Synthesis and Characterization of Red-Emitting Iridium(III) Complexes for Solution-Processable Phosphorescent Organic Light-Emitting Diodes

14 AUTHORS, INCLUDING:

Myungkwan Song
Korea Institute of Materials Science
96 PUBLICATIONS   **927** CITATIONS

SEE PROFILE

Jae-Wook Kang
Chonbuk National University
121 PUBLICATIONS   **4,346** CITATIONS

SEE PROFILE

Sunwoo Kang
Samsung Display, South Korea
54 PUBLICATIONS   **937** CITATIONS

SEE PROFILE

Synthesis and Characterization of Red-Emitting Iridium(III) Complexes for Solution-Processable Phosphorescent Organic Light-Emitting Diodes

By *Seung-Joon Lee, Jin-Su Park, Myungkwan Song, In Ae Shin, Young-Inn Kim, Jae Wook Lee, Jae-Wook Kang, Yeong-Soon Gal, Sunwoo Kang, Jin Yong Lee,* Sung-Hyun Jung, Hyung-Sun Kim, Mi-Young Chae,* and *Sung-Ho Jin**

A new series of highly efficient red-emitting phosphorescent Ir(III) complexes, (Et-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), (Et-CVz-PhQ)$_2$Ir(acac), (EO-CVz-PhQ)$_2$Ir(pic-N-O), (EO-CVz-PhQ)$_2$Ir(pic), and (EO-CVz-PhQ)$_2$Ir(acac), based on carbazole (CVz)-phenylquinoline (PhQ) main ligands and picolinic acid N-oxide (pic-N-O), picolinic acid (pic), and acetylacetone (acac) ancillary ligands, are synthesized for phosphorescent organic light-emitting diodes (PhOLEDs), and their photophysical, electrochemical, and electroluminescent (EL) properties are investigated. All of the Ir(III) complexes have high thermal stability and emit an intense red light with an excellent color purity at CIE coordinates of (0.65,0.34). Remarkably, high-performance solution-processable PhOLEDs were fabricated using Ir(III) complexes with a pic-N-O ancillary ligand with a maximum external quantum efficiency (5.53%) and luminance efficiency (8.89 cd A^{-1}). The novel use of pic-N-O ancillary ligand in the synthesis of phosphorescent materials is reported. The performance of PhOLEDs using these Ir(III) complexes correlates well with the results of density functional theory calculations.

1. Introduction

Organic light-emitting diodes (OLEDs) are currently attracting a lot of attention owing to their potential application in the field of full-color flat panel displays as an efficient and low cost alternative to the widely used liquid crystal displays. Of the light-emitting materials available, phosphorescent materials are particularly promising because they can emit light from both singlet and triplet excitons,[1–6] enabling the fabrication of PhOLEDs with close to 100% internal quantum efficiency. Many PhOLEDs have been prepared by thermal evaporation of up to six organic layers,[1–4] making the fabrication process relatively complicated and expensive especially if large substrates are used. Solution processed OLEDs provide an attractive alternative to those processed by vacuum deposition, mainly due to their significantly reduced production cost. The majority of OLEDs containing solution processed layers has contained oligomers or conjugated polymers[7–12] and more recently dendrimers.[13–18] Several groups have demonstrated the tuning of the phosphorescence wavelength from blue to red by functionalization of the main ligands with electron-withdrawing and electron-donating substituents.[19–22] For example, the emission wavelength of the Ir(III) complexes can cover the whole visible region by modification or variation of cyclometalated 2-arylpyridine main ligands and ancillary ligands.[23]

[*] Prof. J. Y. Lee, S. Kang
Department of Chemistry, Sungkyunkwan University
Suwon, 440-746 (Korea)
E-mail: jinylee@skku.edu
Prof. S. H. Jin, S. J. Lee, J. S. Park, M. Song, I. A. Shin, Prof. Y. I. Kim
Department of Chemistry Education
Interdisciplinary Program of Advanced Information and Display
Materials and Center for Plastic Information System
Pusan National University
Busan, 609-735 (Korea)
E-mail: shjin@pusan.ac.kr
Prof. J. W. Lee
Department of Chemistry, Dong-A University
Busan, 604-714 (Korea)

Dr. J. W. Kang
Department of Surface Technology
Korea Institute of Materials Sciences (KIMS)
Changwon, 641-831 (Korea)
Prof. Y. S. Gal
Polymer Chemistry Lab
College of General Education
Kyungil University
Hayang, 712-701 (Korea)
Dr. S. H. Jung, Dr. H. S. Kim, Dr. M. Y. Chae
Cheil Industries Inc
Uiwang-Si, Gyeonggi-Do, 437-711 (Korea)

Carbazole (CVz) molecules exhibit an inherent electron-donating nature, excellent photoconductivity, and relatively intense luminescence. The thermal stability or glass-state durability of organic compounds can be greatly enhanced by the introduction of a CVz group in the core structure. The CVz group can be easily functionalized at the 3-, 6-, or 9-position and covalently linked to other molecular groups. The N-arylcarbazoles, in which a phenyl or a naphthyl group is attached at the 9-position of CVz, have shown excellent thermal stability and good electro-optical properties.[24–27] Quinolines, in spite of their significant biological activities, are well known for their formation of conjugated molecules and polymers that combine enhanced electronic, optoelectronic, or nonlinear optical properties with excellent mechanical properties.[28–35] Therefore, in this paper, we report the synthesis, redox, photophysical, and electroluminescent (EL) properties of six new red emitting heteroleptic Ir(III) complexes containing the highly efficient main ligands by making use of CVz-containing phenylquinoline (CVz-PhQ) moieties from synergistic effects between CVz and PhQ derivatives for solution processing of the emitting layer in the PhOLED fabrication. To the best of our knowledge, no study to date has explored CVz-PhQ-based Ir(III) complexes for PhOLEDs.

2. Results and Discussion

Two CVz-PhQ derived main ligands, 9-ethyl-3-(4-phenylquinolin-2-yl)-9H-carbazole (Et-CVz-PhQ) (4) and 9-(2-(2-methoxyethoxy)ethyl)-3-(4-phenylquinolin-2-yl)-9H-carbazole (EO-CVz-PhQ) (5) were prepared by an acid-catalyzed Friedlander condensation reaction.[36,37] Condensation of 3-acetyl-N-ethylcarbazole (1) or 3-acetyl-N-2-(2-methoxyethoxy)ethylcarbazole (2) with 2-aminobenzophenone (3) gave the desired donor–acceptor type of CVz-PhQ

(4 and 5) in 80% yield. The diphenylphosphate catalyst was readily removed by precipitation into a 10% triethylamine/ethanol solution. Cyclometalated Ir(III) μ-chloride bridged dimers (6 and 7) were synthesized by iridium trichloride hydrate with an excess of one of our developed main ligands, 4 and 5. The Ir(III) complexes were prepared by 6 and 7 with the corresponding ancillary ligands in 83% (Scheme 1). Compounds 6 and 7 can be easily converted to mononuclear Ir(III) complexes by replacing the two bridging chlorides with bidentate monoanionic ancillary ligands. Among the various types of ancillary ligands, we firstly used picolinic acid N-oxide (pic-N-O), comprising picolinic acid (pic) and acetylacetone (acac) as an ancillary ligand for the synthesis of the Ir(III) complexes. The six Ir(III) complexes, (Et-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), (Et-CVz-PhQ)$_2$Ir-(acac), (EO-CVz-PhQ)$_2$Ir(pic-N-O), (EO-CVz-PhQ)$_2$Ir(pic), and (EO-CVz-PhQ)$_2$Ir(acac), were purified with the silica column method and their structure and purity were characterized using ^{1}H-, ^{13}C-NMR, elemental analysis, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), cyclic voltammetry (CV), UV-visible, and photoluminescent (PL) spectroscopy and computational analysis. These class of Ir(III) complexes were designed on the basis of the following considerations: i) ability to solution process through the introduction of solubilizing groups, ethyl (Et) and methoxyethoxyethyl (EO), on the CVz unit, and ii) modification of the ancillary ligands such as pic-N-O along with of pic and acac to tune the electro-optical properties for enhanced PhOLED performance.

The thermal stability of the Ir(III) complexes was evaluated using TGA and DSC under a nitrogen atmosphere and their 5% weight loss temperatures ($\Delta T_{5\%}$) are given in Figure 1 and are summarized in Table 1. The $\Delta T_{5\%}$ of the TGA curves indicated that all the Ir(III) complexes showed excellent thermal stability (385–344 °C), which enhanced the rigidity of the Ir(III) complexes and prevented the degradation of the emitting layer by the current-induced heat caused by the operation of PhOLEDs. The Et-CVz-PhQ-based Ir(III) complexes with acac ancillary ligand tended to a relatively lower $\Delta T_{5\%}$ than the pic-N-O and pic ancillary ligands. The glass transition temperature of Ir(III) complexes were found to be in the range of 150–287 °C. The Ir(III) complexes with pic-N-O ancillary ligands exhibited a higher thermal stability than the Ir(III) complexes with pic and acac ancillary ligands.

Figure 2a compares the absorption spectra of the Ir(III) complexes and main ligand, Et-CVz-PhQ, in chloroform solution. The photophysical properties of the Ir(III) complexes are summarized in Table 1. In common with most Ir(III) complexes, the absorption spectra can be divided into two regions.[38,39] The intense peaks in the short wavelength region below 400 nm were assigned to the spin-allowed $^1\pi$–π^* transition, which closely resembles the spectrum of the Et-Cvz-PhQ (λ_{max}: 348 nm). The weaker absorption tails that appeared above 400 nm were due to the charge transfer transition.[40] These data suggested that there is
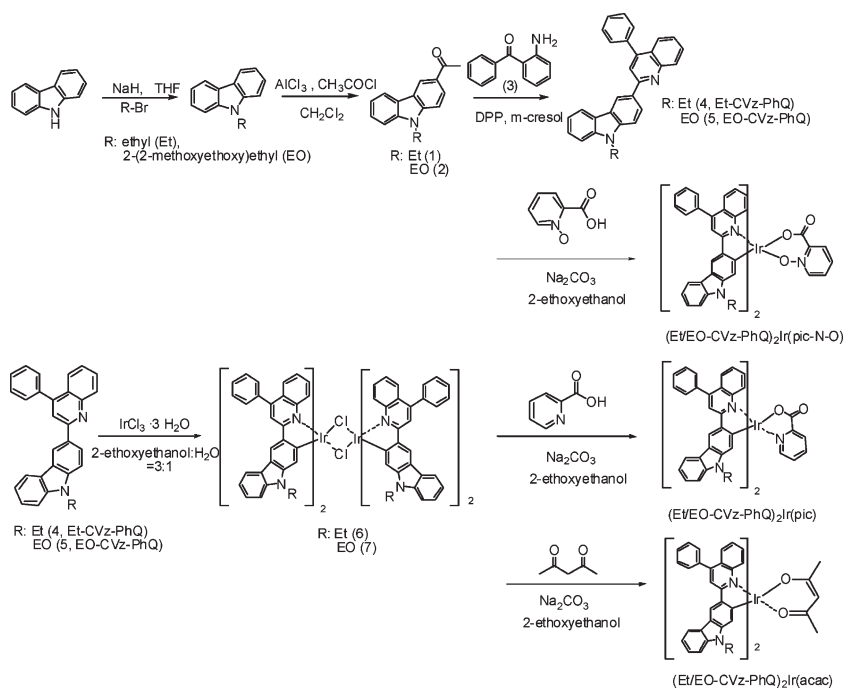
Scheme 1. Synthetic routes of new ligands and their red iridium complexes.
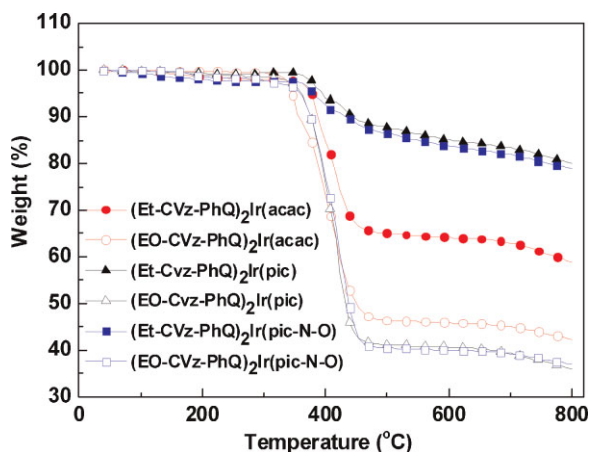
Figure 1. TGA trace of Ir(III) complexes measured at a scan rate of $10\,^\circ\mathrm{C\,min^{-1}}$ under N_2.

a substantial mixing of ligand-based $^3\pi$–π^* states, spin forbidden metal to ligand charge transfer (^{3}MLCT) and higher-lying ^{1}MLCT transition induced by the spin-orbit coupling effect.[41,42] The spin-orbit coupling was enhanced by the presence of closely-spaced π–π^* and MLCT states and the heavy-atom effect of Ir(III) center.[43,44] Under photoexcitation, all the Ir(III) complexes emitted an intense red light as shown in Figure 2b. By comparing with the emission spectrum of Et-Cvz-PhQ which emitted a deep-blue fluorescence at 423 nm, our developed Ir(III) complexes showed strong room-temperature phosphorescent band (λ_{em}: 595–616 nm) from the predominantly ligand-centered $^3\pi$–π^* excited state, which displayed a large Stokes shift (>247 nm). The phosphorescent quantum yields (Φ_{pl}) of Ir(III) complexes in chloroform solution were measured with $(piq)_2Ir(acac)$ as a standard (0.20).[45] The Φ_{pl} for $(Et\text{-}CVz\text{-}PhQ)_2Ir(pic\text{-}N\text{-}O)$, $(Et\text{-}CVz\text{-}PhQ)_2Ir(pic)$, $(Et\text{-}CVz\text{-}PhQ)_2Ir(acac)$, $(EO\text{-}CVz\text{-}PhQ)_2Ir(pic\text{-}N\text{-}O)$, $(EO\text{-}CVz\text{-}PhQ)_2Ir(pic)$, and $(EO\text{-}CVz\text{-}PhQ)_2Ir(acac)$ were in the range of 0.05–0.33, with $(EO\text{-}CVz\text{-}PhQ)_2Ir(pic)$ being the highest.

The emission lifetimes measured with 4 wt % Ir(III) complexes doped PMMA films and found to be well fitted to a single-exponential decay. The observed photoluminescence lifetimes (τ_p) are in the range of sub-microseconds ($\tau_p = 0.91$–1.34), consistent with emission from a triplet excited state (Table 1 and see the Supporting Information, Fig. S2).
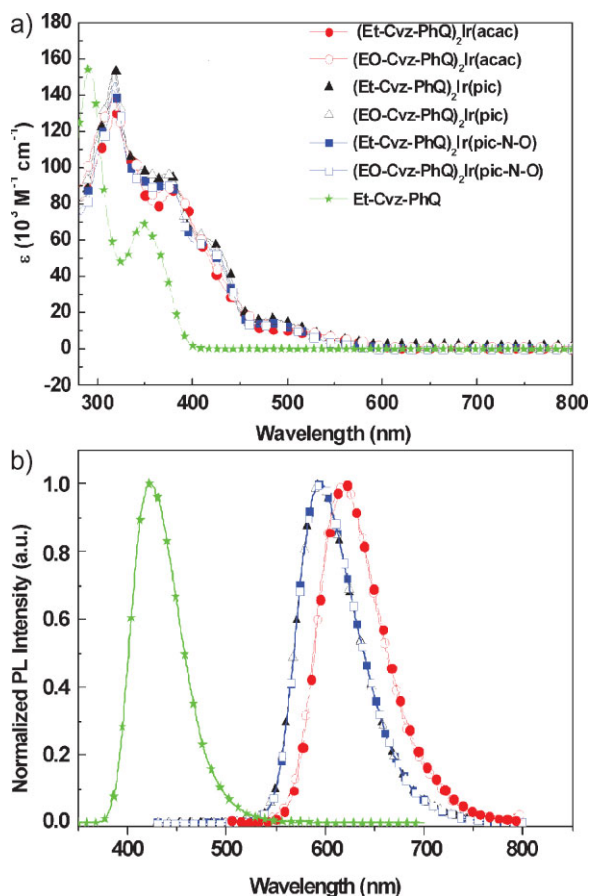
To investigate the charge carrier injection properties of the Ir(III) complexes and evaluate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, we carried out redox measurements using CV. All the Ir(III) complexes showed a reversible redox process over the anodic and cathodic range, suggesting that these Ir(III) complexes stabilized the formation of both cation and anion radicals in PhOLEDs. In the CVz-PhQ-based Ir(III) complexes, the electrochemical behavior and energy levels can be tuned by the ancillary ligands. As shown in Figure 3, the potentials for oxidation and reduction were observed in the range 0.85–0.98 V and -1.53 to -2.51 V, respectively. From these results, the HOMO and LUMO energy levels of the Ir(III) complexes were estimated to be -5.02 to -5.15 eV and 2.50–2.64 eV, respectively. Therefore, the electrochemical band gaps of the Ir(III) complexes were calculated to be in the range 2.50–2.52 eV, which were very similar to the optical band gaps (2.44–2.50 eV) from the onsets of the absorption spectrum. The HOMO and LUMO energy levels are summarized in Table 1.

To illustrate the EL properties of these Ir(III) complexes, typical PhOLEDs were fabricated using $(Et\text{-}CVz\text{-}PhQ)_2Ir(pic\text{-}N\text{-}O)$, $(Et\text{-}CVz\text{-}PhQ)_2Ir(pic)$, $(Et\text{-}CVz\text{-}PhQ)_2Ir(acac)$, $(EO\text{-}CVz\text{-}PhQ)_2Ir(pic\text{-}N\text{-}O)$, $(EO\text{-}CVz\text{-}PhQ)_2Ir(pic)$, and $(EO\text{-}CVz\text{-}PhQ)_2Ir(acac)$ as dopants in the emission layer. The PhOLEDs consisted of multilayer films with a configuration of ITO/PEDOT (40 nm)/ EML (50–60 nm)/BAlq (5 nm)/Alq$_3$ (20 nm)/Liq (0.5 nm)/Al (150 nm) as shown in Figure 4. Prior to organic layer deposition, ITO substrates were exposed to UV–ozone flux for 10 min and then degreased in acetone and isopropyl alcohol. Due to the introduction of the solubilizing group and the high molecular weights of all the Ir(III) complexes, an emitting layer was easily fabricated by spin-coating process. The Ir(III) complexes were doped into m-MTDATA:TPBI (1:1) as an emission layer at a concentration of 7 wt % and were spin-coated with chlorobenzene to give 50–60 nm thick films, after which all organic layers were grown by thermal evaporation at a base pressure of $<5 \times 10^{-8}$ Torr (Torr = 133.32 Pa) for the fabrication of PhOLEDs. The solution processing method offers a simple route for PhOLED fabrication and thus the emitting layers in the PhOLED can be prepared using the spin-coating method. Due to the amorphous nature of our developed Ir(III) complexes, they all possessed very good film-forming properties and good chemical compatibility with the m-MTDATA and TPBI host, resulting in a homogeneous distribution of Ir(III) complexes in the host. The detailed device architecture and molecular structures of m-MTDATA (4,4′,4″-tris[3-methyl-

Table 1. Hotophysical, electrochemical, and thermal data for synthesized red-emitting Ir(III) complexes.

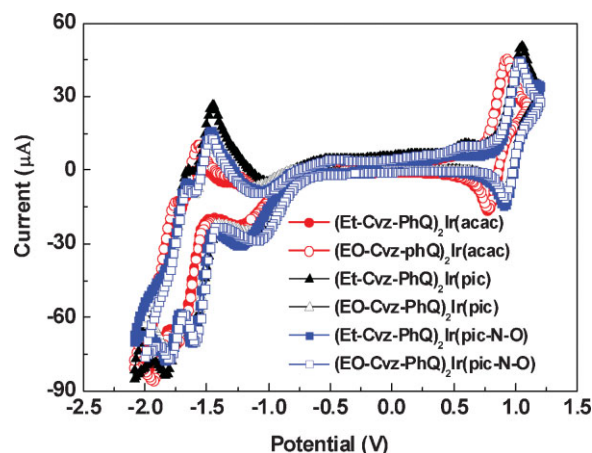| Compound	T_d [$^\circ$C][a]	T_g [$^\circ$C][b]	λ_{abs} [log ε (nm)][c]	λ_{em} [nm][d]	Φ_{pl} [%][e]	τ_p[μs][f]	HOMO/LUMO [ev][g]
(Et-CVz-PhQ)$_2$Ir(acac)	377	248	319(5.1), 383(4.9),413(4.7), 502(4.0)	619	0.05	0.98	−5.02/−2.50
(Et-CVz-PhQ)$_2$Ir(pic)	385	274	318(5.2), 352(5.0),377(5.0), 405(4.8),488(4.2)	595	0.24	1.16	−5.15/−2.63
(Et-CVz-PhQ)$_2$Ir(pic-N-O)	381	287	318(5.2), 353(5.0),375(5.0), 404(4.8), 479 (4.1)	595	0.20	1.12	−5.14/−2.62
(EO-CVz-PhQ)$_2$Ir(acac)	344	150	317(5.1), 378(5.0), 496(4.1),	616	0.03	0.91	−5.03/−2.51
(EO-CVz-PhQ)$_2$Ir(pic)	358	178	317(5.2), 373(5.0),413(4.8), 480(4.2)	595	0.33	1.30	−5.15/−2.63
(EO-CVz-PhQ)$_2$Ir(pic-N-O)	358	182	317(5.2), 373(5.0),406(4.8), 479(4.2)	595	0.30	1.34	−5.14/−2.64

[a] Temperature with 5% mass loss measure by TGA with a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ under N_2. [b] Glass transition temperature, determined by DSC with a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ under N_2. [c] Measured in CHCl$_3$ solution. [d] Maximum emission wavelength, measured in CHCl$_3$ solution. [e] Measured in 1×10^{-5} M degassed CHCl$_3$ solution relative to Ir(piq)$_2$(acac) ($\Phi_{pl} = 0.20$) with 450 nm excitation. [f] Measured emission lifetime at room temperature. [g] Determined from the onset of oxidation and reduction potentials.
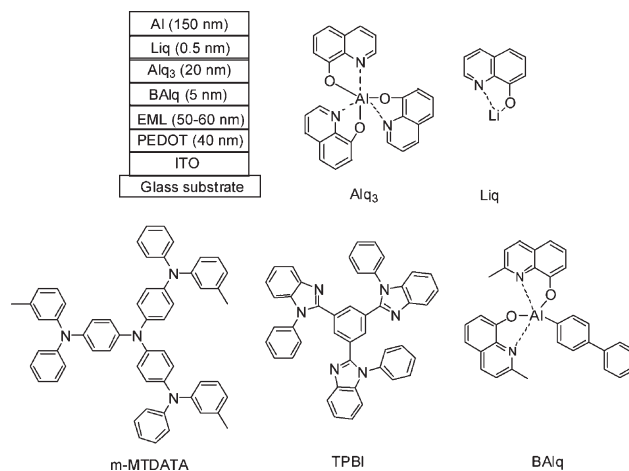
Figure 2. Absorption (a) and PL (b) spectra of Ir(III) complexes in CHCl$_3$ at 25 °C.

Figure 3. Cyclic voltammograms of Ir(III) complexes in tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$) at a scan rate of 100 mV s^{-1}.

Figure 4. Device architectures and chemical structure of the materials used in the PhOLEDs.

phenylphenyl)triphenylamine]), TPBI (1,3,5-tris[2-N-phenyl-benzimidazolyl]benzene), BAlq (bis[2-methyl-8-quinolinato]-4-phenylphenolate aluminum), Alq$_3$ (tris[8-hydroxyquinolinato]aluminum), and Liq (8-hydroxyquinolinatolithium), are shown in Figure 4.
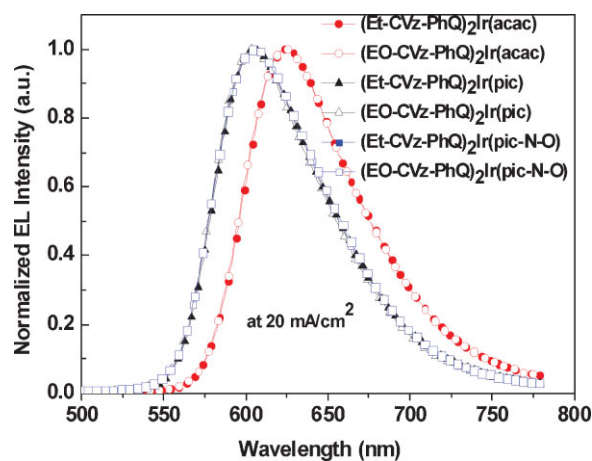
Figure 5 shows the EL spectra of the Ir(III) complexes for PhOLEDs. The EL spectra of all PhOLEDs were almost identical to the PL spectra, indicating that EL and PL are from the same excited state. The absence of any emission peak of m-MTDATA indicated the effective charge trapping on the Ir(III) complexes and/or effective energy transfer to the Ir(III) complexes. The maximum emission peaks of (Et-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), (EO-CVz-PhQ)$_2$Ir(pic-N-O), and (EO-CVz-PhQ)$_2$Ir(pic) were 604 nm, and those of (Et-CVz-PhQ)$_2$Ir(acac) and (EO-CVz-PhQ)$_2$Ir(acac) were 623 nm corresponding to red color. There was no sign of the metal complex aggregation in the fabricated PhOLEDs. The maximum EL peak was dependent on the ancillary ligands. Especially, the EL spectrum of (Et-CVz-PhQ)$_2$Ir(acac) and (EO-CVz-PhQ)$_2$Ir(acac) was also red-shifted by 20 nm compared to that of (Et-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), (EO-CVz-PhQ)$_2$Ir(pic-N-O), and (EO-CVz-PhQ)$_2$Ir(pic) as in the PL emission. Typical Commission Internationale de L'Eclairage (CIE) coordinates versus luminance of the PhOLEDs based on (Et-CVz-PhQ)$_2$Ir(pic-N-O) (0.61, 0.38), (Et-CVz-PhQ)$_2$Ir(pic) (0.60, 0.38), (Et-CVz-PhQ)$_2$Ir(acac) (0.65, 0.34), (EO-CVz-PhQ)$_2$Ir(pic-N-O)

Figure 5. EL spectra of Ir(III) complexes.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
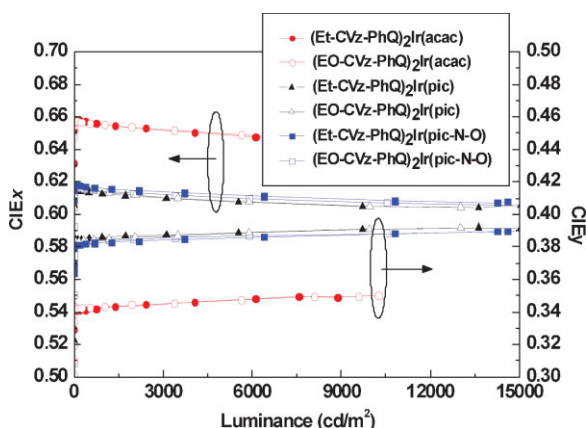
Figure 6. CIE coordinates dependence on the luminance. (closed symbols: CIEx, open symbol: CIEy).
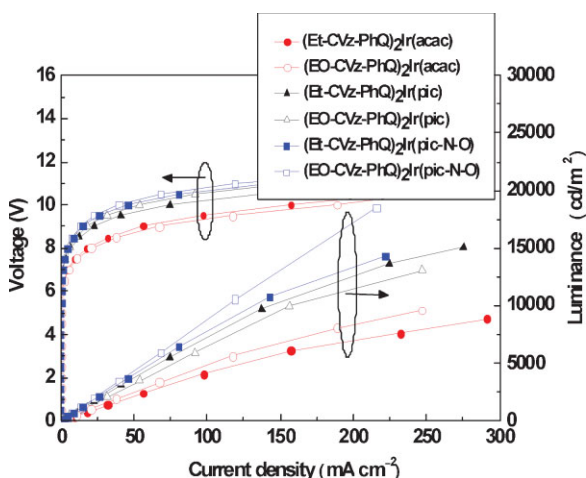
Figure 7. Current density–voltage–luminance characteristics for PhOLEDs.

(0.61, 0.38), (EO-CVz-PhQ)$_2$Ir(pic) (0.60, 0.38), and (EO-CVz-PhQ)$_2$Ir(acac) (0.65, 0.34) are presented in Figure 6. There was little or no variation in the CIE coordinates with luminance for the PhOLEDs using Ir(III) complexes as dopants. The CIE coordinates of the Ir(III) complexes were very close to the National television system committee of red standard with the CIE coordinate of (0.67, 0.33). From these results, stable red EL was obtained from the Ir(III) complexes in the entire active PhOLED area. These

encouraging results showed that the performance of the Ir(III) complexes containing pic-N-O-based PhOLEDs was remarkably higher than that of the Ir(III) complexes containing pic- and acac-based PhOLEDs.

Figure 7 presents the current density–voltage–luminance (J–V–L) characteristics of PhOLEDs using different ancillary ligands and different solubilizing groups at the CVz unit. The PhOLED performance and EL emission characteristics are summarized in Table 2. The PhOLEDs containing the Ir(III) complexes show turn-on voltages of 5–7 V. The slight difference in turn-on voltages of these PhOLEDs was attributed to the difference in the thickness of the spin-coated emission layers. The observed higher current densities at the same voltage of (Et-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), (EO-CVz-PhQ)$_2$Ir(pic-N-O), and (EO-CVz-PhQ)$_2$Ir(pic) relative to (Et-CVz-PhQ)$_2$Ir(acac) and (EO-CVz-PhQ)$_2$Ir(acac) could be due to the higher electron mobilities. Pic-N-O and pic ancillary ligands have a stronger negative inductive effect than the acac ancillary ligand to the Ir(III) complexes. Ir(III) complexes that withdraw electron density by the inductive effect lower the energies of the highest occupied and lowest unoccupied π-MOs, which increase the electron mobility in the Ir(III) complexes.[46] Among the Ir(III) complexes, the maximum brightness of 18 500 cd m^{-2} was obtained at 215 mA cm^{-2} using the (EO-CVz-PhQ)$_2$Ir(pic-N-O) dopant. The external quantum efficiency and luminance efficiency of the Ir(III) complexes as a function of luminance are depicted in Figure 8. With increase in luminance, the external quantum efficiency and luminance efficiency of the Ir(III) complexes were very stable and the PhOLEDs performance was optimized for (EO-CVz-PhQ)$_2$Ir(pic-N-O) with a maximum external quantum efficiency and luminance efficiency of 5.53% and 8.89 cd A^{-1}, respectively, at 3 000 cd m^{-2}. The PhOLED performance was significantly improved by the introduction of the electron-withdrawing pic-N-O ancillary ligand to the Ir(III) complexes.

To understand the structures and orbital properties that are related to the electron and hole mobilities, we performed density functional theory calculations for (Et-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), (Et-CVz-PhQ)$_2$Ir(acac), (EO-CVz-PhQ)$_2$Ir(pic-N-O), (EO-CVz-PhQ)$_2$Ir(pic), and (EO-CVz-PhQ)$_2$Ir(acac) using the Becke's three parameterized Lee-Yang-Parr exchange functional (B3LYP) using a suite of Gaussian 03 program.[47] The split valance 6–31G* basis sets were used except Ir(III) metal for which the LanL2DZ effective core potential was used. The calculated Ir(III) complexes had very similar structures with octahedral geometry. In the case of (Et-CVz-PhQ)$_2$Ir(acac), the N and O atoms of the main ligand (Et-CVz-PhQ) as well as two O atoms of the acac ancillary ligand are coordinated to the Ir(III) metal. Similarly, in

Table 2. EL performance of red PhOLED based on a solution processed emitting layer.

EML	EQE [%][a]	CE [cd/A][a]	PE [lm/W][a]	EQE [%][b]	LE [cd/A][b]	PE [lm/W][b]	CIE (x, y)[b]
(Et-CVz-PhQ)$_2$Ir(acac)	4.08 (8.5)	4.31	1.79 (6.5)	4.04 (8.0)	4.25	1.65	(0.65, 0.34)
(Et-CVz-PhQ)$_2$Ir(pic)	4.45 (8.5)	7.70	3.26 (7.0)	4.41 (9.0)	7.65	2.70	(0.60, 0.38)
(Et-CVz-PhQ)$_2$Ir(pic-N-O)	4.98 (8.5)	8.36	3.50 (7.0)	4.90 (9.5)	8.30	2.80	(0.61, 0.38)
(EO-CVz-PhQ)$_2$Ir(acac)	4.74 (8.5)	5.08	2.13 (7.0)	4.72(8.0)	5.03	1.97	(0.65, 0.34)
(EO-CVz-PhQ)$_2$Ir(pic)	3.80 (9.5)	6.51	2.37 (8.0)	3.79 (9.0)	6.46	2.20	(0.60, 0.38)
(EO-CVz-PhQ)$_2$Ir(pic-N-O)	5.53(10.0)	8.89	3.41 (7.0)	5.51(9.5)	8.52	2.82	(0.61, 0.38)

[a] Maximum efficiency. [b] Values collected at a current density of 20 mA cm^{-2}.
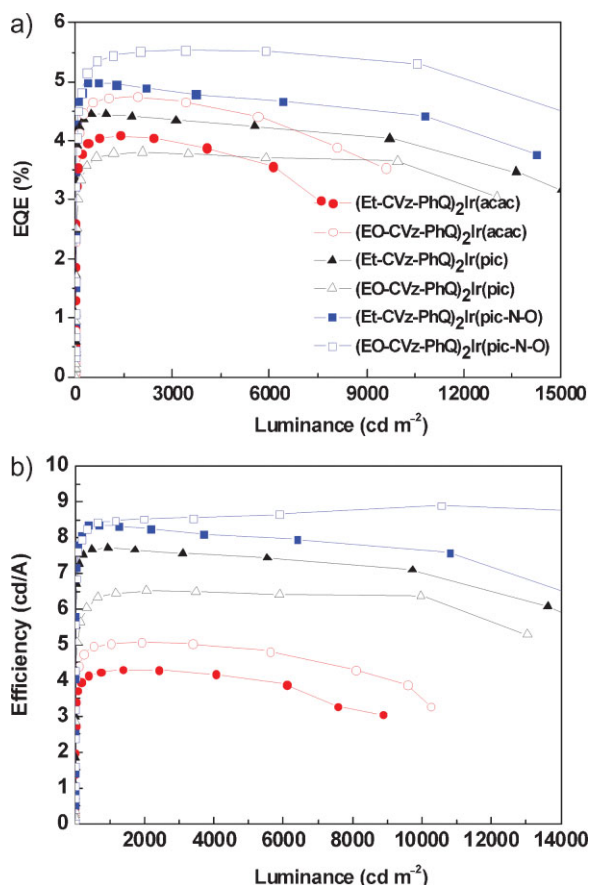
Figure 8. External quantum efficiency (a) and luminance efficiency (b) as a function of luminance for PhOLEDs.

(Et-CVz-PhQ)$_2$Ir(pic-N-O)/(Et-CVz-PhQ)$_2$Ir(pic), (two O atoms of pic-N-O)/(one N and one O atom) are coordinated to the Ir(III) metal. The other Ir(III) complexes, where the Et solubilizing group is replaced by the EO solubilizing group, (EO-CVz-PhQ)$_2$Ir(acac), (EO-CVz-PhQ)$_2$Ir(pic-N-O), and (EO-CVz-PhQ)$_2$Ir(pic) had the same coordination geometry.

The HOMOs and LUMOs shown in Figure 9 looked quite similar, despite the slight change for the Et and EO solubilizing groups. The HOMO-LUMO energy gaps for (Et-CVz-PhQ)$_2$Ir(acac), (Et-CVz-PhQ)$_2$Ir(pic-N-O), and (Et-CVz-PhQ)$_2$Ir(pic) were calculated as 2.99 eV, 2.91 eV, and 2.86 eV, which corresponded to the absorption wavelengths of 414, 425, and 434 nm, respectively. For (EO-CVz-PhQ)$_2$Ir(acac), (EO-CVz-PhQ)$_2$Ir(pic-N-O) and (EO-CVz-PhQ)$_2$Ir(pic), these values were 3.02, 2.99, and 2.86 eV with 410, 414, and 434 nm, respectively. These calculated results were in good agreement with the experimentally observed absorption peaks at around 300–400 nm, considering that the calculated absorption peak is often blue-shifted with respect to the experimental value. It is generally accepted that the transport of excess electrons/holes in organic materials takes place via charge carrier hopping. Consequently, the electron and hole mobilities can be roughly estimated from the transfer integral between the frontier molecular orbitals such as HOMO-1, HOMO, LUMO, and LUMO+1.[48] As such, the transfer integrals for (Et-CVz-PhQ)$_2$Ir(acac), (EO-CVz-PhQ)$_2$Ir(acac), (Et-CVz-PhQ)$_2$Ir(pic-N-

O), (EO-CVz-PhQ)$_2$Ir(pic-N-O), (Et-CVz-PhQ)$_2$Ir(pic), and (EO-CVz-PhQ)$_2$Ir(pic) were calculated to be 0.041, 0.068, 0.068, 0.041, 0.123, and 0.068 eV, respectively. This was consistent with the experimental finding that the Ir(III) complexes with pic-N-O or pic ancillary ligands had higher electron mobility than those with the acac ancillary ligand.
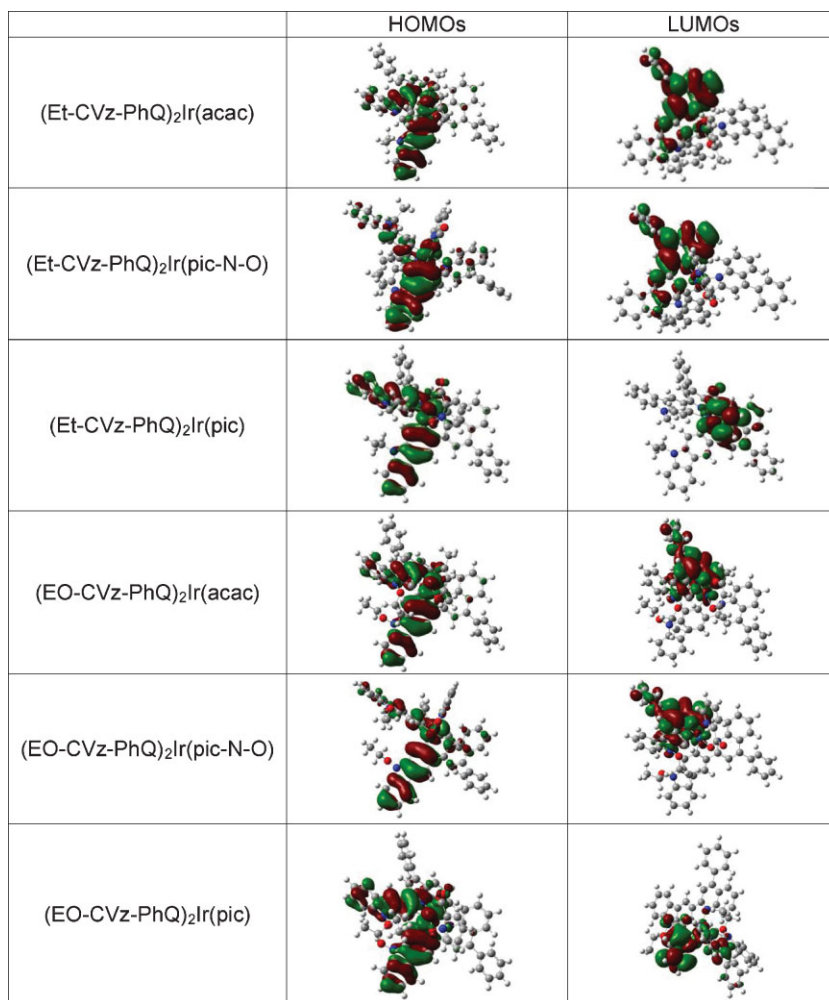
3. Conclusions

We have demonstrated for the first time the synthesis of Ir(III) complexes using the CVz-PhQ main ligands and pic-N-O ancillary ligand for the fabrication of PhOLEDs. The fabricated PhOLEDs showed reasonably high brightness, external quantum efficiency and luminance efficiency of 18 500 cd m^{-2}, 5.53%, and 8.89 cd A^{-1}, respectively. These performances of the Ir(III) complexes are some of the highest ever reported for solution processable PhOLEDs. The combination of good efficiency and color purity elevates the material to a promising candidate for red phosphorescent dopants for PhOLEDs.

4. Experimental

General Information: Unless otherwise specified, all reactions were carried out under a N$_2$ atmosphere using standard Schlenk techniques. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture free atmosphere. Column chromatography was performed using silica gel (Merck, 250–430 mesh). ^{1}H- and ^{13}C-NMR spectra were recorded using a Bruker AM-300 spectrometer and the chemical shifts were recorded in ppm units. The thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e, DSC 822e analyzer under an N$_2$ atmosphere at a heating rate of 10 °C min^{-1}. CV was carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV s^{-1} in a 0.1 M solution of tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$) in anhydrous acetonitrile/benzene (1:1.5 v/v). A platinum wire was used as the counter electrode and an Ag/AgNO$_3$ electrode was used as the reference electrode. All of the electrochemical experiments were performed in a glove box under an Ar atmosphere at room temperature. The absorption and PL spectra were measured by using a Jasco V-570 UV–Vis spectrometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively.

General Procedure for the Synthesis of (Et-CVz-PhQ)$_2$Ir(pic-N-O): The cyclometalated Ir(III) μ-chloro-bridged dimer was synthesized by the method reported by Nonoyama [49]. 9-Ethyl-3-(4-phenylquinolin-2-yl)-9H-carbazole (Et-CVz-PhQ) (3.34 g, 8.36 mmol) and IrCl$_3$·H$_2$O (1.14 g, 3.34 mmol) were added to a mixture of 2-ethoxyethanol and water (130 mL, 3:1 v/v). The reaction mixture was stirred at 140 °C for 20 h and a brown precipitate was obtained after cooling to room temperature. The precipitate was collected and washed with deionized water (100 mL) and methanol (50 mL). Subsequently, the cyclometalated iridium dimer was dried under vacuum to afford a brown solid. Cyclometalated iridium dimer (2.8 g, 1.37 mmol) and pic-N-O (0.95 g, 6.85 mmol) were mixed with Na$_2$CO$_3$ (1.45 g, 13.7 mmol) in 2-ethoxyethanol (100 mL). The mixture was refluxed for 12 h under a N$_2$ atmosphere. After cooling at room temperature, the crude solution was poured onto water and extracted with ethyl acetate, dried over anhydrous MgSO$_4$ and evaporated in a vacuum. The residue was purified by silica gel chromatography (hexane:ethyl acetate = 1:4) as an eluent and further purified by recrystallization twice using dichloromethane/hexane mixture to afford a red solid complex (1.25 g, 84%). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.92 (d, J = 8.7 Hz, 1H), 8.78 (s, 1H), 8.64 (s, 1H), 8.26 (s, 2H), 8.14 (d, J = 7.5 Hz, 1H), 8.04 (t, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.80–7.55 (m, 14H), 7.49–7.10 (m, 10H), 7.02 (s, 1H), 6.78 (t, 1H), 6.31 (s, 1H), 3.92–3.60 (m, 4H), 0.95

	HOMOs	LUMOs
(Et-CVz-PhQ)₂Ir(acac)		
(Et-CVz-PhQ)₂Ir(pic-N-O)		
(Et-CVz-PhQ)₂Ir(pic)		
(EO-CVz-PhQ)₂Ir(acac)		
(EO-CVz-PhQ)₂Ir(pic-N-O)		
(EO-CVz-PhQ)₂Ir(pic)		

Figure 9. Calculated HOMOs and LUMOs of Ir(III) complexes.

(m, 8H), 7.38–7.26 (m, 8H), 7.15–7.12 (m, 4H), 6.59 (s, 2H), 4.76 (s, 1H), 3.85–3.66 (m, 4H), 1.58 (s, 6H), 0.82 (t, J = 7.2Hz, 6H), ^{13}C NMR (300 MHz, CDCl₃, δ): 185.5, 170.1, 149.6, 149.4, 148.7, 141.7, 139.6, 139.1, 138.3, 129.9, 129.8, 128.7, 127.0, 125.9, 125.3, 125.0, 124.4, 124.2, 119.0, 118.8, 118.4, 118.3, 117.2, 115.1, 108.1, 100.2, 36.9, 31.5,28.3, 22.6, 14.1, 12.9. Anal. calcd. for C63H49N4O2Ir: C 69.66, H 4.55, N 5.16; found: C 69.47, H 4.65, N 5.17.

General Procedure for the Synthesis of (EO-CVz-PhQ)₂Ir(pic-N-O): (EO-CVz-PhQ)₂Ir(pic-N-O) was prepared in a similar procedure to that described for (Et-CVz-PhQ)₂Ir(pic-N-O) except that 9-(2-(2-methoxyethoxy)ethyl)-3-(4-phenylquinolin-2-yl)-9H-carbazole (EO-CVz-PhQ) was used instead of Et-CVz-PhQ. (EO-CVz-PhQ)₂Ir(pic-N-O) was obtained as a red solid in 82% yield. 1H NMR (300 MHz, CDCl₃, δ): 8.90 (d, J = 8.7 Hz, 1H), 8.77 (s, 1H), 8.64 (s, 1H), 8.26 (s, 2H), 8.13 (d, J = 7.5 Hz, 1H), 8.04 (t, 2H), 7.89 (d, J = 7.5 Hz, 2H), 7.80–7.11 (m, 23H), 7.04 (s, 1H), 6.79 (t, 1H), 6.34 (s, 1H), 4.08–3.77 (m, 4H), 3.47–2.90 (m, 18H), ^{13}C NMR (300 MHz, CDCl₃, δ): 172.0, 170.5, 168.8, 152.8, 150.1, 148.7, 148.5, 148.2, 147.9, 146.4, 142.7, 142.2, 140.3, 140.2, 138.9, 138.0, 137.7, 137.6, 137.3, 131.1, 129.7, 129.6, 128.9, 128.7, 128.6, 128.0, 127.1, 126.3, 125.8, 125.5, 124.9, 124.6, 124.5, 124.0, 123.8, 119.6, 119.1, 118.9, 118.5, 117.9, 116.9, 115.0, 113.7, 108.9, 108.6, 71.5, 71.4, 70.2, 70.1, 68.1, 67.7, 58.8, 58.7, 42.0. Anal. calcd. for C70H58N5O7Ir: C 66.02, H 4.59, N 5.50; found: C 65.62, H 4.65, N 5.50.

Other Ir(III) complexes, (EO-CVz-PhQ)₂Ir(pic) and (EO-CVz-PhQ)₂Ir(acac) were also prepared from the same main ligand and different ancillary ligands by a similar procedure. (EO-CVz-PhQ)₂Ir(pic). ^{1}H NMR (300 MHz, CDCl₃, δ): 8.93 (d, J = 8.7 Hz, 1H), 8.79 (s, 1H), 8.67 (s, 1H), 8.29 (s, 2H), 8.14 (d, J = 7.5 Hz, 1H), 8.06 (t, 2H), 7.90 (d, J = 7.5 Hz, 2H), 7.91–7.11 (m, 23H), 7.07 (s, 1H), 6.82 (t, 1H), 6.39 (s, 1H), 4.07–3.80 (m, 4H), 3.48–2.90 (m, 18H), ^{13}C NMR (300 MHz, CDCl₃, δ): 172.0, 170.4, 168.7, 152.6, 150.0, 148.6, 148.3, 148.1, 147.8, 146.2, 142.6, 142.0, 140.2, 140.1, 138.7, 137.8, 137.5, 137.3, 137.2, 131.1, 129.5, 128.8, 128.6, 128.5, 127.8, 127.1, 126.9, 126.2, 125.7, 125.4, 124.8, 124.5, 124.4, 123.9, 123.7, 119.4, 119.0, 118.7, 118.4, 117.7, 116.8, 114.9, 113.5, 108.7, 108.4, 71.3, 70.0, 67.9, 67.5, 58.0, 41.9. Anal. calcd. for C70H58N5O6Ir: C 66.86, H 4.65, N 5.57; found: C 66.56, H 4.65, N 5.58.

(EO-CVz-PhQ)₂Ir(acac) ^{1}H NMR (300 MHz, CDCl₃, δ): 8.66 (s, 2H), 8.27 (s, 2H), 8.06 (d, J = 7.5 Hz, 2H), 7.92–7.81 (m, 4H), 7.72–7.61 (m, 8H), 7.43–7.22(m, 8H), 7.17–7.12 (m, 4H), 6.65 (s, 2H), 4.75 (s, 1H), 4.08–3.87 (m, 4H), 3.38–2.95 (m, 18H), 1.59 (s, 6H), ^{13}C NMR (300 MHz, CDCl₃, δ): 185.4, 170.1, 149.6, 149.5, 149, 142.0, 140.0, 139.4, 138.2, 129.8, 128.7, 127.0, 126.0, 125.4, 124.3, 119.1, 118.5, 118.4, 117.2, 115.0, 108.6, 100.1, 71.6, 70.2, 68.0, 59.8, 41.9, 28.3. Anal. calcd. for C69H61N4O6Ir: C 67.13, H 4.98, N 4.54; found: C 66.79, H 5.01 N 4.58.

Device Fabrication: To measure EL properties, prior to spin coating with the PEDOT:PSS layer, the ITO was pre-cleaned and UV-ozone treated. Then a 40 nm-thick PEDOT:PSS layer was spin coated onto the ITO and baked in a N₂ environment at 120 °C for 10 min. Then, a 50–60 nm-thick emitting layer was prepared by spin-coating in chlorobenzene solution at 7 wt % of Ir(III) complexes doped into the m-MTDATA:TPBI (1:1). Successively, BALq, Alq₃, Liq and Al were evaporated at a base pressure of 5 × 10⁻⁸ Torr. The film thickness was measured with an α-Step IQ surface profiler (KLA Tencor, San Jose, CA, USA). Emission lifetimes were obtained by exponential fit of emission decay curves recorded on PMT (Hamamatsu) attached monochromator (Acton Research Corp.) with excitation of 355 nm wavelength (Nd-YAG laser, 10 ns pulse width).

(t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H), ^{13}C NMR (300 MHz, CDCl₃, δ): 172.0, 170.6, 168.9, 153.0, 150.1, 148.9, 148.2, 148.1, 148.0, 146.5, 142.4, 142.0, 139.7, 139.6, 138.6, 137.9, 137.8, 137.7, 137.3, 131.3, 129.8, 129.7, 128.9, 128.8, 128.7, 128.1, 127.2, 127.1, 127.0, 126.3, 125.8, 125.7, 125.5, 125.4, 124.8, 124.6, 124.4, 124.2, 124.0, 119.3, 119.1, 119.0, 118.8, 118.4, 117.9, 116.9, 115.1, 113.7, 108.5, 108.1, 37.0, 36.9, 13.1, 12.5. Anal. calcd. for C64H46N5O3Ir: C 68.31, H 4.12, N 6.22; found: C 67.97, H 4.20, N 6.15.

Other Ir(III) complexes, (Et-CVz-PhQ)₂Ir(pic), and (Et-CVz-PhQ)₂Ir-(acac) were also prepared from the same main ligand and different ancillary ligands by a similar procedure. (Et-CVz-PhQ)₂Ir(pic). ^{1}H NMR (300 MHz, CDCl₃, δ): 8.93 (d, J = 8.7 Hz, 1H), 8.79 (s, 1H), 8.65 (s, 1H), 8.28 (s, 2H), 8.15 (d, J = 7.5 Hz, 1H), 8.04 (t, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.81–7.56 (m, 14H), 7.52–7.11 (m, 10H), 7.03 (s, 1H), 6.79 (t, 1H), 6.33 (s, 1H), 3.93–3.58 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H), ^{13}C NMR (300 MHz, CDCl₃, δ): 172.0, 170.7, 168.9, 153.0, 150.1, 148.9, 148.3, 148.1, 148.0, 146.5, 142.4, 142.0, 139.8, 139.7, 138.7, 137.9, 137.8, 137.7, 137.3, 131.3, 129.8, 129.7, 128.9, 128.8, 128.7, 128.1, 127.2, 127.1, 126.3, 125.9, 125.7, 125.6, 125.5, 124.8, 124.4, 124.2, 124.0, 119.3, 119.2, 119.0, 118.9, 118.4, 117.9, 116.9, 115.1, 113.8, 108.6, 108.1, 37.1, 36.8, 13.1, 12.5. Anal. calcd. for C64H46N5O2Ir: C 69.29, H 4.18, N 6.31; found: C 68.89, H 4.25, N 6.25.

(Et-CVz-PhQ)₂Ir(acac). ^{1}H NMR (300 MHz, CDCl₃, δ): 8.63 (s, 2H), 8.24 (s, 2H), 8.05 (d, J = 7.5Hz, 2H), 7.90–7.79 (m, 4H), 7.71–7.62

The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. To characterize the PhOLEDs, the J–V–L changes were measured using a current/voltage source meter (Keithley 238) and an optical power meter (CS-1000, LS-100). All processes and measurements were carried out in the open air at room temperature.

Acknowledgements

[1] N. Bera, N. Cumpstey, P. L. Burn, I. D. W. Samuel, *Adv. Funct. Mater.* **2007**, *17*, 1149.

[2] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.

[3] M. A. Baldo, D. F. O'Brien, M. E. Thompson, S. R. Forrest, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *60*, 14 422.

[4] C. Adachi, M. A. Baldo, D. F. O'Brien, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2001**, *90*, 5048.

[5] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, *Appl. Phys. Lett.* **2001**, *79*, 156.

[6] S. C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata, I. D. W. Samuel, *Adv. Mater.* **2002**, *14*, 975.

[7] X. H. Yang, F. I. Wu, D. Neher, C. H. Chien, C. F. Shu, *Chem. Mater.* **2008**, *20*, 1629.

[8] Y. J. Pu, M. Higashidate, K. I. Nakayama, J. Kido, *J. Mater. Chem.* **2008**, *18*, 4183.

[9] S. C. Lo, G. J. Richards, J. P. I. Markham, E. B. Naamdas, S. Sharma, P. L. Burn, I. D. W. Samuel, *Adv. Funct. Mater.* **2005**, *15*, 1451.

[10] P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, *Nature* **1999**, *356*, 6364.

[11] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.

[12] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539.

[13] J. Ding, J. Lü, Y. Cheng, Z. Xie, L. Wang, X. Jing, F. Wang, *Adv. Funct. Mater.* **2008**, *18*, 2754.

[14] B. Liang, L. Wang, Y. Xu, H. Shi, Y. Cao, *Adv. Funct. Mater.* **2007**, *17*, 3580.

[15] G. Zhou, W. Y. Wong, B. Yao, Z. Xie, L. Wang, *Angew. Chem. Int. Ed.* **2007**, *46*, 1149.

[16] A. W. Freeman, S. C. Koene, P. R. L. Malenfant, M. E. Thompson, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2000**, *122*, 12385.

[17] M. Halim, J. N. G. Pillow, I. D. W. Samuel, P. L. Burn, *Adv. Mater.* **1999**, *11*, 371.

[18] P. W. Wang, Y. J. Lui, C. Devadoss, P. Bharathi, J. S. Moore, *Adv. Mater.* **1996**, *8*, 237.

[19] H. J. Bolink, E. Coronado, S. G. Santamaria, M. Sessolo, N. Evans, C. Klein, E. Baranoff, K. Kalyanasundaram, M. Gräetzel, Md, K. Nazeeruddin, *Chem. Commun.* **2007**, 3276.

[20] P. Coppo, E. A. Plummer, L. De Cola, *Chem. Commun.* **2004**, 1774.

[21] T. Sajoto, P. I. Djurovich, A. B. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes, S. R. Forrest, *Inorg. Chem.* **2005**, *44*, 7992.

[22] Y. You, S. Y. Park, *J. Am. Chem. Soc.* **2005**, *127*, 12438.

[23] C. Yang, X. Zhang, H. You, L. Zhu, L. Chen, L. Zhu, Y. Tao, D. Ma, Z. Shuai, J. Qin, *Adv. Funct. Mater.* **2007**, *17*, 651.

[24] C. L. Ho, W. Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, *Adv. Funct. Mater.* **2008**, *18*, 928.

[25] Y. Tao, Q. Wang, C. Yang, K. Zhang, Q. Wang, T. Zou, J. Qin, D. Ma, *J. Mater. Chem.* **2008**, *18*, 4091.

[26] K. R. J. Thomas, J. T. Lin, Y. T. Tao, C. W. Ko, *Adv. Mater.* **2000**, *12*, 1949.

[27] K. R. J. Thomas, J. T. Lin, Y. T. Tao, C. W. Ko, *J. Am. Chem. Soc.* **2000**, *123*, 9404.

[28] C. L. Ho, W. Y. Wong, Z. Q. Gao, C. H. Chen, K. W. Cheah, B. Yao, Z. Xie, Q. Wang, D. Ma, L. Wang, X. M. Yu, H. S. Kwok, Z. Lin, *Adv. Funct. Mater.* **2008**, *18*, 319.

[29] C. J. Tonzola, A. P. Kulkarni, A. P. Gifford, W. Kaminsky, S. A. Jenekhe, *Adv. Funct. Mater.* **2007**, *17*, 863.

[30] A. P. Kulkarni, X. Kong, S. A. Jenekhe, *Adv. Funct. Mater.* **2006**, *16*, 1057.

[31] A. P. Kulkarni, P. T. Wu, T. W. Kwon, S. A. Jenekhe, *J. Phys. Chem. B* **2005**, *109*, 19584.

[32] Y. Zhu, A. P. Kulkarni, S. A. Jenekhe, *Chem. Mater.* **2005**, *17*, 5225.

[33] J. Huang, T. Watanabe, K. Ueno, Y. Yang, *Adv. Mater.* **2007**, *19*, 739.

[34] J. K. Stille, *Macromolecules* **1981**, *14*, 870.

[35] A. K. Agrawal, S. A. Jenekhe, *Macromolecules* **1991**, *24*, 6806.

[36] A. K. Agrawal, S. A. Jenekhe, *Chem. Mater.* **1992**, *4*, 95.

[37] S. J. Lee, J. S. Park, K. J. Yoon, Y. I. Kim, S. H. Jin, S. K. Kang, Y. S. Gal, S. Kang, J. Y. Lee, J. W. Kang, S. H. Lee, H. D. Park, J. J. Kim, *Adv. Funct. Mater.* **2008**, *18*, 3922.

[38] C. L. Ho, W. Y. Wong, G. J. Zhou, Z. Xie, L. Wang, *Adv. Funct. Mater.* **2007**, *17*, 2925.

[39] S. C. Lo, C. P. Shipley, R. N. Bera, R. E. Harding, A. R. Cowley, P. L. Burn, I. D. W. Samuel, *Chem. Mater.* **2006**, *18*, 5119.

[40] P. J. Hay, *J. Phys. Chem. A* **2002**, *106*, 1634.

[41] A. P. Wilde, K. A. King, R. J. Watts, *J. Phys. Chem.* **1991**, *95*, 629.

[42] M. C. Columbo, A. Hauser, H. U. Güdel, *Top. Curr. Chem.* **1994**, *171*, 143.

[43] Y. Wang, N. Herron, V. V. Grushin, D. LeCloux, V. Petrov, *Appl. Phys. Lett.* **2001**, *79*, 449.

[44] F. O. Garces, K. A. King, R. J. Watts, *Inorg. Chem.* **1998**, *27*, 3464.

[45] Y. J. Su, H. L. Huang, C. L. Li, C. H. Chien, Y. T. Tao, P. T. Chou, S. Dataa, R. S. Liu, *Adv. Mater.* **2003**, *15*, 884.

[46] I. Avilov, P. Minoofar, J. Cornil, L. De Cola, *J. Am. Chem. Soc.* **2007**, *129*, 8247.

[47] Gaussian 03, Revision A1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc.: Pittsburgh, PA, **2003**.

[48] E. F. Valeev, V. Coropceanu, D. A. da Silva Filho, S. Salman, J. L. Bredas, *J. Am. Chem. Soc.* **2006**, *128*, 9882.

[49] M. Nonoyama, *J. Organomet. Chem.* **1975**, *86*, 263.