Novel iridium(III) complexes bearing dimesitylboron groups with nearly 100% phosphorescent quantum yields for highly efficient organic light-emitting diodes†

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A series of cyclometalated iridium(III) complexes, Ir-B-1, Ir-B-2, Ir-B-3, and Ir-B-4, were synthesized with the 2-phenylpyridine (ppy) type main ligand possessing a dimesitylboron group and the auxiliary ligand containing other main-group element units showing unique charge injection/transporting features. Their thermal stability, photophysical and electrochemical properties, and electroluminescent (EL) performances have been characterized. Time-dependent density functional theory (TD-DFT) calculations were carried out to study the photophysical properties of these complexes. All these complexes can emit intense orange phosphorescence with extremely high quantum yields of nearly 100% measured in neat films at room temperature. Moreover, the solution-processed organic light-emitting devices (OLEDs) using these complexes as orange emitters can show very high EL efficiencies with the maximum luminance efficiency (η_lum) of 85.1 cd A⁻¹, corresponding to a power efficiency (η_p) of 69.7 lm W⁻¹ and an external quantum efficiency (η_ext) of 28.1%.

Introduction

Organic light-emitting devices (OLEDs) possess the merits of thin thickness, high brightness, flexibility, and fast response, etc., which make them suitable as prospective candidates for next-generation flat-panel displays and energy-saving solid-state lighting sources.¹⁻¹⁰ At the early stage, fluorescent emitters could only utilize 25% of the excitons generated by the charge recombination process, furnishing very low electroluminescence (EL) efficiency. Later on, owing to the strong spin-orbital coupling effect of the iridium center, OLEDs based on phosphorescent iridium(III) complexes were shown to harness both the singlet and triplet excitons in the EL process. Accordingly, the internal quantum efficiency (IQE) of the resultant EL devices can possibly reach 100% theoretically,⁴,¹⁰⁻²⁰ which ensures the high performance of the EL devices using phosphorescent iridium(III) complexes as emitters.

Regarded as the most promising candidates of future solid-state lighting sources, white organic light-emitting diodes (WOLEDs) based on phosphorescent emitters with high efficiency and less pollution have drawn enormous attention from both the scientific research and industrial community. One of the critical factors ensuring the practical application of WOLEDs as energy-saving lighting sources should be their EL efficiencies, which can be influenced by the properties of the emitters involved in the devices. As an essential parameter to characterize the performance of the phosphorescent EL devices, external quantum efficiency (EQE, η_ext) is defined as

η_ext = η_intη_ph = γ_e-hη_p,⁴,¹²,²¹,²²

where η_int is internal quantum efficiency (IQE) defined as the total number of photons generated from each injected electron–hole pair in the device, η_ph is the light out-coupling efficiency, γ_e-h is the ratio of injected electrons to holes (or vice versa) and typically γ_e-h ≤ 1, η_p is the emissive exciton ratio, which is regarded as 1.0 for the phosphorescent (triplet) emitters, and Φ_p is the intrinsic quantum yield for the radiative decay of phosphorescence, i.e. the phosphorescent quantum yield of the triplet emitters. As is shown in the above equation, improving the Φ_p of the phosphorescent...
materials can be an important outlet to enhance the EL efficiencies of both monochromatic OLEDs and WOLEDs with respect to the positive correlation between $\Phi_p$ and $\eta_{\text{ext}}$

According to our previous work, introducing a dimesityl-boron –B(Mes)$_2$ unit to the ppy-type ligands of iridium(III) complexes can result in a remarkable enhancement of their $\Phi_p$s. Besides, Wang and coworkers reported a series of cyclometalated platinum(II) complexes with the –B(Mes)$_2$ moiety, showing high $\Phi_p$ as well. Therefore, introducing the –B(Mes)$_2$ moiety to the cyclometalated metal complexes should represent an efficient strategy for developing phosphorescent iridium(III) or platinum(II) complexes with high $\Phi_p$. In addition, many researchers reported iridium(III) complexes with functional groups that exhibit excellent electron injection/transporting (EI/ET) abilities, such as –B(Mes)$_2$, aryl phosphine oxide (–POPh$_2$), and diarylsulfone moieties (–SO$_2$Ph), etc. Meanwhile, introducing triphenylamine (TPA) and carbazole (Cz) moieties to the complexes can confer good hole injection/transporting (HI/HT) properties to the iridium(III) complexes, whereas the basis set used for C, H, O, N, P, S, and B atoms was 6-31G(d,p). The energies of the excited states of the iridium(III) phosphorescent complexes can also effectively promote their EL efficiencies.

Herein, a series of orange phosphorescent iridium(III) complexes bearing –B(Mes)$_2$ moieties and other functional groups with charge carrier injection/transporting features have been designed and synthesized. Their photophysical properties, electrochemical characters, and EL performances have been fully investigated. With such rational molecular design, these orange iridium(III) complexes can show outstanding $\Phi_p$s in both CH$_2$Cl$_2$ solution and doped PMMA films. These admirable results suggest that these orange cyclometalated iridium(III) complexes have great application value in developing either monochromatic OLEDs or WOLEDs with decent EL properties.

**Experimental section**

**General information**

All the reactions were conducted under a nitrogen atmosphere and no special precautions were required during the workup. The solvents were purified by routine procedures and distilled under dry nitrogen before use. Commercially available reagents were used without further purification unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) purchased from Merck & Co., Inc. Flash column chromatography and preparative TLC were carried out using silica gel from Shanghai Qingdao (200–300 mesh).

**Physical characterization**

UV/vis spectra were measured on a Perkin-Elmer UV/VIS NIR Spectrometer Lambda 950. The photoluminescent properties and the phosphorescent lifetimes of the iridium(III) complexes were obtained using a spectrophotometer from Edinburgh Instruments (FLS920). The relative phosphorescence quantum yields ($\Phi_p$) were determined in CH$_2$Cl$_2$ solution relative to the $\Phi_p$-[Ir(ppy)$_3$] standard ($\Phi_p = 40\%$). Absolute $\Phi_p$ for the CH$_2$Cl$_2$ solution and neat films was obtained by a Hamamatsu Photonics KK E7536 model measurement system. Cyclic voltammetry was performed using a Princeton Applied Research model 2273A potentiostat with a glassy carbon working electrode, a platinum sheet counter electrode, and a platinum-wire reference electrode with the scan rate of 50 mV s$^{-1}$. The supporting electrolyte used was 0.1 M [nBu$_4$N][BF$_4$] solution in degassed CH$_2$Cl$_2$ with ferrocene (Fc) as the calibrant. The oxidation ($E_{\text{ox}}$) and reduction ($E_{\text{red}}$) potentials were used to determine the HOMO and LUMO energy levels using the equations $E_{\text{HOMO}} = (E_{\text{ox}} + 4.8)$ eV and $E_{\text{LUMO}} = (E_{\text{red}} + 4.8)$ eV which were calculated using the internal standard ferrocene value of 4.8 eV with respect to the vacuum level. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded in CDCl$_3$, CD$_3$OD or DMSO-$d_6$ on a Bruker Advance 400 MHz spectrometer and chemical shifts were referenced to the solvent residual peak at $\delta$ 7.26 ppm for $^1$H and 77.0 ppm for $^{13}$C, respectively. Elemental analyses were performed on a Flash EA 1112 elemental analyzer. High resolution mass spectra (HRMS) were recorded on Waters Vion IMS Qtof spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 214 under a nitrogen flow at a heating rate of 10 K min$^{-1}$ to obtain the glass transition temperature ($T_g$). The thermal gravimetric analysis (TGA) was conducted on a METTLER TOLEDO TGA2 star system under nitrogen with a heating rate of 20 K min$^{-1}$.

**Computational details**

Geometrical optimizations were conducted using the popular B3LYP density functional theory (DFT). The effective core potentials with the LanL2dz basis set were employed for the Ir atom, whereas the basis set used for C, H, O, N, P, S, and B atoms was 6-31G(d,p). The energies of the excited states of the complexes were computed by TD-DFT (time-dependent density functional theory) based on all the ground-state geometries. All the calculations were carried out by using the Gaussian 09 program.

**Synthesis**

**TPAPicMe.** Under a nitrogen atmosphere, methyl 5-bromo-picolinate (0.400 g, 1.185 mmol), TPA-B (0.660 g, 2.283 mmol), and Pd(PPh$_3$)$_4$ (0.110 g, 0.095 mmol) were added to 10 mL degassed toluene and 2 M Na$_2$CO$_3$ (4 mL). The reaction mixture was heated to 110 °C and stirred for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3 × 30 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure, then purified by column chromatography over silica gel using CH$_2$Cl$_2$/ethyl acetate (15:1, v:v) as the eluent. A yellow solid of the title compound was obtained (0.680 g, 91%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.94 (d, $J = 4.0$ Hz, 1H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.97 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.26-7.31 (m, 4H), 7.12-7.17 (m, 6H), 7.08 (t, $J = 8.0$ Hz, 2H), 4.01 (s, 3H, OCH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 165.58, 148.83, 147.71, 147.13, 145.62, 139.17, 134.12, 129.43, 127.96, 125.20, 124.99, 123.66, 122.66, 52.82. HRMS $m/z$ [M + H]$^+$ calc'd for C$_{22}$H$_{20}$NO$_2$: 321.1598, found 318.1606. C$_{22}$H$_{20}$NO$_2$: calcd C 78.93, H 5.30, N 7.36; found C 78.88, H 5.22, N 7.19.
The organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silica gel using ethyl acetate as the eluent. A white solid of CzPicMe was obtained (0.430 g, 88%). 1H NMR (400 MHz, CDCl$_3$, δ): 8.90 (d, J = 1.6 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 2H), 8.13 (dd, J = 8.0, 2.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.42–7.50 (m, 4H), 7.32 (t, J = 8.0 Hz, 2H), 4.07 (s, 3H, OCH$_3$). 13C NMR (100 MHz, CDCl$_3$): δ: 165.55, 148.21, 146.72, 140.53, 138.88, 138.56, 135.44, 135.18, 134.06, 132.95, 132.85, 132.43, 131.34, 130.89, 130.79, 129.83, 129.45, 129.27, 129.16, 128.93, 128.72, 128.65, 128.32, 128.25, 127.40, 127.27, 127.19, 52.90; 31P NMR (162 MHz, CDCl$_3$): δ: 28.71 (P=O). HRMS m/z [M + Na]$^+$ calcd for C$_{25}$H$_{20}$NO$_3$P 436.1073, found 436.1052. C$_{14}$H$_{13}$NO$_3$S: calcd C 66.86, H 4.05, N 4.33; found C 66.74, H 4.36, N 4.24.

**L1. TPAPicMe** (0.600 g, 1.577 mmol) was dissolved in 5 mL THF (tetrahydrofuran) and 5 mL MeOH. Then, NaOH (0.190 g, 4.750 mmol) was added to the solution and the mixture was stirred at room temperature for 8 h. Water (10 mL) was added and the pH value of the mixture was adjusted to ca. 6.0 with concentrated HCl. After extraction with ethyl acetate (3 × 15 mL), the combined organic layer was dried over anhydrous Na$_2$SO$_4$. After the removal of the solvent, the white solid obtained was washed with hexane (3 × 15 mL) and the product was obtained in high yield (0.560 g, 99%). 1H NMR (400 MHz, CD$_2$OD, δ): 8.91 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.08 (dd, J = 8.0, 2.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 4H), 7.16 (d, J = 8.0 Hz, 6H), 7.10 (t, J = 8.0 Hz, 2H). 13C NMR (100 MHz, CD$_2$OD, δ): 164.63, 149.12, 147.03, 145.92, 143.54, 134.90, 132.47, 132.00, 125.11, 124.13, 123.82, 122.79. HRMS m/z [M + Na]$^+$ calcd for C$_{24}$H$_{18}$NO$_2$ 389.1260, found 389.1272. C$_{24}$H$_{18}$NO$_2$: calcd C 76.67, H 4.95, N 7.65; found C 78.57, H 4.86, N 7.50.

**L2. CzPhPicMe** (0.200 g, 0.528 mmol) was dissolved in 10 mL THF. Then, 50% NaOH (2 mL) was added to the solution and the mixture was stirred at room temperature for 8 h. Water (10 mL) was added and the pH value of the mixture was adjusted to ca. 6.0 with concentrated HCl. After the extraction with ethyl acetate (3 × 15 mL), the combined organic layer was dried over anhydrous Na$_2$SO$_4$. After the removal of the solvent, the white solid obtained was washed with hexane (3 × 15 mL) and the product L2 was obtained in high yield (0.190 g, 96%). 1H NMR (400 MHz, DMSO-d$_6$, δ): 8.97 (d, J = 2.0 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.24 (dd, J = 8.4, 2.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.43–7.50 (m, 4H), 7.33 (td, J = 7.0, 1.2 Hz, 2H). 13C NMR (100 MHz, DMSO-d$_6$, δ): 166.84, 147.79, 140.41, 137.80, 137.22, 135.79, 135.54, 134.21, 129.38, 127.77, 126.85, 125.08, 123.36, 121.08, 120.76, 119.19. HRMS m/z [M + Na]$^+$ calcd for C$_{24}$H$_{18}$NO$_2$ 387.1104, found 387.1118. C$_{24}$H$_{18}$NO$_2$: calcd C 79.11, H 4.43, N 7.69; found C 79.03, H 4.50, N 7.56.

**L3. POBpicMe** (0.220 g, 0.532 mmol) was dissolved in 5 mL THF and 5 mL MeOH. Then, NaOH (0.060 g, 1.500 mmol) was added to the solution and the mixture was stirred at room temperature for 8 h. Water (10 mL) was added and the pH value of the mixture was adjusted to ca. 6.0 with concentrated HCl. After the extraction with ethyl acetate (3 × 15 mL), the combined organic layer was dried over anhydrous Na$_2$SO$_4$. After removing the solvent, the resulting white solid was washed with hexane (3 × 15 mL). The product L3 was obtained in high yield (0.210 g, 99%). 1H NMR (400 MHz, CDCl$_3$, δ): 9.03 (d, J = 1.6 Hz, 1H), 8.38 (dd, J = 8.4, 2.4 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.99 (dd, J = 8.4, 2.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.69–7.75 (m, 6H), 7.59–7.64 (m, 4H). 13C NMR (100 MHz, CDCl$_3$, δ): 168.21, 149.60, 142.75, 140.80, 138.54, 134.96, 134.85, 134.82, 134.79, 134.01, 133.91, 133.79, 132.73, 131.01, 130.89, 130.79, 129.83, 129.71, 127.28; 31P NMR (162 MHz, CDCl$_3$): δ: 31.91. HRMS m/z [M + Na]$^+$ calcd for C$_{22}$H$_{16}$NO$_3$P 422.0917, found 422.0932. C$_{22}$H$_{16}$NO$_3$P: calcd C 72.18, H 4.54, N 3.51; found C 72.09, H 4.47, N 3.36.
L4. KMnO4 (0.029 g, 0.183 mmol) and SO2-CHO (0.030 g, 0.093 mmol) were added to 5 mL acetone/H2O (4:1, v:v). The reaction mixture was refluxed for 2 h. After cooling to room temperature, the mixture was filtered to remove the residual MnO2 and obtain the colorless filtrate. Then, the solution was acidified with concentrated HCl to the pH value at ca. 6.0 and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous Na2SO4. After removing the solvent, the white solid obtained was washed with hexane (3 × 15 mL). The product L4 was obtained in high yield (0.030 g, 95%).

1H NMR (400 MHz, DMSO-d6, δ): 9.05 (s, 1H), 8.32 (d, J = 7.2 Hz, 1H), 8.10–8.15 (m, 3H), 8.04 (t, J = 7.6 Hz, 4H), 7.72 (t, J = 7 Hz, 1H), 7.66 (t, J = 7.2 Hz, 2H). 13C NMR (100 MHz, DMSO-d6, δ): 166.35, 148.48, 141.66, 141.56, 141.34, 137.02, 136.42, 134.39, 130.34, 129.16, 128.66, 127.92, 125.27. HRMS m/z [M + Na]+ caked for C82H75B2IrN4O3P 1418.5254, found 1418.5272. C82H75B2IrN4O3P: calcd C 70.59, H 5.42, N 3.01; found C 70.48, H 5.36, N 2.90.

General procedure for the synthesis of iridium(Ⅲ) complexes

Under a N2 atmosphere, 1.0 equiv. of the cyclometalated iridium (Ⅲ) μ-chlorobridge dimer [IrppyB]2Cl2 (Scheme S1, ES†), 2.2 equiv of the picolinic acid derivative and 2.2 equiv. of Na2CO3 were added to 2-ethoxyethanol and the mixture was heated to 70 °C for 0.5 h. After cooling to room temperature and the addition of water, the colored precipitate was collected by filtration and washed with water and dried. The crude product was chromatographed on a silica column using an appropriate solvent, the white solid obtained was washed with hexane (3 × 10 mL). The combined organic layer was dried over anhydrous Na2SO4. After removing the solvent, the white solid obtained was washed with hexane (3 × 15 mL). The product L4 was obtained in high yield (0.030 g, 95%).

1H NMR (400 MHz, DMSO-d6, δ): 9.05 (s, 1H), 8.32 (d, J = 7.2 Hz, 1H), 8.10–8.15 (m, 3H), 8.04 (t, J = 7.6 Hz, 4H), 7.72 (t, J = 7 Hz, 1H), 7.66 (t, J = 7.2 Hz, 2H). 13C NMR (100 MHz, DMSO-d6, δ): 166.35, 148.48, 141.66, 141.56, 141.34, 137.02, 136.42, 134.39, 130.34, 129.16, 128.66, 127.92, 125.27. HRMS m/z [M + Na]+ caked for C82H75B2IrN4O3P 1418.5254, found 1418.5272. C82H75B2IrN4O3P: calcd C 63.71, H 3.86, N 4.13; found C 63.59, H 3.78, N 4.01.

**OLED fabrication and measurements**

The ITO glass substrates were pre-cleaned with ethanol, acetone and deionized water under an ultrasonic bath, and then exposed to UV–ozone for 30 min. Then, PEDOT:PSS was deposited on the surface of the ITO glass by the spin-coating method, and after being cured at 120 °C for half an hour in the air, a 45 nm thick hole-injection layer was formed. The emission layer (30 nm) was prepared by the spin-coating method using the chlorosor form of phosphorescent dopant (x wt%) in 4,4’,4”-tri(9-carbazolyl)triphenylamine (TCTA) at different concentrations. The obtained OLED chip was dried in a vacuum oven at 60 °C for 10 min and it was transferred to the deposition system for organic and metal deposition. Then, 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBI) (45 nm), LiF (1 nm) and an Al cathode (100 nm) were successively evaporated at a base pressure less than 10−6 Torr. A PR650 spectra colorimeter was used to measure the EL spectra and the CIE coordinates of the OLEDs. A Keithley 2400/2000 source meter was used to obtain the f-V-L characters of the OLEDs. All the experiments and measurements were carried out under ambient conditions.

**Results and discussion**

Synthetic strategies and structural characterization

The chemical structures and detailed synthetic pathway of the cyclometalated iridium(Ⅲ) phosphorescent complexes are
shown in Scheme 1. The starting materials methyl 5-bromopicolinate, 5-bromopicolinoldehyde, TPA-B, CzPh-B, PO-Bpin and SO$_2$-Bpin can be easily prepared according to the literature methods.$^{53-56}$ The synthetic method of the Ir(III)-$\mu$-chloride-bridged dimer [IrppyB]$_2$Cl$_2$ is provided in the ESI† (Scheme S1). The aromatic esters TAPicMe, CzPhPicMe and POPicMe were obtained by Suzuki–Miyaura cross coupling between methyl 5-bromopicolinate and the appropriate aromatic boronic acid or boronic acid pinacol cyclic ester. Then, the auxiliary ligands L$_1$, L$_2$ and L$_3$ were obtained by the alkaline hydrolysis of the aromatic esters with NaOH. Ligand L$_4$ was prepared by different methods. 5-Bromopicolinoldehyde was coupled with SO$_2$-Bpin via Suzuki–Miyaura cross coupling to obtain SO$_2$-CHO. Then, L$_4$ was synthesized in high yield by SO$_2$-CHO by using potassium permanganate as the oxidant. After obtaining all the key picolinate-type auxiliary ligands, the designed iridium(III) complexes could be easily prepared with the conventional procedure between the auxiliary ligands L$_1$, L$_2$, L$_3$ or L$_4$ and [IrppyB]$_2$Cl$_2$ in the presence of Na$_2$CO$_3$. All the complexes are orange-red solids and air stable. The chemical structures of these iridium(III) complexes have been fully characterized by $^1$H, $^{13}$C and $^{31}$P NMR spectroscopy. In their $^1$H NMR spectra, the existence of a single peak at ca. 8.8 ppm can be assigned to the H atom adjacent to the carboxyl group on the pyridine ring of the auxiliary ligands while the chemical shifts at ca. 8.1 ppm can be assigned to the H atom on the 6-position of the pyridyl ring in the ppy-type ligands. The signals with chemical shifts at ca. 1.9 and 2.3 ppm can be ascribed to the protons of the methyl groups in the –B(Mes)$_2$ moieties, whereas those at ca. 6.8 ppm can be ascribed to the aromatic protons of the –B(Mes)$_2$ moieties. The $^{13}$C NMR spectra also indicate the expected structural features of these compounds. Signals of the carbonyl group from the auxiliary ligands and methyl group derived from –B(Mes)$_2$ moieties can be found at ca. 170 ppm and 20 ppm, respectively. Furthermore, in the $^{31}$P NMR spectra of Ir-B-3, the strong resonance peak at ca. 31.91 ppm clearly indicates the presence of a –P=O unit from L$_3$. Therefore, all the NMR data can safely reveal the chemical structures of these cyclometalated iridium(III) complexes.

Scheme 1  Synthetic pathway of the cyclometalated iridium(III) complexes.
Table 1 Photophysical and thermal data for the cyclometalated iridium(III) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption $\lambda_{abs}$ (nm) 298 K</th>
<th>Relative $\Phi_p$ (%) 298 K</th>
<th>Absolute $\Phi_p$ solution$^a$</th>
<th>$\tau_s$ solution$^b$</th>
<th>$\tau_d$ solution$^c$</th>
<th>$\tau_l$ film$^d$ (µs) 298 K</th>
<th>$\Delta T_{50}^g{T_h}^h$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-B-1</td>
<td>292 (4.73), 340 (4.82), 405 (4.33), 499 (3.89)</td>
<td>105</td>
<td>95/100</td>
<td>0.17/0.91</td>
<td>1.86</td>
<td>907</td>
<td>240/190</td>
</tr>
<tr>
<td>Ir-B-2</td>
<td>289 (5.15), 340 (5.22), 405 (5.15), 498 (4.25)</td>
<td>107</td>
<td>98/100</td>
<td>0.16/1.03</td>
<td>1.91</td>
<td>1029</td>
<td>246/190</td>
</tr>
<tr>
<td>Ir-B-3</td>
<td>277 (4.79), 336 (4.72), 403 (3.88), 499 (3.90)</td>
<td>105</td>
<td>97/100</td>
<td>0.17/0.94</td>
<td>1.84</td>
<td>943</td>
<td>220/183</td>
</tr>
<tr>
<td>Ir-B-4</td>
<td>280 (4.93), 336 (4.84), 403 (4.04), 499 (4.01)</td>
<td>96</td>
<td>86/93</td>
<td>0.22/0.70</td>
<td>1.89</td>
<td>780</td>
<td>220/180</td>
</tr>
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</table>

$^a$ Measured in CH2Cl2 at $10^{-5}$ M and log $ε$ values are shown in parentheses. $^b$ Measured in CH2Cl2 relative to fac-[Ir(ppy)3] ($\Phi_p = 40\%$), $\lambda_{abs} = 360$ nm. $^c$ Measured in an integrating sphere with 6 wt% doped PMMA film on quartz as a sample and the excitation wavelength set at 360 nm. $^d$ Measured in an integrating sphere with 6 wt% doped PMMA film on quartz. $^e$ The triplet radiative lifetimes were deduced from $\tau_s = \tau_p/\Phi_p$. $^f$ The excitation wavelength was set at $\lambda_{exc}$. $^g$ Using 6 wt% doped PMMA film on quartz. $^h$ The triplet radiative lifetimes were deduced from $\tau_s = \tau_p/\Phi_p$. $^i$ The excitation wavelength was set at $\lambda_{exc}$. $^j$ Using 6 wt% doped PMMA film on quartz.

Thermal and photophysical properties

Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) characterized the thermal properties of these iridium(III) complexes under a nitrogen flow. The TGA results show that these complexes have high thermal stability with the 5% weight-reduction temperatures ($\Delta T_{50}$) higher than 220 °C (Fig. S1, ESI† and Table 1). DSC traces for all these cyclometalated iridium(III) complexes imply no melting and crystallization processes but only glass-transition behavior (Fig. S1, ESI†). Each of them exhibits a high glass-transition temperature ($T_g$) ranging from 180 to 190 °C, which should be induced by the motion of –B(Mes)2, TPA, Cz2, –POPh3, and –SO2Ph moieties. This good thermal property will guarantee the stabilities of the OLEDs based on these complexes.

The UV-vis absorption spectra of these cyclometalated iridium(III) phosphorescent complexes can be seen in Fig. 1. There are two noticeable absorption bands in their absorption spectra. According to the literature results for their analogues,15,23 the intense absorption bands before 400 nm of these cyclometalated iridium(III) complexes can be safely assigned to the spin-allowed $^3\pi-\pi^*$ transitions of the organic ligands, which can also be ascertained by their large extinction coefficients (log $ε$ ca. 5.0). However, the weaker, low-energy features beyond 400 nm extended to the visible region should be induced by both singlet ($^1$MLCT) and triplet ($^3$MLCT) excitations (MLCT = metal-to-ligand charge transfer).

Under UV light irradiation at 360 nm, these complexes emit intense orange phosphorescence. The photoluminescent (PL) spectra of all these cyclometalated iridium(III) complexes shown in Fig. 2 have virtually identical line-shapes, indicating that the same excited states and ground states are involved in the radiative transitions. The maximum emission wavelengths of the spectra measured in PMMA (polymethylmethacrylate) films (at ca. 6 wt% doping level) are almost the same as those measured in their dilute solution of less polar toluene at 298 K (Fig. 2). However, the PL spectra measured in CH2Cl2, THF and DMF show bathochromic shift and the emission bands are broadened with the increase of the polarity of the solvents due to the solvatochromism effect.57–61 All these complexes have similar peak emission wavelengths in the same medium, indicating that the phosphorescent emission is mainly dominated by –B(Mes)2 moieties on the ppy-type ligands.

In order to interpret the photophysical behavior of these cyclometalated iridium(III) complexes, TD-DFT calculations have been carried out. Detailed calculation results for these iridium(III) complexes are shown in Table 2. From the data in Table 2, it can be seen that HOMO $\rightarrow$ LUMO (H $\rightarrow$ L) and HOMO $\rightarrow$ LUMO+1 (H $\rightarrow$ L+1) can represent the characters of S1 and T1 states due to their large coefficient in CI expansion with the corresponding lowest excited states. From the MO pattern illustrated in Fig. 3, the lowest unoccupied molecular orbitals (LUMOs) of these complexes are mainly located on the ppy-type ligands with substantial contributions from both the pyridine ring and –B(Mes)2 moiety, whereas the highest occupied molecular orbitals (HOMOs) are predominately located in the phenyl ring of the ppy-type ligand and the dπ orbitals of the Ir center. For some exception from L4 to the LUMO and LUMO+1 of Ir-B-4 due to the strong electron-withdrawing ability of the –SO2Ph moiety, the auxiliary ligands make negligible contributions to the key frontier MOs of these cyclometalated iridium(III) complexes (Fig. 3). This result clearly indicates the similarity of the lowest excited states involved in these complexes. Hence, it is reasonable that these cyclometalated iridium(III) complexes can exhibit similar absorption and phosphorescent spectra (Fig. 2). The bathochromic effect of the strong absorption band in Ir-B-1 is induced by the triphenylamine (TPA) unit (Fig. 1), which can be supported by the absorption behavior of the analogues bearing a TPA group.15,25,62 Comparing the different patterns of their HOMO, LUMO and LUMO+1, the transitions generating the lowest excited S1 and T1 states in these cyclometalated iridium(III) complexes exhibit obvious MLCT features, despite the fact that some inter-ligand charge...
transfer (ILCT) features from the ppy-type ligand to auxiliary ligand L4 might be involved in Ir-B-4. Hence, these cyclometalated iridium(III) complexes can show the low-energy MLCT absorption features beyond 400 nm, including both 1MLCT and 3MLCT absorption bands (Fig. 1). The structureless line-shape of the PL spectra for these cyclometalated iridium(III) complexes also clearly indicates the MLCT features associated with the T1 states which induce the phosphorescent signal (Fig. 2 and Fig. S2, ESI†). Clearly, the experimental and theoretical results can corroborate each other very well, indicating the validity of the theoretical results.

The relative phosphorescent quantum yields (Φp) of these cyclometalated iridium(III) complexes were measured in degassed dichloromethane with fac-[Ir(ppy)3] (Φp = 40%) as the standard (Table 1). After several repeated measurements, the Φp s for Ir-B-1, Ir-B-2 and Ir-B-3 are even higher than 100%. Therefore, the absolute Φp s of the same solution samples have been measured by using an integrating sphere (Table 1), and the Φp s in ca. 95% for Ir-B-1, 98% for Ir-B-2 and 97% for Ir-B-3, respectively. For Ir-B-4, the Φp of ca. 86% is slightly lower than that of the other three analogues. When doped in PMMA film at ca. 6 wt% doping level, these cyclometalated iridium(III) complexes can still show exceptionally high absolute Φp s. For Ir-B-1, Ir-B-2 and Ir-B-3 dispersed in the PMMA rigid matrix, their absolute Φp s can be as high as ca. 100%. Similarly, Ir-B-4 also possesses a slightly lower absolute Φp of ca. 93%. These results can possibly be due to the following reasons: (1) According to the TD-DFT calculation (Fig. 3), the excited states of Ir-B-4 exhibit some inter-ligand charge-transfer (ILCT) characteristics, which show prohibited transition behavior instead of that for the allowed transition. Hence, it will restrain the radiative decay in Ir-B-4. (2) The much smaller –SO2Ph moiety in Ir-B-4 can rotate more easily in solution compared with the larger TPA, Cz and –POPh2 groups in Ir-B-1, Ir-B-2 and Ir-B-3, respectively. (3) The strong electron-withdrawing –SO2Ph moiety can provide a larger molecular dipole to induce the molecular interaction and hence slight phosphorescence quenching to some extent. This conclusion might get support from the shortest phosphorescent lifetime (τp) of

<table>
<thead>
<tr>
<th>Compound</th>
<th>Contribution of metal d to HOMO (%)</th>
<th>Contribution of metal d to LUMO (%)</th>
<th>The largest coefficient in CI expansion of the T1 state</th>
<th>Contribution of H → L/H → L+1 to the T1 state (%)</th>
<th>The largest coefficient in CI expansion of the S1 state</th>
<th>Contribution of H → L to the S1 state (%)</th>
<th>f</th>
<th>S0 → S1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-B-1</td>
<td>39.15 1.12</td>
<td></td>
<td>H → L: 0.6470 (533 nm)</td>
<td>83.7/10.7</td>
<td>H → L: 0.7013 (525 nm)</td>
<td>98.4</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>Ir-B-2</td>
<td>38.91 1.72</td>
<td></td>
<td>H → L: 0.5511 (525 nm)</td>
<td>60.7/28.3</td>
<td>H → L: 0.7013 (516 nm)</td>
<td>98.4</td>
<td>0.0014</td>
<td></td>
</tr>
<tr>
<td>Ir-B-3</td>
<td>38.79 1.08</td>
<td></td>
<td>H → L: 0.4416 (524 nm)</td>
<td>39.0/45.4</td>
<td>H → L: 0.7012 (513 nm)</td>
<td>98.3</td>
<td>0.0017</td>
<td></td>
</tr>
<tr>
<td>Ir-B-4</td>
<td>38.54 0.85</td>
<td></td>
<td>H → L: 0.4558 (526 nm)</td>
<td>41.6/30.0</td>
<td>H → L: 0.6831 (505 nm)</td>
<td>93.3</td>
<td>0.0039</td>
<td></td>
</tr>
</tbody>
</table>

- The data have been obtained by exporting DFT results with the software AOMix. H → L represents the HOMO to LUMO transition. CI stands for configuration interaction.

Fig. 2 PL spectra for (a) Ir-B-1, (b) Ir-B-2, (c) Ir-B-3 and (d) Ir-B-4 measured in different media at 298 K (PMMA film: 6 wt% doping level).
Ir-B-4 in the PMMA film (Table 1). At a low temperature of 77 K to restrain the rotation of the SO$_2$Ph moiety, the $\tau_p$ of Ir-B-4 is still similar to that of the other complexes and just like the situation in solution at 298 K. However, in the solid matrix of PMMA to restrain the rotation of the SO$_2$Ph moiety as well, the $\tau_p$ of Ir-B-4 is obviously shorter than that of the other analogues, which can be ascribed to the molecular interaction of Ir-B-4. Hence, besides the ILCT character of excited states, the interaction among the molecules of Ir-B-4 can also account for its lower $\Phi_p$. Owing to the MLCT features associated with the phosphorescent signal aforementioned, the $\tau_p$ of these cyclometalated iridium(III) complexes is relatively short at ca. 1 μs in PMMA film. Both the exceptionally high $\Phi_p$ and short $\tau_p$ will definitely indicate these cyclometalated iridium(III) complexes to be outstanding phosphorescent emitters for application in high performance OLEDs.

**Electrochemical properties**

In order to characterize the electrochemical properties of these cyclometalated iridium(III) complexes, Ir-B-1, Ir-B-2, Ir-B-3 and Ir-B-4, cyclic voltammetry (CV) measurements have been carried out under a nitrogen atmosphere, calibrated with a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple as an internal reference. The experimental data are listed in Table 3. The reduction potential ($E_{\text{red}}$) at ca. 0.72–0.80 V can be assigned to the oxidation of iridium centers of these complexes. For Ir-B-1 and Ir-B-2, the lower potential at ca. 0.62 and 0.58 V can be assigned to the oxidation process of the electron-rich aromatic amine moiety TPA and Cz, respectively (Table 3).$^{15,19,62,66}$ Owing to the attached electron-withdrawing picolinic acid unit, the oxidation potential of the TPA and Cz units moves to the more positive region. Based on our previous study,$^{15,23,67}$ the first reduction potential ($E_{\text{red}}$) at ca. $-2.10$ V for these cyclometalated iridium(III) complexes (ca. $-2.06$ V for Ir-B-1, $-2.13$ V for Ir-B-2, $-2.12$ V for Ir-B-3 and $-2.02$ V for Ir-B-4) can be induced by the reduction of the –B(Mes)$_2$ moieties on the ppy-type ligands (Table 3). The large contribution from the –B(Mes)$_2$ moieties to the LUMOs of these iridium(III) complexes can properly support this conclusion. Considering its stronger electron-withdrawing ability than the –POPh$_2$ moiety, the –SO$_2$Ph moiety might have moved the first $E_{\text{red}}$ of Ir-B-4 (ca. $-2.03$ V) to the less negative potential region compared with that of Ir-B-3 (ca. $-2.12$ V) (Table 3).$^{15,68}$ The reduction waves located at the more negative potential region can be ascribed to the reduction of the pyridyl rings on the ligands of these cyclometalated iridium(III) complexes.$^{23}$

**Electroluminescence devices**

Inspired by their outstanding $\Phi_p$, OLEDs have been constructed with the cyclometalated iridium(III) complexes as phosphorescent emitters by the spin-coating approach to evaluate their EL performance. Considering the electronic features of the functional groups attached to these cyclometalated iridium(III) complexes, Ir-B-2 with both EI/ET and HI/HT moieties can furnish these cyclometalated iridium(III) complexes with balanced charge carrier injection/transporting features, which is essential to help enhance the EL performance of the OLEDs based on these phosphorescent complexes.
have been selected as the phosphorescent emitters to fabricate OLEDs. The devices based on these two phosphorescent iridium(III) complexes have been constructed with the configuration of ITO/PEDOT:PSS (45 nm)/Ir x wt%:TCTA (30 nm)/TPBi (45 nm)/LiF/Al (1:100 nm) (Fig. 4). The thin PEDOT:PSS layer can play the role of hole injection. The host material for the phosphorescent dopant is 4,4',4'-tri(N-carbazolyl)-triphenylenamine (TCTA). Due to its excellent electron transporting (ET) ability and low HOMO level of ca. 6.3 eV, the layer of 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) can serve the purpose of both electron transporting and hole blocking, whereas LiF can fulfill the function of the electron injection layer (EIL). With the aim of optimizing the EL performances, OLEDs with different doping levels have also been fabricated (Fig. 4). Devices A1–A3 and B1–B3 have the doping level of 4.0, 6.0 and 8.0 wt%, respectively.

Table 4 summarizes the obtained EL data of the solution-processed OLEDs. At proper driving voltage, all these OLEDs exhibit intense orange electroluminescence. As depicted in Fig. 4, for the devices A2 and B2, the EL maximum is located at 576 nm with the Commission Internationale de L’Eclairage (CIE) coordinates of (0.51, 0.49). Their EL spectral profiles are similar to the typical PL spectra of the corresponding iridium(III) complexes in TCTA film (Fig. 5, Fig. S3 and S4, ESI†), indicating that the EL emission is indeed generated from the triplet excited state of the iridium(III) complexes. For devices A1 and B1, the emerged emission peak at around 400 nm can be assigned to the EL band for the host material TCTA, which is caused by the relatively insufficient energy transfer from the host to the phosphorescent guest (Fig. S4, ESI†). Hence, devices A1 and B1 show lower EL efficiencies than A2 and B2. However, the EL band from the TCTA host cannot be detected noticeably in the spectra for A2, A3, B2 and B3, implying the efficient forward energy-transfer from the host to the phosphorescent guest (Fig. 5). The current density–voltage–luminance (J–V–L) characteristics and the EL efficiency–luminance curves can be seen in Fig. 6 and 7, and the ESI† (Fig. S5 and S6). All these devices show low turn-on voltages from 3.4 to 3.9 V (Table 4). As the iridium(III) complexes exhibit very high ΦP and excellent charge carrier transporting/injection features, the OLEDs fabricated with these phosphorescent iridium(III) complexes can show exceptionally high EL performance. It turns out that the 6.0 wt% doped device A2 based on cyclometalated iridium(III) complex Ir-B-2 as the emitter exhibits the best EL performance, which gives a turn-on voltage (Vturn-on) of 3.6 V, a maximum luminance (Lmax) of 14940 cd m−2 at 23.6 V, a peak luminance efficiency (ηL) of 85.1 cd A−1, corresponding to a peak power efficiency (ηP) of 69.7 lm W−1 and a peak external quantum efficiency (ηext) of 28.1% (Table 4). Besides, device B2 with Ir-B-3 as an emitter can show remarkable EL performances with Vturn-on of 3.4 V, Lmax of 15894 cd m−2 at 21.9 V, ηL of 73.0 cd A−1, ηP of 63.9 lm W−1, and ηext of 24.6%. The devices A3 and B3 with high doping levels of ca. 8.0 wt% might induce triplet–triplet annihilation (TTA) among the phosphorescent molecules, which should account for their lower EL efficiencies compared with A2 and B2. Despite the relatively lower EL efficiencies compared with those of devices A2 and B2, devices A1, A3, B1 and B3 still possess attractive EL data.

In order to clarify the high EL performance for these OLEDs, ΦP for Ir-B-2 and Ir-B-3 doped in TCTA films with different doping levels were measured (Table S1, ESI†). All these doped films can also possess very high ΦP of 100% to guarantee their high EL efficiencies.21,22,25 In addition, as compared with the TCTA host in both hole-only and electron-only devices, both Ir-B-2 and Ir-B-3 can show lower HI/HT and higher EI/ET abilities (Fig. S7, ESI†), i.e. ambipolar properties, benefiting their EL performances as well. These are the two main factors to furnish very high EL efficiencies to Ir-B-2 and Ir-B-3. Differently, without HI/HT units, Ir-B-3 just possesses the EI/ET functional groups of –B(Mes)2 and –POPh2. So, Ir-B-3 might show an insufficient HI/HT ability to balance its high EI/ET capacity.

Table 3 Redox properties of these cyclometalated iridium(III) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eox (V)</th>
<th>Ered (V)</th>
<th>EHOMO (eV)</th>
<th>ELUMO (eV)</th>
<th>Eopt (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-B-1</td>
<td>0.62a, 0.80b</td>
<td>−2.06c, −2.27c</td>
<td>−5.42</td>
<td>−2.74</td>
<td>2.25</td>
</tr>
<tr>
<td>Ir-B-2</td>
<td>0.58c, 0.80b</td>
<td>−2.13c, −2.61c</td>
<td>−5.38</td>
<td>−2.67</td>
<td>2.29</td>
</tr>
<tr>
<td>Ir-B-3</td>
<td>0.72b</td>
<td>−2.12c, −2.34c</td>
<td>−5.52</td>
<td>−2.68</td>
<td>2.29</td>
</tr>
<tr>
<td>Ir-B-4</td>
<td>0.74b</td>
<td>−2.03b, −2.30c, −2.60b</td>
<td>−5.38</td>
<td>−2.77</td>
<td>2.29</td>
</tr>
<tr>
<td>Ir[ppy]2[pic]</td>
<td>0.61b</td>
<td>−2.38b</td>
<td>−5.41</td>
<td>−2.42</td>
<td>2.88</td>
</tr>
</tbody>
</table>

a Irreversible or quasi-reversible. The value was derived from the anodic or cathodic peak potential. b Reversible. The value was set as E1/2 = (Eox + Ered) / 2 and E opt = (Eox + Ered) / 2. Eox is the E1/2 of the first reversible oxidation wave or the onset potential of the first irreversible oxidation wave. Ered is the E1/2 of the first reversible reduction wave or the onset potential of the first irreversible reduction wave. c Optical energy gap Eopt calculated from the absorption onset of the UV-vis absorption spectra.
As a result, Ir-B-3 exhibits lower EL efficiencies than Ir-B-2. At high luminance, all the devices show an obvious efficiency roll-off effect (Fig. 7 and Fig. S6, ESI†). Owing to the high EL efficiencies, the recombination efficiency between holes and electrons should be high to form excitons. Accordingly, the density of excitons should be very high at high driving voltage or luminance, which should greatly increase the chance of exciton quenching. So, an obvious efficiency roll-off effect can be observed in the OLEDs at high luminance.

Several research groups have studied OLEDs using phosphorescent complexes containing –B(Mes)₂ moieties as emitters.15,23,24,66,70,71 EL devices based on borylated iridium(III) complexes can show EL efficiencies of 14.7%, 21.4 cd A⁻¹ and 22.2 lm W⁻¹, while OLEDs showing 10.1%, 35.0 cd A⁻¹ and

**Table 4** EL performance for the devices made from the cyclometalated iridium(III) complexes Ir-B-2 and Ir-B-3

<table>
<thead>
<tr>
<th>Device</th>
<th>Phosphor dopant</th>
<th>( V_{\text{turn-on}} ) (V)</th>
<th>Luminance ( \eta_{\text{lum}} ) (L/cd m⁻²)</th>
<th>( \eta_{\text{ext}} ) (%)</th>
<th>( \eta_{\text{le}} ) (cd A⁻¹)</th>
<th>( \eta_{\text{LP}} ) (lm W⁻¹)</th>
<th>( \lambda_{\text{max}} ) (nm) (CIE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Ir-B-2 (4 wt%)</td>
<td>3.9</td>
<td>14 681 (19.1)</td>
<td>20.2 (5.1)°</td>
<td>61.0 (3.1)</td>
<td>46.4 (3.9)</td>
<td>576 (0.50, 0.49)</td>
</tr>
<tr>
<td>A2</td>
<td>Ir-B-2 (6 wt%)</td>
<td>3.6</td>
<td>14 940 (23.6)</td>
<td>28.1 (5.3)°</td>
<td>85.1 (5.3)</td>
<td>69.7 (3.6)</td>
<td>576 (0.51, 0.49)</td>
</tr>
<tr>
<td>A3</td>
<td>Ir-B-2 (8 wt%)</td>
<td>3.9</td>
<td>10 736 (25.0)</td>
<td>24.2 (5.1)°</td>
<td>73.3 (5.1)</td>
<td>54.1 (3.9)</td>
<td>580 (0.52, 0.48)</td>
</tr>
<tr>
<td>B1</td>
<td>Ir-B-3 (4 wt%)</td>
<td>3.4</td>
<td>12 849 (23.3)</td>
<td>24.3 (4.8)°</td>
<td>66.6 (4.8)</td>
<td>55.1 (3.4)</td>
<td>576 (0.51, 0.49)</td>
</tr>
<tr>
<td>B2</td>
<td>Ir-B-3 (6 wt%)</td>
<td>3.4</td>
<td>15 894 (21.9)</td>
<td>24.6 (4.8)°</td>
<td>73.0 (4.8)</td>
<td>63.9 (3.4)</td>
<td>576 (0.51, 0.49)</td>
</tr>
<tr>
<td>B3</td>
<td>Ir-B-3 (8 wt%)</td>
<td>3.7</td>
<td>14 536 (25.3)</td>
<td>23.5 (3.7)°</td>
<td>66.1 (3.7)</td>
<td>55.4 (3.7)</td>
<td>576 (0.51, 0.49)</td>
</tr>
</tbody>
</table>

° Maximum values. Values in parentheses are the voltages at which they were obtained. ° Values were collected at 100 cd m⁻². ° Values were collected at 1000 cd m⁻². ° Values were collected at 8 V and CIE coordinates (x, y) are shown in parentheses.

Fig. 5 EL spectra of the optimized devices A2 and B2 at ca. 10 V.

Fig. 6 J–V–L curves for the optimized devices A2 and B2.

Fig. 7 Relationship between the electroluminescence efficiency and luminance for the optimized devices (a) A2 and (b) B2.
36.6 lm W\(^{-1}\) were fabricated with organoboron platinum(II) complexes.\(^{24}\) Compared with these reported impressive EL data, the EL efficiencies of the solution-processed OLEDs using these cyclometalated iridium(III) complexes are even higher than the aforementioned vacuum evaporated devices with phosphorescent complexes containing –B[Mes]\(_2\) moieties. There are also many highly efficient phosphorescent OLEDs fabricated with orange-emitting heavy-metal complexes using the solution process technique.\(^{7,2-80}\) Our recently reported asymmetric phosphors with a 9-phenyl-9-phosphaphluorene oxide moiety and –B[Mes]\(_2\) moiety can achieve 17.3%, 53.4 cd A\(^{-1}\) and 31.6 lm W\(^{-1}\).\(^ {115}\) Devices based on a dendritic host and an orange-emitting iridium complex give 17.6%, 49.7 cd A\(^{-1}\) and 43.9 lm W\(^{-1}\).\(^ {1,74}\) The OLEDs with phosphorescent iridium(III) complexes can show 29.6%, 87.9 cd A\(^{-1}\) and 46.0 lm W\(^{-1}\), representing the top performances of the solution-processed orange-emitting phosphorescent OLEDs to date.\(^ {7,5,76}\) Except for the higher EL efficiency aforementioned, the orange phosphorescent complexes typically show \(\eta_{\text{ext}}\) < 20%, \(\eta_{\text{L}}\) < 50 cd A\(^{-1}\) and \(\eta_{\text{P}}\) < 40 lm W\(^{-1}\).\(^ {7,0}\) So, EL efficiencies of 28.1%, 85.1 cd A\(^{-1}\) and 69.7 lm W\(^{-1}\) achieved by these cyclometalated iridium(III) complexes with extremely high quantum yield should definitely show their great potential in OLEDs. All these results can clearly show the importance of the concerned molecular design concept, which can provide valuable guidance for synthesizing novel phosphorescent emitters with high EL efficiency. To the best of our knowledge, the peak \(\eta_{\text{P}}\) of device A2 is the highest \(\eta_{\text{P}}\) among the orange OLEDs made from the phosphorescent complexes using the solution process technique.

**Conclusion**

In summary, four phosphorescent cyclometalated iridium(III) complexes with –B[Mes]\(_2\) groups have been developed. Notably, these phosphorescent emitters show extremely high \(\Phi_{\text{P}}\) of nearly 100% at room temperature in both solution and a solid matrix. In addition, the high \(\Phi_{\text{P,s}}\) as well as their good charge carrier injection/transporting ability, endow the OLEDs made from these iridium(III) complexes with exceptional EL efficiencies of maximum \(\eta_{\text{L}}\) of 85.1 cd A\(^{-1}\), \(\eta_{\text{P}}\) of 69.7 lm W\(^{-1}\) and \(\eta_{\text{ext}}\) of 28.1% and the CIE coordinates of (0.51, 0.49). All these decent data will certainly offer the great prospect of using these cyclometalated iridium(III) complexes with very high \(\Phi_{\text{P}}\) in the field of OLEDs. Hence, these results can afford valuable clues for developing highly efficient phosphorescent emitters for practical applications.

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**References**


