ChemPubSoc Europe

DOI: 10.1002/chem.201400243

CHEMISTRY
A European Journal
Communication

Electrochemistry

An Easy Route to Red Emitting Homoleptic Ir^{III} Complex for Highly Efficient Solution-Processed Phosphorescent Organic Light-Emitting Diodes

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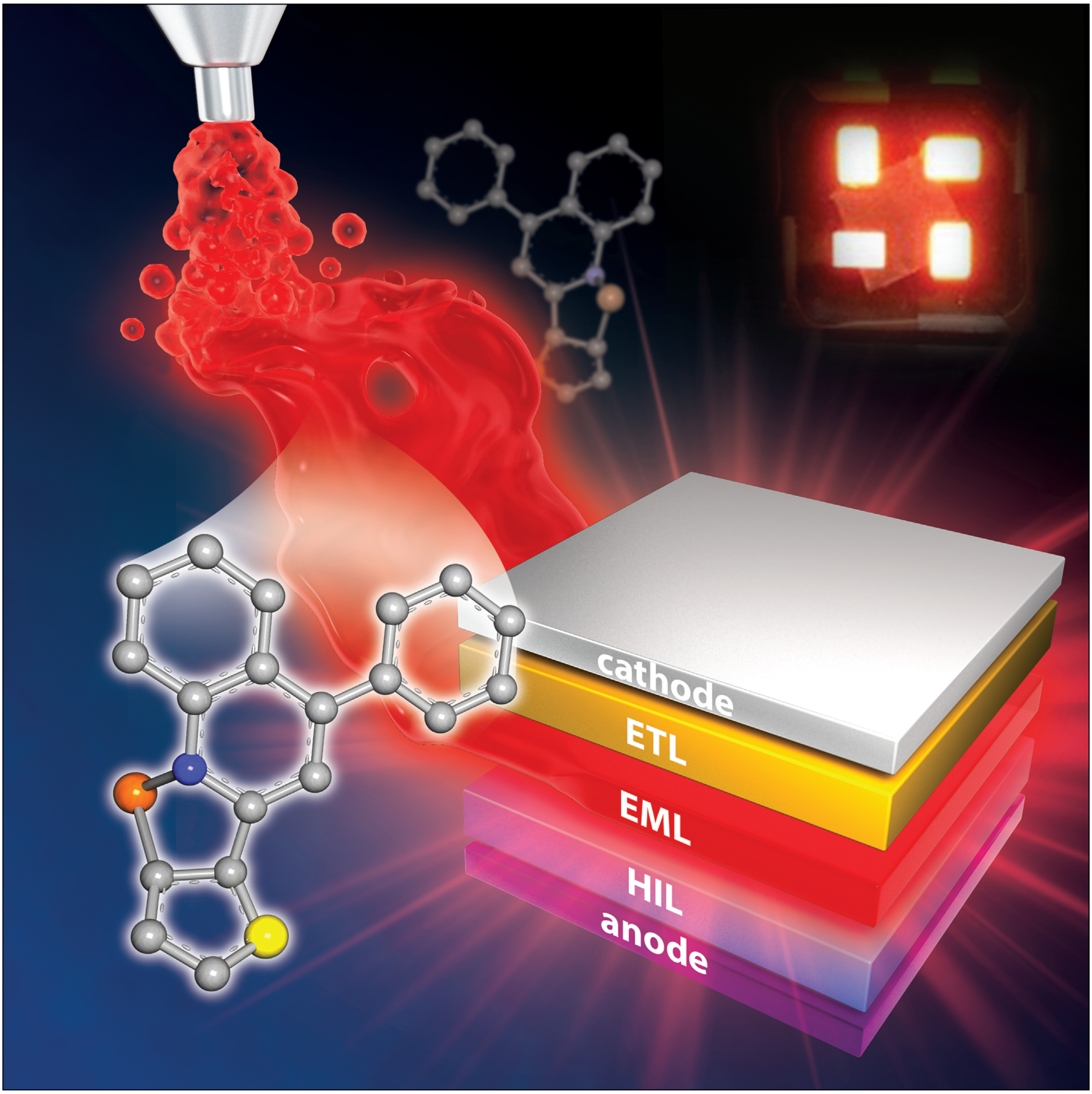

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Abstract: A thiophene-phenylquinoline-based homoleptic Ir^{III} complex, $[Ir(Th\text{-}PQ)_3]$, has been synthesised by a simple route and utilised as a dopant in solution-processed phosphorescent organic light-emitting diodes (PhOLEDs). It shows the current efficiency of approximately 26 $cd\,A^{-1}$ and the external quantum efficiency of about 21 %, which are the highest values reported to date for PhOLEDs prepared by solution-process.

Phosphorescent organic light-emitting diodes (PhOLEDs) have potential applications in flat-panel displays and solid-state lighting sources.[1] The use of phosphorescent dopants can greatly increase the PhOLED efficiency due to harvesting both singlet and triplet excitons; this can provide nearly 100 % internal quantum efficiency.[2] Among the phosphorescent emitters, Ir^{III} complexes have been considered as the most efficient triplet dopant in high efficiency PhOLEDs due to their excellent colour tunability and relatively short phosphorescence lifetimes.[3] When compared to the green phosphors, the design and synthesis of red- and near-infrared emitting phosphors are more complicated because the luminescence quantum yields tend to decrease with longer wavelengths according to the energy-gap law.[4] Therefore, the design and synthesis of red phosphors for highly efficient PhOLEDs remain to be further developed.

The general approach to increase quantum efficiency of particular phosphorescent dopants is to replace electron-donating or electron-withdrawing groups with heteroatoms in the cyclometalated ligand systems.[5] However, ligands containing two heteroatoms that increase the efficiency and luminance half-lifetime of Ir^{III} complexes have seldom been reported.[6] For this purpose, quinolone-based compounds have been investigated because of their elevated electron affinities in opto-electronic materials.[7] These compounds are stable at high current density and possess short phosphorescence lifetimes to suppress triplet–triplet annihilation, thereby improving device quantum efficiency.[8,9]

Fabrication of PhOLEDs by the solution process has more advantages, such as low cost fabrication and large area applications, than their highly expensive vacuum-deposition counterparts.[10] The luminous efficiency achieved in polymeric materials is comparatively lower than that of small-molecule-based OLEDs.[11,12] In contrast, the design and synthesis of highly soluble small molecular phosphorescent emitter for solution-processed PhOLEDs is very scarce. Very recently, Wu et al. reported the solution processed small molecule PhOLEDs with the highest external quantum efficiency (EQE) of 15 %. However, they achieved the homoleptic Ir^{III} complex by multi-step synthetic routes.[13]

In this work, we have synthesised tris(4-phenyl-2-(thiophen-2-yl)quinoline)iridium, $[Ir(Th\text{-}PQ)_3]$, and utilised it as a dopant for solution-processed PhOLEDs. The ligand of this Ir^{III} complex was synthesised from two commercially available starting materials.

Introduction of electron-donating thiophene unit into the ligand frame of $[Ir(Th\text{-}PQ)_3]$ improves the quantum yield, and red shifts the photoluminance (PL) maximum compared to their benzene counterparts due to the decrease in the ligand's triplet energy with increasing π conjugation.[14] On the other hand, the strong electron-accepting character of the quinoline group can effectively reduce the ^{3}MLCT exited energy of the $[Ir(Th\text{-}PQ)_3]$. The simple solution-processed PhOLEDs were fabricated using $[Ir(Th\text{-}PQ)_3]$ as a dopant and achieved the luminous current efficiency of approximately 26 $cd\,A^{-1}$ and the EQE of about 21 %, which are the highest values reported to date for PhOLEDs prepared by the solution-process.

$[Ir(Th\text{-}PQ)_3]$ was synthesised according to the route shown in Scheme 1 and its structure was confirmed by ^{1}H, ^{13}C NMR, HRMS spectral techniques and single-crystal X-ray analysis. The synthetic details are provided in the Supporting Information. The single crystal was grown by the diffusion of hexane into a dichloromethane solution of $[Ir(Th\text{-}PQ)_3]$. The ORTEP representation of the $[Ir(Th\text{-}PQ)_3]$ is shown in Figure 1 a. It has tetragonal geometry with three Th-PQ main ligands around the metal centre.

The thermal stability of the Ir^{III} complex was investigated by thermal gravimetric analysis (TGA; Figure S1 in the Supporting Information). The onset decomposition temperature of $[Ir(Th\text{-}PQ)_3]$ was observed at 409 °C indicating its high thermal stability. The UV–visible absorption spectrum of $[Ir(Th\text{-}PQ)_3]$ in chloroform solution is shown in Figure 1 b. It shows two absorption bands at 312 and 421 nm corresponding to the spin-allowed $^1\pi\rightarrow\pi^*$ transition of the cyclometalated ligands and a well-resolved shoulder at 459 nm originating from the singlet metal-to-ligand charge transfer (MLCT) transitions. A structure-less weak band at 578 nm was attributed to the spin-forbidden ^{3}MLCT transition. The PL spectrum of $[Ir(Th\text{-}PQ)_3]$ is shown in Figure 1 b. It shows an emission maximum at 601 nm in chloroform solution due to the presence of donor–acceptor interactions between the electron-donor thiophene and electron-acceptor quinoline (Th-PQ) groups in the cyclometalated ligand. The donor–acceptor character is caused by the interaction between electron-rich thiophene and electron-deficient quinoline units.[14]

The electrochemical properties of $[Ir(Th\text{-}PQ)_3]$ were studied using cyclic voltammetry and the corresponding cyclic voltammogram is shown in Figure 2 a. Appearance of good redox waves confirms the presence of both anionic and cationic radi-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201400243.

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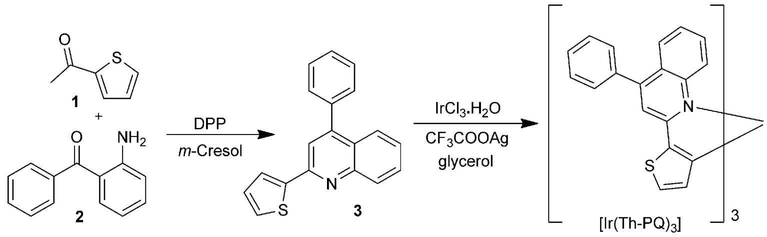

Scheme 1. Synthesis of $[Ir(Th-PQ)_3]$.

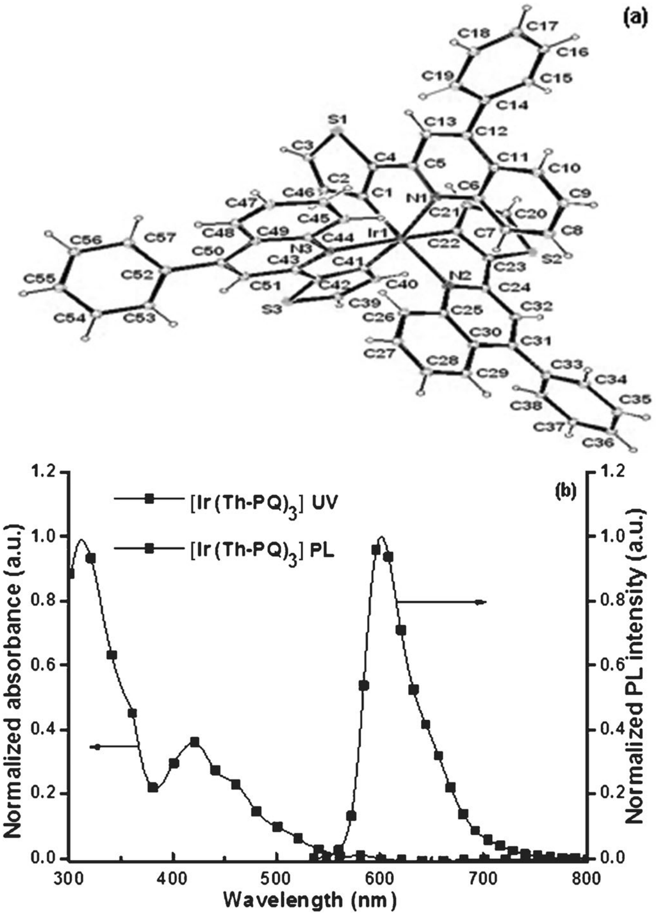

Figure 1. a) ORTEP representation, 50% probability, and b) UV–visible absorption and PL spectra of $[Ir(Th-PQ)_3]$ in $CHCl_3$ solution.

cal states. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were determined from the onsets of the oxidation and reduction potentials and were found to be −5.17 and −3.08 eV, respectively. These energy levels are well matched with adjacent layer of the devices as shown in Figure 2b. The calculated band gap was 2.09 eV. The reduction and oxidation generally occurred due to the presence of quinoline and thiophene units, respectively, in the cyclometalated ligand. The narrow band gap may be due to the elevation of the HOMO energy level with the introduction of an electron-rich thiophene moiety. The electrochemical switching property of $[Ir(Th-PQ)_3]$ was reversible over 100 successive scans indicating its electrochemical stability. The triplet energy level (T_1) of $[Ir(Th-PQ)_3]$ was estimated to be approximately 2.06 eV by using the first phosphorescent emission peak of low temperature PL measured at 77 K (Figure S2 in the Supporting Information).

Here, we have used a high-performance polymeric hole injection layer (HIL) that has a gradient ionisation potential which gradually increases from bottom-to-top surface of the HIL film due to self-organisation (surface work function ~5.95 eV)[15,16] (Figures S3, S4 and Table S1 in the Supporting Information). This gradient HIL (GraHIL) provides efficient hole injection from the ITO anode to an overlying emitting layer (EML), which has a large energy band gap and a deep HOMO energy level (e.g., HOMO of TCTA ~5.7 eV). The GraHIL also has a self-organised surface-enriched insulating property that provides efficient electron blocking and quenching of excitons.[17] Therefore, the PhOLED does not require an additional layer for hole injection and electron blocking between the HIL and the EML as shown in Figure 3a. The EML consists of a mixed host system of a hole-transporting host, 4,4′,4′′-tris(N-carbazolyl)triphenylamine (TCTA), and an electron-transporting host, 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBI), in 1:1 weight ratio with 15 wt% $[Ir(Th-PQ)_3]$. The mixed host EML can provide more efficient injection and transport of both charge carriers to the EML from the adjacent HIL and from the electron trans-

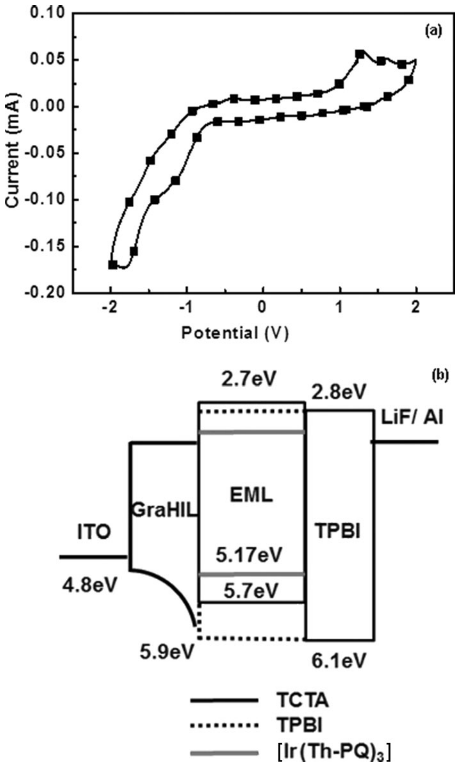

Figure 2. a) Cyclic voltammogram of $[Ir(Th-PQ)_3]$ measured in MC at a scan rate of 100 mV s^{-1}, and b) energy-level diagram of simple-structured red emitting PhOLEDs.

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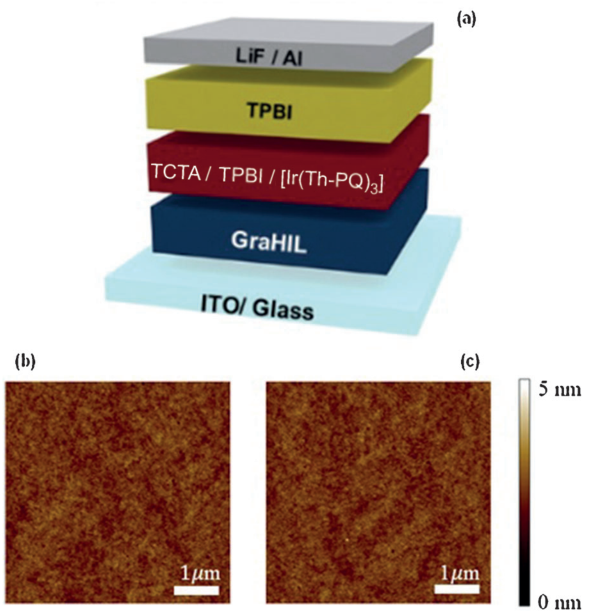

Figure 3. a) Schematic illustration of the device structure, and b) AFM topographic images of TCTA/TPBI, and c) TCTA/TPBI/[Ir(Th-PQ)$_3$] films formed by the spin-coating process.

porting layer (ETL, TPBI) than can a single host EML.[17] Because both hole and electron transport in the mixed host system can be facilitated by a hole-transporting host (TCTA) and an electron-transporting host (TPBI), better balance of holes and electrons can be achieved in the mixed host EML than in single-host EML.[17] In addition, good charge transport of both charge carriers and charge-carrier balance in the mixed-host device can uniformly distribute the recombination region in EML, thereby providing an effective energy transfer from host to phosphorescent dopant with decreased non-radiative decay.[17]

Because a good solubility and thin-film formability of the mixed-host EML materials are prerequisites for fabricating high-performance solution-processed PhOLEDs, we observed surface morphology of the EML using atomic force microscopy (AFM). Figure 3 b and c display AFM topographic images of 40 nm thick mixed-host (TCTA/TPBI) and 15 wt % of [Ir(Th-PQ)$_3$]-doped EML film (TCTA/TPBI/[Ir(Th-PQ)$_3$]). The root-mean-square (RMS) surface roughness value of [Ir(Th-PQ)$_3$] doped EML film was 2.41 Å, which is highly smooth and comparable to that of undoped mixed-host film (TCTA/TPBI; 2.47 Å). This very smooth surface roughness of the EML, without localised protruding regions leading to leakage current in the device, can provide a base for achieving a high luminous efficiency.[18,19]

The PhOLED was fabricated as a configuration shown in Figure 3 a by simple solution-process and measured-device characteristics, that is, current density, luminance, current efficiency, and external quantum efficiency (EQE), as shown in Figure 4. The device exhibited a very high maximum luminous current efficiency of about 26 cd A^{-1} and EQE of approximately 21 %. To the best of our knowledge, this luminous efficiency and EQE are the highest ever reported for solution-processed red-emitting PhOLEDs (Table S2 and Figure S5 in the Supporting Information). This high luminous efficiencies can be attributed to good thin-film formability, efficient hole injection from high work function GraHIL, and good charge balance in the mixed host EML.

PhOLEDs with [Ir(Th-PQ)$_3$] exhibited a narrow, red EL spectrum at 1000 cd m^{-2} with a maximum peak intensity at 608 nm, which matches well with the PL spectrum of [Ir(Th-PQ)$_3$] (Figure 5 a). This spectral result indicates that energy transfer from host-to-dopant materials is efficient and the device architecture is well optimised. The Commission Internationale de l'Éclairage (CIE) coordinates of the device is (0.64, 0.34), which is nearly identical to the red of the National Television System Committee (NTSC) 1987 (0.64, 0.33) at 1000 cd m^{-2} (Figure 5 b).

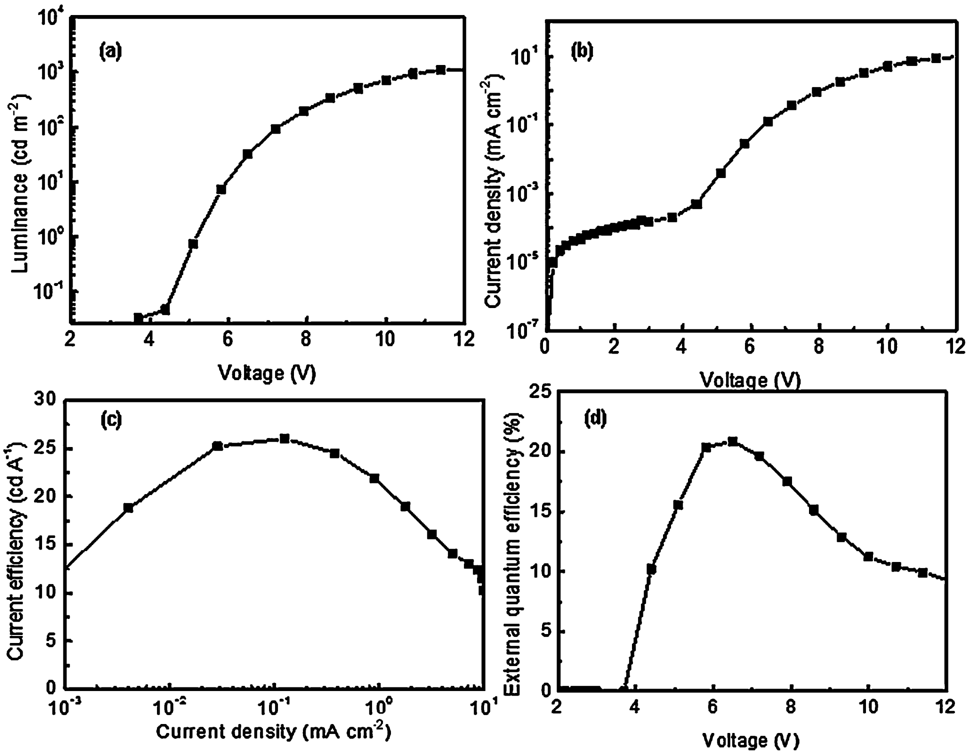

Figure 4. a) Current density, b) luminance characteristics versus voltage, c) current efficiency, and d) external quantum efficiency of the [Ir(Th-PQ)$_3$] solution processed PhOLEDs.

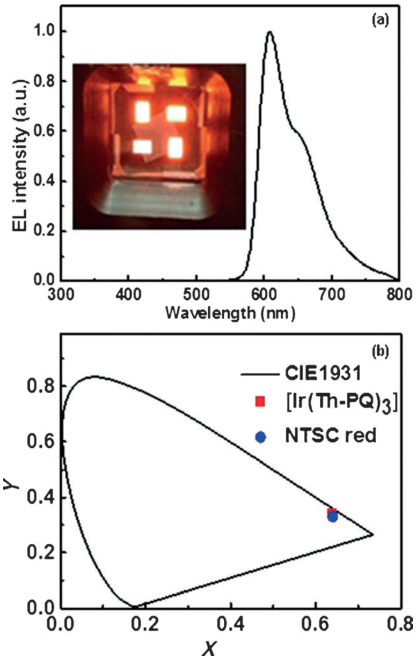

Figure 5. a) Electroluminescent spectrum, and b) CIE coordinates of the [Ir(Th-PQ)$_3$] solution processed PhOLEDs.

In summary, we report a highly efficient and soluble red-emitting tris(4-phenyl-2-(thiophen-2-yl)quinoline)iridium(III) complex, [Ir(Th-PQ)$_3$], that was designed and successfully synthesised for use in solution-processed PhOLEDs. Upon replacing the benzene in the cyclometalated phenylquinoline main ligand by thiophene the PL emission is shifted to red and the thermal stability is enhanced. PhOLEDs with [Ir(Th-PQ)$_3$] were successfully fabricated with a GraHIL as high work function HIL and a mixed-host EML, which is composed of electron- and hole-transporting host materials (TCTA, TPBI). Using this simple structure, we achieved a PhOLED with very high luminous current efficiency of approximately 26 cd A^{-1} and EQE of about 21% with good CIE coordinates (0.64, 0.34). This achievement shows the possibility of using low-cost solution-processing methods to fabricate small-molecule-based PhOLEDs for use in applications such as large-area flat-panel displays or solid-state lighting.

Acknowledgements

This work was supported by a grant from the National Research Foundation of Korea (NRF) of the Ministry of Science, ICT & Future Planning (MSIP) of Korea (NRF-2011-0028320) and the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT & Future Planning (MSIP) of Korea (NRF-2013M3C1A3065522) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP; NRF-2013R1A2A2A01068753).

Keywords: electrochemistry · iridium · phenylquinoline · PhOLEDs · solution processing

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Received: January 21, 2014

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