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Synthesis of a high-efficiency red phosphorescent emitter for organic light-emitting diodes

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Four novel red phosphorescent emitter compounds bis(1-phenylisoquinolinato-$N,C^{2'}$)iridium(acetylacetonate), $(\mathrm{piq})_2\mathrm{Ir(acac)}$, bis(1-(1′-naphthyl)isoquinolinato-$N,C^{2'}$)iridium(acetylacetonate), $(1\text{-niq})_2\mathrm{Ir(acac)}$, bis(1-(2′-naphthyl)isoquinolinato-$N,C^{2'}$)iridium(acetylacetonate), $(2\text{-niq})_2\mathrm{Ir(acac)}$ and bis(1-phenyl-5-methylisoquinolinato-$N,C^{2'}$)iridium(acetylacetonate), $(\text{m-piq})_2\mathrm{Ir(acac)}$, have been synthesized and fully characterized. Electroluminescent devices with a configuration of ITO/NPB/CBP:dopant/BCP/$\mathrm{AlQ_3}$/Al were fabricated. All devices emitted in the red region with an emission ranging from 624 to 680 nm. $(\text{m-piq})_2\mathrm{Ir(acac)}$ shows a maximum brightness of 17 164 cd m^{-2} at a current density of $J = 300$ mA cm^{-2} and the best luminance efficiency of 8.91 cd A^{-1} at a current density of $J = 20$ mA cm^{-2}. $(1\text{-niq})_2\mathrm{Ir(acac)}$ exhibits pure-red emission with 1931 CIE (Commission International de L'Eclairage) chromaticity coordinates $x = 0.701$, $y = 0.273$.

Introduction

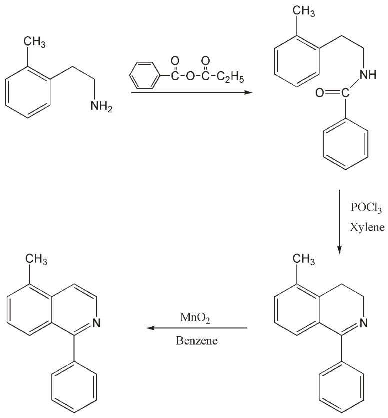
In the past decade, great progress has been made in organic light-emitting diodes (OLEDs).[1–3] Both red-emitting fluorescent and phosphorescent dopants have been investigated. Fluorescent dyes, including [2-methyl-6-[2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizin-9-yl]-4*H*-pyran-4-ylidene]propanedinitrile (DCM2) and 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyl-julolidyl-9-enyl)-4*H*-pyran (DCJTB) series, usually exhibit a maximum external quantum efficiencies limited to 1–2%.[4,5] However, by employing triplet-based phosphorescent dyes in OLEDs where both singlet and triplet excited states participate, the external quantum efficiency can reach as high as 5–6%.[6,7] Recently, the photophysics of cyclometalated metal complexes has been the subject of extensive studies. OLEDs based on the triplet emitters such as Ir(III),[8,9] Pt(II),[10] Ru(II),[11] and Os(II)[12] have been demonstrated with high efficiency. The best performing phosphorescent dopants have been shown to be those based on iridium complexes.[10,13] These iridium complexes are highly suitable for OLED applications due to their relatively short excited state lifetime, high photoluminescence efficiencies and excellent color tunability.[13]

Lately, Okada and coworkers demonstrated a high efficiency red OLED,[14] $\mathrm{Ir(piq)_3}$ [tris(1-phenylisoquinolinato-N,C^{2})iridium-(III)], which exhibits a maximum emission peak at 623 nm, and efficiency of the electroluminescence device is 8.0 lm W^{-1}, 9.3 cd A^{-1} at 100 cd m^{-2}, 6.3 lm W^{-1}, 8.4 cd A^{-1} at 300 cd m^{-2}; its CIE-coordinates are (0.68, 0.33). In this paper, we report a series of high efficiency red phosphorescent iridium complexes based on the isoquinoline derivatives.

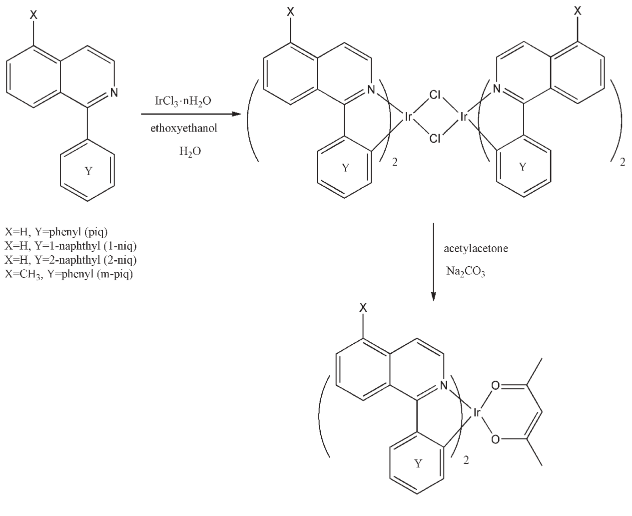
Results and discussion

Isoquinoline ligands were synthesized from 3,4-dihydroisoquinoline as shown in Scheme 1.[15] We prepared 1-phenylisoquinoline (piq), 1-(1′-naphthyl)isoquinoline (1-niq), 1-(2′-naphthyl)isoquinoline (2-niq) and 1-phenyl-5-methylisoquinoline (m-piq) for metal complexes. Only the synthesis of 1-phenyl-5-methylisoquinoline (m-piq) is described in the Experimental section.

Scheme 2 outlines the synthetic process for red phosphorescent iridium complexes: $(\mathrm{piq})_2\mathrm{Ir(acac)}$, $(1\text{-niq})_2\mathrm{Ir(acac)}$, $(2\text{-niq})_2\mathrm{Ir(acac)}$ and $(\text{m-piq})_2\mathrm{Ir(acac)}$. The iridium complexes were prepared from the isoquinoline ligands and iridium trichloride



Scheme 1 Synthesis of 1-phenyl-5-methylisoquinoline (m-piq).



Scheme 2 Synthesis of the iridium complexes.

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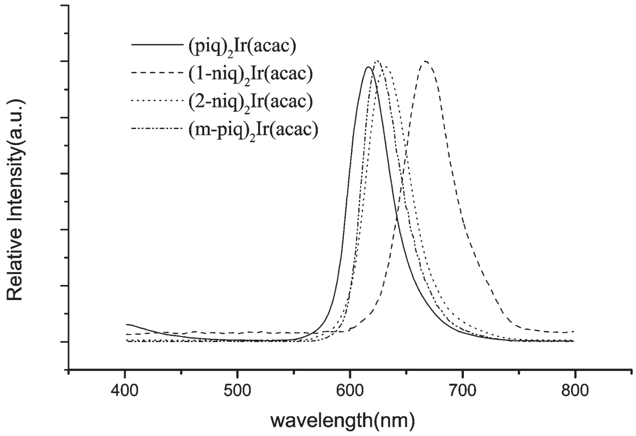

Fig. 1 PL Spectra of the Ir complexes in CH_2Cl_2.

to form a dimer, $[(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2]$, followed by the reaction with acetylacetone in the presence of sodium carbonate.[8] All procedures involving Ir(III) species were carried out under nitrogen gas atmosphere. All these materials were characterized by ^1H and ^{13}C NMR as well as mass spectrometry.

The signals in the ^1H NMR spectrum could be exactly assigned to the various hydrogen atoms when the iridium was chelated with ligands (see Experimental section). In the mass spectrum, all these compounds show the corresponding ion peaks of acetylacetonate and ligand. After using vacuum sublimation to purify these complexes, we found that (1-niq)$_2$Ir(acac) has poor thermal stability. Therefore, we only report the mass spectral data of this complex.

The photoluminescence (PL) and electroluminescence (EL) spectra are shown in Fig. 1 and Fig. 2, respectively. The PL and EL spectra show the same trends. The PL spectrum of (piq)$_2$Ir(acac) in CH_2Cl_2 shows an emission band at 618 nm. The other complexes exhibit bathochromic shifts at 664.8, 633 and 623.4 nm. The EL spectra of these devices based on these four iridium complexes were recorded at a current density of $J = 50$ mA cm^{-2}. The EL spectrum of (piq)$_2$Ir(acac) and (m-piq)$_2$Ir(acac) show the same emission band at 624 nm, (2-niq)$_2$Ir(acac) shows the band at 633 nm, and (1-niq)$_2$Ir(acac) shows the maximum bathochromic shift at 680 nm. AC-2 measurements showed that these compounds have high HOMO values in the range -5.11 to -5.35 eV.

Devices were fabricated by high vacuum (10^{-6} Torr) thermal evaporation on pre-cleaned indium–tin oxide (ITO) glass substrates as shown in Fig. 3. With a base pressure of $\sim 1 \times 10^{-6}$ Torr, the organic and metal cathode layers were grown successively. In this device, 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) acted as a hole transport layer, 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole blocking layer, tris-(8-hydroxyquinoline)aluminium(III) (AlQ_3) as an electron transport layer, 4,4′-bis(N-carbazolyl)biphenyl (CBP) as the host material, and iridium complexes as the dopant. The corresponding CIE coordinates are $x = 0.679$, $y = 0.318$ for (piq)$_2$Ir(acac), $x = 0.701$, $y = 0.273$ for (1-niq)$_2$Ir(acac), $x = 0.697$, $y = 0.299$ for (2-niq)$_2$Ir(acac) and $x = 0.677$, $y = 0.321$ for (m-piq)$_2$Ir(acac) (as shown in Fig. 4) All four devices show red to deep-red emissions, these were close to the National Television Standards Committee recommended red for a video display.

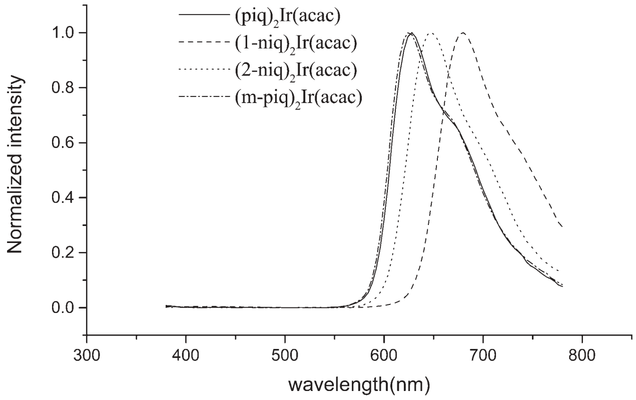

Fig. 2 EL Spectra of iridium complexes at $J = 50$ mA cm^{-2}.

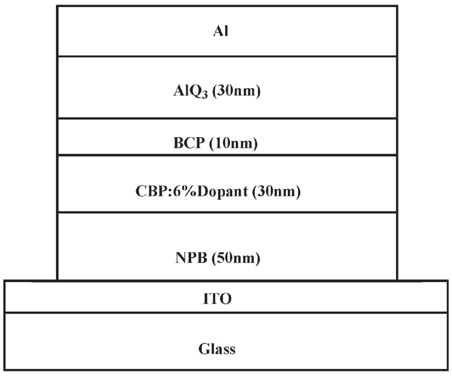

Fig. 3 Configuration of the device.

Electrophosphorescence data for the iridium complexes are summarized in Table 1. In these complexes, we change the substituent at C-1 of isoquinoline from phenyl to 1-naphthyl and 2-naphthyl. The data show that (1-niq)$_2$Ir(acac) and (2-niq)$_2$Ir(acac) as the dopant give better bathochromic shifts (680 and 634 nm, respectively), but have poor brightness and luminance efficiency. In contrast, when we retain the isoquinoline C-1 substituent group as phenyl and change the C-5 substituent group from hydrogen to methyl, a better performance in brightness and luminance can be achieved. (m-piq)$_2$Ir(acac) showed a better performance than (piq)$_2$Ir(acac) in both brightness and luminance efficiency. When (m-piq)$_2$Ir(acac) was used as the dopant, a maximum brightness of 17 164 cd m^{-2} was achieved at a current density of $J = 300$ mA cm^{-2}.

In summary, we have designed and synthesized cyclometalated iridium complexes suitable for use as red dopant materials in OLEDs. In comparison to the known derivatives of this

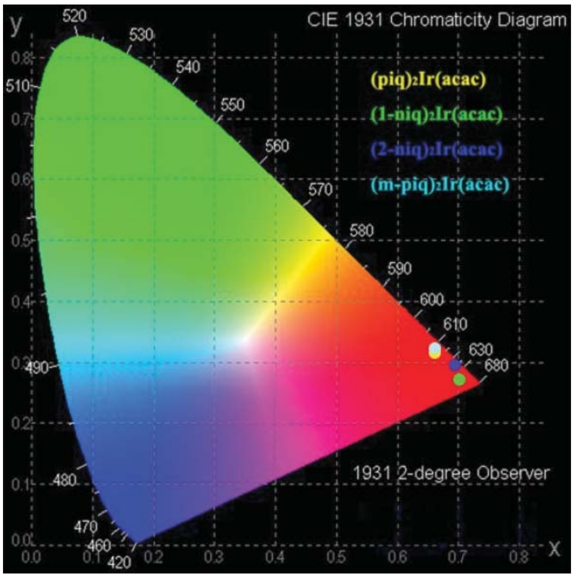

Fig. 4 CIE coordinates of (piq)$_2$Ir(acac) (0.679, 0.318), (1-niq)$_2$Ir(acac) (0.701, 0.273), (2-niq)$_2$Ir(acac) (0.697, 0.299) and (m-piq)$_2$Ir(acac) (0.677, 0.321).

Table 1 Electrophosphorescence data for iridium complexes

Compound	Brightness/ cd m^{-2}	LE/ cd A^{-1}	Voltage/ V	CIE coordinates	HOMO/ eV
(piq)$_2$Ir(acac)	1566[a]	7.83	8.7	x = 0.679;	−5.25
	3505[b]	7.01	9.8	y = 0.318	
	6431[c]	6.43	11.0		
	11362[d]	5.68	12.4		
	15621[e]	5.21	13.6		
(1-niq)$_2$Ir(acac)	48[a]	0.240	11.9	x = 0.701;	−5.11
	106[b]	0.218	13.2	y = 0.273	
	210[c]	0.210	14.4		
	415[d]	0.207	16.1		
	591[e]	0.197	17.1		
(2-niq)$_2$Ir(acac)	758[a]	3.79	10.7	x = 0.697;	−5.14
	1709[b]	3.42	12.1	y = 0.299	
	3043[c]	3.04	13.4		
	5664[d]	2.83	15.2		
	7895[e]	2.63	16.6		
(m-piq)$_2$Ir(acac)	1781[a]	8.91	9.6	x = 0.677;	−5.35
	3959[b]	7.91	11.1	y = 0.321	
	7246[c]	7.25	12.8		
	12375[d]	6.19	15.1		
	17164[e]	5.72	16.9		

For each parameter, the data in different rows correspond to those measured at different current density: [a] 20 mA cm^{-2}, [b] 50 mA cm^{-2}, [c] 100 mA cm^{-2}. [d] 200 mA cm^{-2}, [e] 300 mA cm^{-2}.

class,[16] (m-piq)$_2$Ir(acac) shows better efficiency and equivalent CIE coordinates data. Although (2-niq)$_2$Ir(acac) can not give brightness and luminance efficiency as high as (piq)$_2$Ir(acac), it produces a more pure red color than (m-piq)$_2$Ir(acac) and can be used in special applications as indicated by its CIE data. We believe the efficiency can be further improved by using a more suitable host material for the emitting layer, or a more suitable device structure.[7]

Experimental

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were measured using a Bruker AMX-400 (400 MHz), FAB mass spectra were collected with a Bruker APEX II, and Photoluminesence spectra were recorded with a HITACHI F-4500. The melting point data were measured with a PYRIS Diamond TG/DTA-10 at a heating rate of 20 °C min^{-1}.

N-(2-*o*-Tolylethyl)benzamide

Benzoic acid (12.2 g, 100 mmol) was dissolved in 100 ml of dry dimethylformamide. While the solution was cooled with ice with stirring, triethylamine (11.5 g) and ethyl chloroformate (11 g) were added. After a lapse of 30 min, 2-methylphenethylamine (14 g, 104 mmol) was added dropwise. The mixture was stirred at room temperature for 1 h and then at 50–60 °C for 1 h, and poured into ice-water. The crystallized precipitates were washed in water, dried, and recrystallized from cyclohexane to afford *N*-(2-*o*-tolylethyl)benzamide (14.66 g, 61.3 mmol).

5-Methyl-1-phenyl-3,4-dihydroisoquinoline

N-(2-*o*-Tolylethyl)benzamide (14.66 g, 61.3 mmol) was heated with stirring at 130 °C for 4 h together with 150 ml of xylene, 50 ml of phosphorus oxychloride and 50 g of phosphorus pentoxide. The reaction mixture was decanted to remove the solvent. The residue was carefully decomposed with ice-water, and made weakly alkaline with 45% sodium hydroxide. The crystals which precipitated were extracted with benzene (2 × 100 ml). The organic layer was washed with water (3 × 100 ml) and dried over MgSO$_4$.

1-Phenyl-5-methylisoquinoline

All of the organic layer above was reacted for 16 h together with active manganese dioxide (100 g). After the reaction, the manganese dioxide was removed by filtration, and the benzene was distilled off. Recrystallization of the resulting crystals from cyclohexane afforded 1-phenyl-5-methylisoquinoline as yellow crystals (11.94 g, 54.5 mmol).

1-Phenylisoquinoline (piq) (yield 33%)

T_m = 95 °C, EIMS: *m/z* 205, [M]$^+$; ^{1}H NMR (acetone-d$_6$, 400 MHz): δ 8.57 (d, J = 5.6 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.79–7.69 (m, 4H), 7.62 (t, J = 8 Hz, 1H), 7.58–7.50 (m, 4H).

1-(1′-Naphthyl)isoquinoline (1-niq) (yield 30%)

T_m = 106.4 °C, EIMS: *m/z* 255, [M]$^+$; ^{1}H NMR (acetone-d$_6$, 400 MHz): δ 8.66 (d, J = 5.6 Hz, 1H), 8.08–8.02 (m, 3H), 7.89 (d, J = 5.9 Hz, 1H), 7.75 (td, J = 8, 1.3 Hz, 1H), 7.69 (td, J = 7.3, 1.38 Hz, 1H), 7.58–7.45 (m, 4H), 7.35–7.32 (m, 2H).

1-(2′-Naphthyl)isoquinoline (2-niq) (yield 41%)

T_m = 163.3 °C, EIMS: *m/z* 255, [M]$^+$; ^{1}H NMR (acetone-d$_6$, 400 MHz): δ 8.62 (d, J = 5.6 Hz, 1H), 8.23–8.18 (m, 2H), 8.09–8.01 (m, 4H), 7.87 (dd, J = 8.4, 1.6 Hz, 1H), 7.82–7.76 (m, 2H), 7.65–7.58 (m, 3H).

1-Phenyl-5-methylisoquinoline (m-piq) (yield 54.5%)

T_m = 61.2 °C, EIMS: *m/z* 219, [M]$^+$; ^{1}H NMR (acetone-d$_6$, 400 MHz): δ 8.60 (d, J = 5.6 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.87 (dd, J = 5.95, 0.69 Hz, 1H), 7.68–7.66 (m, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.57–7.47 (m, 4H).

Preparation of red phosphorescence iridium complexes, (piq)$_2$Ir(acac), (1-niq)$_2$Ir(acac), (2-niq)$_2$Ir(acac) and (m-piq)$_2$Ir(acac)

All procedures involving IrCl$_3$·H$_2$O were carried out in nitrogen gas atmosphere. Cyclometalated Ir(III) μ-chloro-bridged dimers were synthesized by the method reported by Nonoyama.[17] IrCl$_3$·H$_2$O (Next Chimica) and 2.5 equiv. of ligand were heated in a 3:1 mixture of 2-ethoxyethanol and water. This slurry was heated at 100 °C for 24 h. After cooling to room temperature, the precipitate was filtered off and washed with water. The obtained solid was placed in a flask and dispersed in 2-ethoxyethanol. Acetylacetone and sodium carbonate were added to the solution and the mixture were heated at 120 °C for 12–16 h. After cooling to room temperature, the crude product was filtered off and washed with water, followed by two portions of *n*-hexane and ether. The solid was dried in vacuum and zone sublimed to give pure product which was used for advanced analysis and device fabrication.

Bis(1-phenylisoquinolinato-*N*,*C*$^{2'}$)iridium(acetylacetonate) (piq)$_2$Ir(acac) (yield 53.8%)

T_m = 372.9 °C, FAB MS: *m/z* 700, [M + 1]$^+$; ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 9.01 (d, J = 6.4 Hz, 2H), 8.51 (dd, J = 6.4,1.2 Hz, 2H), 8.25 (d, J = 8 Hz, 2H), 7.99 (m, 2H), 7.76 (m, 4H), 7.57 (d, J = 6.4 Hz, 2H), 6.97 (t, J = 7.6 Hz, 2H), 6.69 (t, J = 7.6 Hz, 2H), 6.37 (d, J = 7.6 Hz, 2H), 5.35 (s, 1H), 1.81 (s, 6H). ^{13}C NMR (CD$_2$Cl$_2$, 400 MHz) δ: 175.1, 158.9, 141.8, 137.0, 130.6, 127.4, 123.8, 120.9, 119.9, 118.9, 118.0, 117.5, 116.8, 116.5, 110.6, 110.4, 90.7, 18.5.

Bis(1-(1′-naphthyl)isoquinolinato-$N,C^{2'}$)iridium(acetylacetonate) - (1-niq)$_2$Ir(acac) (yield 34.5%)

T_m = 369.8 °C, FAB MS: *m*/*z* 800, $[M + 1]^+$.

Bis(1-(2′-naphthyl)isoquinolinato-$N,C^{2'}$)iridium(acetylacetonate) (2-niq)$_2$Ir(acac) (yield 64.4%)

T_m = 370 °C, FAB MS: *m*/*z* 800, $[M + 1]^+$; ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.21 (m, 2H), 8.75 (s, 2H), 8.60 (d, J = 6.4 Hz, 2H), 8.08 (m, 2H), 7.86 (m, 4H), 7.77 (m, 2H), 7.67 (d, J = 6.4 Hz, 2H), 7.17 (m, 6H), 6.69 (s, 2H), 5.32 (s, 1H), 1.79 (s, 6H). ^{13}C NMR (CD_2Cl_2, 400 MHz) δ: 175.2, 158.0, 137.1, 133.3, 131.0, 127.4, 124.4, 121.9, 121.0, 120.1, 119.9, 119.7, 119.4, 118.6, 117.8, 117.2, 116.9, 115.0, 111.1, 108.6, 90.7, 18.6.

Bis(1-phenyl-5-methylisoquinolinato-$N,C^{2'}$)iridium(acetylacetonate) (m-piq)$_2$Ir(acac) (yield 41.8%)

T_m = 383.7 °C, FAB MS: *m*/*z* 728, $[M + 1]^+$; ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.85 (d, J = 8 Hz, 2H), 8.49 (d, J = 6.4 Hz, 2H), 8.22 (d, J = 8 Hz, 2H), 7.71 (d, J = 6.4 Hz, 2H), 7.61 (m, 4H), 6.93 (td, J = 6.4, 1.2 Hz, 2H), 6.65 (td, J = 6.4, 1.2 Hz, 2H), 6.34 (dd, J = 7.6, 1.2 Hz, 2H), 5.32 (s, 1H), 2.77 (s, 6H), 1.80 (s, 6H). ^{13}C NMR (CD_2Cl_2, 400 MHz) δ: 175.1, 159.2, 141.7, 137.2, 130.5, 126.8, 124.4, 123.8, 121.4, 120.2, 118.8, 117.6, 116.6, 115.0, 110.6, 106.7, 90.6, 18.5, 9.4.

OLED Fabrication and measurement

Pre-patterned ITO glass with an effective device of area 0.16 cm^2 was cleaned in detergent for 10 min, and then washed with a large amount of doubly distilled water. After sonication in pure water for 5 min, the glass was dried in an oven at 180 °C for 90 min. The organic layers were deposited thermally at a rate of 0.1 nm s^{-1} and pressure of $\sim 1 \times 10^{-6}$ Torr in a deposition system. Aluminium was deposited as the cathode. The HOMO value of iridium complexes were measured with a RIKEN Photoelectron Spectrometer AC-2. The electrophosphorescence data were measured with a SpectraScan PR650. These devices were fixed in the device holder and collected the light from the front face.

Acknowledgements

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16 The (piq)$_2$Ir(acac) complex has been described in a recent paper by Su *et al.* The device based on this complex gave η_{ext} = 8.46% at J = 20 mA cm^{-2}. In this paper, we treat (piq)$_2$Ir(acac) as the standard while (m-piq)$_2$Ir(acac) shows better luminance efficiency and brightness. We predict that (m-piq)$_2$Ir(acac) should exhibit a better η_{ext} than (piq)$_2$Ir(acac). See: Y. J. Su, H. L. Huang, C. L. Li, C. H. Chien, Y. T. Tao, P. T. Chou, S. Datta and R. S. Liu, *Adv. Mater.*, 2003, **15**, 884.
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