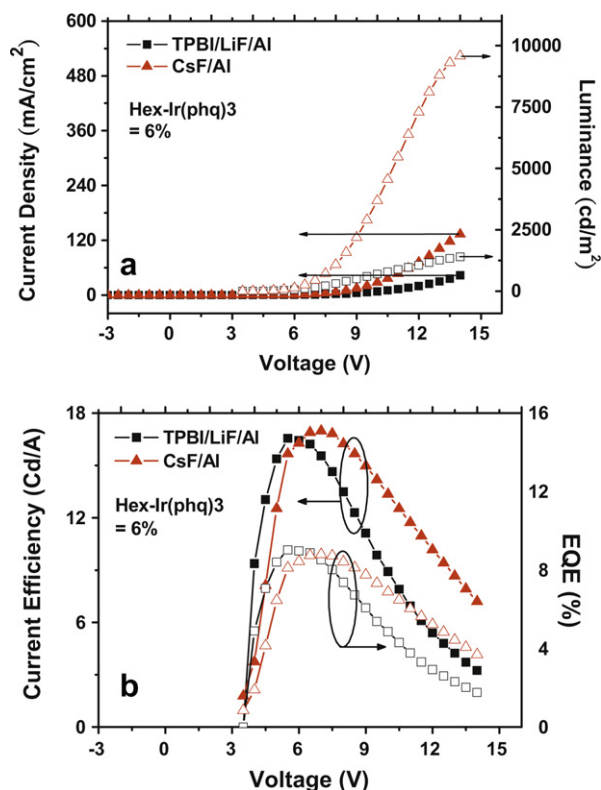


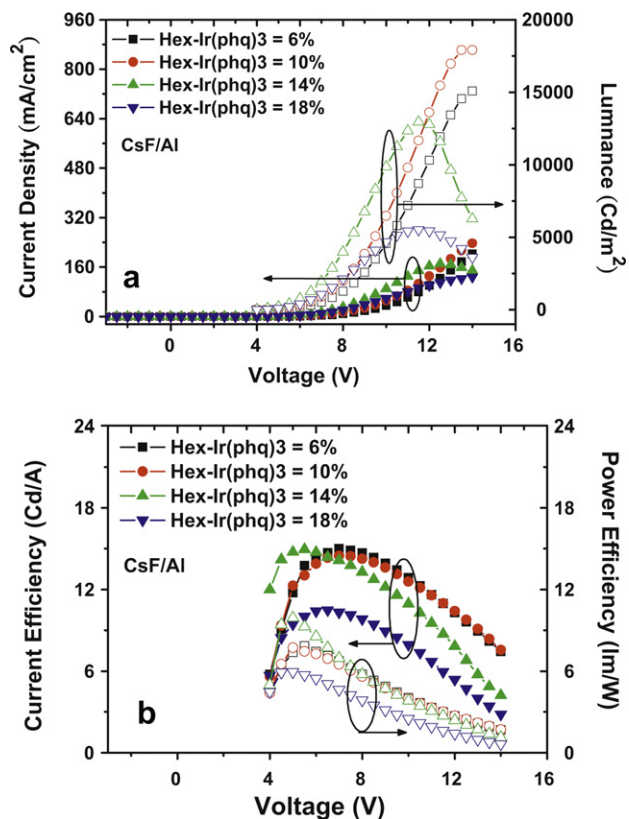
Fig. 2.  $^1\text{H}$  NMR spectrum of (a) Hex-Ir(phq)3 and (b) Hex-Ir(piq)3 in  $\text{CDCl}_3$ .

luminance and current density increased as the emitter concentration increased up to 14%. The luminance and current density is then decreased as the emitter concentration further increased to 18%. The peak luminance of  $15,090 \text{ cd/m}^2$  (at 14 V),  $17,910 \text{ cd/m}^2$  (at 14 V),  $12,950 \text{ cd/m}^2$  (at 11.5 V), and  $5511 \text{ cd/m}^2$  (at 11.5 V) are obtained for Hex-Ir(phq)3 device with blending ratios of 6%, 10%, 14%, and 18%, respectively. For devices with 6–14% of emitters, the current efficiency is roughly the same. The maximum current efficiency of 15 cd/A (at 7 V), 14.5 cd/A (at 7 V), and 14.9 cd/A (at 5.5 V) are obtained for Hex-Ir(phq)3 device with blending ratios of 6%, 10%, and 14%, respectively. The current efficiency of the device with 18% of emitter is low. The tendency of the power efficiency of the devices varies with doping concentration is similar to the current efficiency. The maximum power efficiency of 7.9 lm/W (at 5.5 V), 7.7 lm/W (at 5 V), and 9.9 lm/W (at 5 V) are obtained for Hex-Ir(phq)3 device with blending ratios of 6%, 10%, and 14%, respectively. The reason why high efficiency can keep up to 14% of emitters is a good mixing of the Hex-Ir(phq)3 with polymer host. The decrease in current density, luminance, and efficiency as the Hex-Ir(phq)3 doping concentration increased to 18% may result from the occurrence of Hex-Ir(phq)3 aggregation.

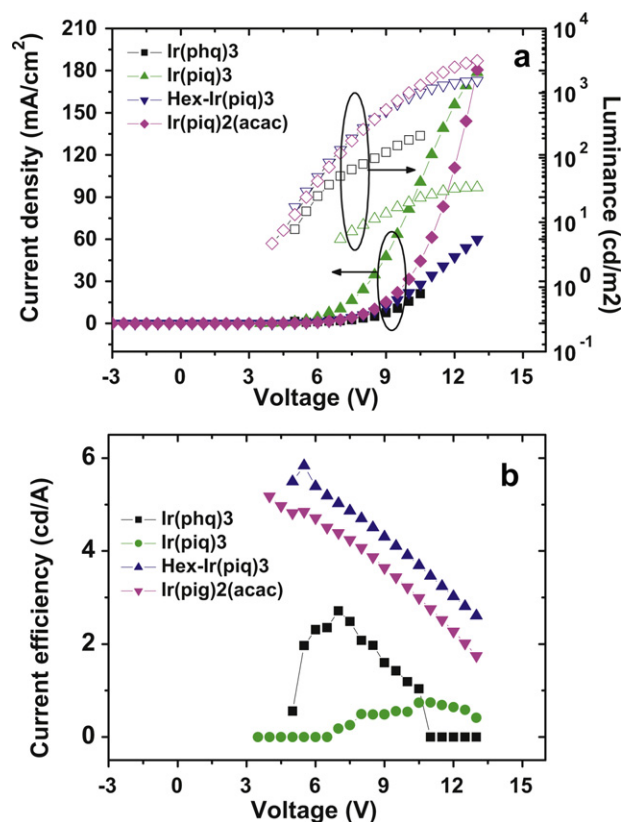
In order to verify the idea of attaching long-side-chain to the ligand, Ir(phq)3, Ir(piq)3, and Ir(piq)2(acac), three Ir complexes similar to Hex-Ir(phq)3 and Hex-Ir(piq)3 but without long-side-chain, are used to demonstrate the necessity of the side chain. The solubilities of Hex-Ir(phq)3 and Hex-Ir(piq)3 are over 3 wt% in chlorobenzene in sharp contrast to solubility of Ir(piq)2(acac), Ir(phq)3, and Ir(piq)3. The solubility of Ir(piq)2(acac) is about 0.25 wt%, while the solubilities of Ir(phq)3 and Ir(piq)3 are less than 0.1 wt%. Unlike Hex-Ir(phq)3 and Hex-Ir(piq)3 can be dissolved in chlorobenzene immediately, Ir(piq)2(acac), Ir(phq)3, and Ir(piq)3 only can be completely dissolved after the solution being heated overnight. The poor solubility of Ir(piq)2(acac), Ir(phq)3, and Ir(piq)3 make the performance of the devices poor as shown in Fig. 5(a) and (b). The current efficiency of the Ir(piq)2(acac), Ir(phq)3, and Ir(piq)3 device are about 5 cd/A (at 4 V), 2.7 cd/A (at 7 V), and 0.74 cd/A (at 10.5 V), respectively. These current efficiency are inferior to those of Hex-Ir(phq)3 and Hex-Ir(piq)3 devices. From the atomic force microscopy images of EMLs shown in Fig. 6, the roughness of EMLs contain Ir(phq)3 and Ir(piq)3 are higher than EMLs contain Hex-Ir(phq)3 and Hex-Ir(piq)3. Many particulate aggregates can be observed on the surface of EMLs contains



**Fig. 3.** (a) The current density and luminance of the bi-layer PLED and tri-layer PLED under 6% Hex-Ir(phq)3 doping concentration. The device structure of bi-layer and tri-layer PLED are ITO/PEDOT:PSS/TFB/EML/CsF/Al and ITO/PEDOT:PSS/TFB/EML/TPBI/LiF/Al, respectively. (b) The current efficiency and EQE of the bi-layer PLED and tri-layer PLED under 6% Hex-Ir(phq)3 doping concentration.



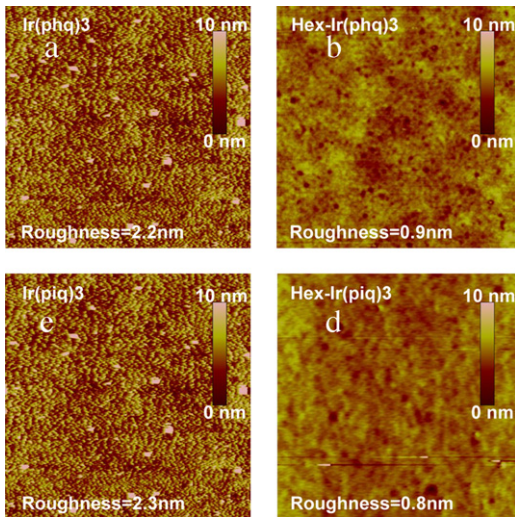
**Fig. 4.** (a) The current density and luminance of the bi-layer PLED with various host-to-emitter ratio. (b) The current efficiency and power efficiency of the bi-layer PLED with various host-to-emitter ratio.



**Fig. 5.** (a) The current density and luminance of the PLED with Ir(phq)3, Ir(piq)3, Hex-Ir(piq)3, and Ir(piq)2(acac) as triplet emitters. (b) The current efficiency of the PLED with Ir(phq)3, Ir(piq)3, Hex-Ir(piq)3, and Ir(piq)2(acac) as triplet emitters. (c) The spectrum of four triplet emitters Ir(phq)3, Hex-Ir(phq)3, Ir(piq)3, Hex-Ir(piq)3, and Ir(piq)2(acac). The inset shows the enlarged spectrum around 450 nm.

Ir(phq)3 and Ir(piq)3. Non-uniform dispersion of Ir(piq)2(acac), Ir(phq)3, and Ir(piq)3 are evidenced by the presence of (TPD<sup>+</sup>PBD<sup>-</sup>)<sup>\*</sup> exciplexes emission in the devices as shown in Fig. 5(c). The inset in Fig. 5(c) shows the enlarged spectrum around 450 nm. The residual blue emission from (TPD<sup>+</sup>PBD<sup>-</sup>)<sup>\*</sup> exciplexes [14–16] in the host is strongest in Ir(piq)3 device. This may result from the dispersion of Ir(piq)3 is the poorest one. As for the Hex-Ir(phq)3 and Hex-Ir(piq)3 devices, the residual blue emission from the host is invisible which indicates that the high efficiency of the Hex-Ir(phq)3 and Hex-Ir(piq)3 devices come from the uniform dispersion of the emitter. The necessity of the long-side-chain on ligand is confirmed.

In conclusion, highly soluble red Ir complexes tris[2-(4-n-hexyl-phenyl)quinoline]iridium(III) and tris[(4-n-hexylphenyl)isoquinoline]iridium(III) are synthesized to demonstrate the necessity of long-side-chain. High efficiency



**Fig. 6.** Atomic force microscopy images of emissive layer contains (a) Ir(phq)<sub>3</sub>, (b) Hex-Ir(phq)<sub>3</sub>, (c) Ir(piq)<sub>3</sub>, and (d) Hex-Ir(piq)<sub>3</sub>.

multi-layer solution-processed red organic light-emitting diodes are demonstrated. Uniform dispersion of this triplet emitter in polymer host is achieved. Multi-layer structure is obtained by blade coating method. Similar quantum efficiency and current efficiency are achieved for the device with CsF/Al cathode and for the device with an electron-transport layer and LiF/Al cathode. With the high efficiency and easy fabrication process, large-area solution-processed organic electronics is possible.

## Acknowledgment

This work is supported by the National Science Council of Taiwan under grant number NSC 98-2120-M-009-003 and NSC 98-2811-M-009-048.

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