



Highly efficient red iridium(III) complexes based on phthalazine derivatives for organic light-emitting diodes

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ABSTRACT

Two novel bis-cyclometalated iridium(III) complexes, **Ir(ECPC)₂(pic)** and **Ir(TPC)₂(pic)** (**HECPC**, 3-(4-(9H-carbazol-9-yl)phthalazin-1-yl)-9-ethyl-9H-carbazole; **HTPC**, 4-(4-(9H-carbazol-9-yl)phthalazin-1-yl)-N,N-diphenylaniline, pic = 2-picolinic acid) were synthesized in moderate yield under mild synthetic conditions, and their electrical and photophysical properties were characterized with respect to their application as a phosphorescent emitter in polymer light-emitting diodes (PLEDs). The devices based on these complexes with the structure of ITO/PEDOT:PSS (40 nm)/70%PVK:30%PBD:x% iridium(III) complex (70 nm)/TPBI (30 nm)/Ba (1.5 nm)/Al (120 nm) were fabricated with highly external quantum efficiency. The device based on **Ir(ECPC)₂(pic)** exhibited a maximum external quantum efficiency of 16.3% and a luminance of 1484 cd/cm²; while the device based on **Ir(TPC)₂(pic)** showed a maximum external quantum efficiency of 11.9% and a Commission International de L'Eclairage (CIE) coordinates of (0.695,0.289). The results showed that the two new bis-cyclometalated iridium(III) complexes can be used as emitters and applied in saturated red phosphorescent organic light-emitting diodes (PHOLEDs).

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1. Introduction

Organic light-emitting diodes (OLEDs) has become a hot research field because of its high efficiency, high brightness, low drive voltage, wide viewing angle, fast response time and easy to realize lower cost large-area flat-panel displays [1]. The organic electrophosphorescent materials have generated great interests for their better luminous efficiency and energy conversion rate [2,3]. The heavy metal complexes used as electrophosphorescent materials in organic light-emitting diodes in recent years because these complexes can generate a strong spin-orbit coupling of triplet excitons to promote phosphorescent radiation, thus substantially improving the luminous efficiency. The internal quantum efficiency theoretically is up to 100%, which is four times of the fluorescent materials [4–9]. In these heavy metal complexes, iridium(III) complexes have attracted more and more attention due to their high luminescence quantum yields, excellent color tuning and

relatively short excited-state lifetime. Generally, both the electroluminescent efficiency and the emission wavelength of devices based on iridium(III) complexes were affected mainly by the cyclometalated ligands. So the emission color could be adjusted tuning and the luminescent properties could be promoted by modifying of the ligands [10]. For practical application of phosphorescent complexes in flat-panel displays, three primary colors, blue, green, red, were essential. Compared with highly efficient green phosphorescent materials, the main problems of red phosphorescent materials were poor color purity, low efficiency and low luminance, et al. So it was an urgent problem to design and synthesize the appropriate red materials.

Phthalazine compounds have a distorted heterocyclic biphenyl structure with two adjacent N-atoms in one aromatic ring and had been widely used in red phosphorescent iridium(III) complexes with excellent luminescent properties. Compared with the common C=N=CH iridium(III) complexes, these C=N=N iridium(III) complexes had high thermal stabilities and easy formed tris-cyclometalated iridium(III) complexes under mild synthetic conditions [11]. Recently, some tris-cyclometalated iridium(III) complexes with C=N=N structure such as phthalazine and pyridazine derivatives as ligands were reported and proved to be

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strong phosphorescent materials with good thermal stabilities. Tong et al. [12] reported a red device using tris(1-(2,6-dimethylphenoxy)-4-(4-chloro-phenyl)phthalazine)iridium ($\text{Ir}(\text{MPCPPZ})_3$) as the dopant by solution process with internal quantum efficiency of nearly 100%. Mi et al. [13] reported the excellent works of iridium(III) complexes containing $\text{C}=\text{N}=\text{N}$ ligands, tris(3,6-bis(phenyl)pyridazine)iridium ($\text{Ir}(\text{BPPya})_3$) and tris(1,4-bis(phenyl)phthalazine)iridium ($\text{Ir}(\text{BPPa})_3$). These tris-cyclometalated iridium(III) complexes based on $\text{C}=\text{N}=\text{N}$ ligands were more promising for optoelectronic applications compared with iridium(III) complexes with simple $\text{C}=\text{N}=\text{CH}$ ligands because of their high thermal stability, high electroluminescent efficiency and high photoluminescent efficiency. Fang et al. [14–16] synthesized several tris-cyclometalated iridium(III) complexes based on phthalazine derivatives containing various functional units. The iridium(III) complexes-based OLEDs had a maximum external quantum efficiency of 20.2%. Based on the results, it was reasonable to believe that ligands with $\text{C}=\text{N}=\text{N}$ structure was beneficial for the performance of iridium(III) complexes. Additionally, excellent performance of the bis-cyclometalated iridium(III) complexes can be obtained in high yields when 1,4-positions of phthalazine derivatives were replaced by conjugate units [17]. It is well known that carbazole has been widely used in OLEDs due to their high triplet energy and good hole-transporting ability [18–20]. Triphenylamine groups which possess superior hole-transport mobility, low ionization, high thermal stability and strong fluorescent properties, are extensively used as hole transporting materials in electroluminescence (EL) [21]. In this article, two novel cyclometalated ligands (**HECPC**, **HTPC**) containing $\text{C}=\text{N}=\text{N}$ structure by introducing carbazole or triphenylamine unit into phenylphthalazine derivatives were synthesized and their bis-cyclometalated iridium(III) complexes were obtained in moderate yield under mild synthetic conditions. The photophysical and electrochemical properties of these complexes were studied. The devices using these complexes as dopants were fabricated by solution process and exhibited saturated red phosphorescent and high external quantum efficiency.

2. Experimental

2.1. General information

All commercially available reactants were purchased and used as received without further purification. Dimethylformamide (DMF), acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and chloroform (CHCl_3) were dried by standard procedures before use. The poly(*N*-vinylcarbazole) (PVK), 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD), 1,3,5-tris(*N*-phenyl-benzimidazol-2-yl)benzene (TPBI), CsF were purchased from Aldrich while poly(ethylenedioxythiophene)-poly(styrenesulfonic acid) (PEDOT:PSS) (Baytron P4083) was from Bayer. The NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer with TMS as the internal standard and $\text{CDCl}_3/\text{DMSO}-d_6$ as solvent. GC-MS spectra were collected on a Shimadzu GC-MS-QP2010 Plus mass spectrometer and electron spray ionization (ESI) mass spectra on a Thermo LCQDECAXP mass spectrometer. Melting points were measured on SGW X-4 micro melting point spectrometer. UV–Vis absorption spectra were obtained at room temperature in HPLC grade CH_2Cl_2 solutions on a Shimadzu UV-3600 UV–Vis spectrometer. Photoluminescence spectra were recorded in CH_2Cl_2 solutions at 298 K by Shimadzu RF-5301PC fluorescence spectrometer. Cyclic voltammetry experiments were performed with a CHI660C electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working

electrode, an auxiliary electrode, and a nonaqueous Ag/AgNO_3 reference electrode. The solvent used was CH_2Cl_2 and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Oxidation potential was calibrated with that of ferrocene. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was estimated from the UV–Vis absorption spectrum edge.

2.2. Synthesis

2.2.1. 2-(9-Ethyl-9H-carbazole-3-carbonyl)benzoic acid [22]

To a suspension of O-phthalic anhydride (2.31 g, 15.6 mmol) in CH_2Cl_2 (20 mL), AlCl_3 (2.78 g, 21 mmol) was added in portions at 0 °C. A solution of 9-ethyl-9H-carbazole (3.56 g, 18 mmol) in CH_2Cl_2 (10 mL) was added, and the mixture was stirred overnight at room temperature. The mixture was poured into diluted hydrochloric acid solution and extracted with 50 mL of CH_2Cl_2 . The extract was dried and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel to give 0.62 g of 2-(9-ethyl-9H-carbazole-3-carbonyl)benzoic acid. Yield: 57%. m.p.: 204–205 °C. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ (ppm): 1.29–1.32 (t, 3H), 4.43–4.48 (q, 2H), 7.20–7.24 (t, 1H), 7.43–7.45 (d, $J = 7.2$ Hz, 1H), 7.47–7.51 (t, 1H), 7.64–7.66 (d, $J = 7.5$ Hz, 3H), 7.71–7.73 (t, 2H), 8.00–8.02 (d, $J = 7.6$ Hz, 1H), 8.17–8.19 (d, $J = 7.7$ Hz, 1H), 8.49 (s, 1H). ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz) δ (ppm): 30.39, 30.47, 118.69, 120.95, 122.39, 128.34, 129.62, 130.09, 130.23, 130.74, 132.54, 135.13, 139.56, 143.37, 146.61, 153.40, 167.68, 198.21. GC-MS (m/z): 299 ($\text{M}^+ - \text{CO}_2$).

2.2.2. 2-(4-(Diphenylamino)benzoyl)benzoic acid

Yield: 43.9%. m.p.: 168–169 °C. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ (ppm): 6.96–6.98 (d, $J = 7.7$ Hz, 2H), 7.01–7.03 (d, $J = 6.4$ Hz, 1H), 7.11–7.13 (d, $J = 8.6$ Hz, 3H), 7.27–7.29 (d, $J = 8.1$ Hz, 1H), 7.35–7.39 (t, 2H), 7.54–7.56 (d, $J = 8.7$ Hz, 1H), 7.59–7.63 (t, 5H), 7.69–7.71 (d, $J = 7.4$ Hz, 1H), 7.95–7.97 (d, $J = 7.6$ Hz, 2H). EI-MS (m/z): 349 ($\text{M} - \text{CO}_2$).

2.2.3. 4-(9-Ethyl-9H-carbazol-3-yl)phthalazin-1(2H)-one [22]

A solution of 2-(9-ethyl-9H-carbazole-3-carbonyl)benzoic acid (1.01 g, 2.9 mmol) and hydrazine hydrate (80%) (5 mL) in ethanol (10 mL) was refluxed for 8 h. After cooled, the resulting white precipitate was filtered, washed with ethanol and dried to give 0.62 g of 4-(9-ethyl-9H-carbazol-3-yl)phthalazin-1(2H)-one. Yield: 62.1%. m.p.: 249–251 °C. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ (ppm): 1.33–1.37 (t, 3H), 4.48–4.53 (q, 2H), 7.19–7.23 (t, 1H), 7.47–7.50 (t, 1H), 7.63–7.64 (d, $J = 3.9$ Hz, 1H), 7.66 (s, 1H), 7.75–7.80 (m, 2H), 7.88–7.90 (t, 2H), 8.21–8.23 (d, $J = 7.7$ Hz, 1H), 8.34–8.37 (m, 1H), 8.38 (t, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 29.70, 30.91, 118.85, 120.01, 123.29, 124.95, 127.37, 128.57, 128.90, 128.99, 129.88, 131.38, 132.50, 132.91, 137.05, 140.63, 148.06, 154.89, 164.82. GC-MS (m/z): 339 (M^+).

2.2.4. 4-(4-(Diphenylamino)phenyl)phthalazin-1(2H)-one

Yield: 58%. m.p.: 269–270 °C. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ (ppm): 7.05–7.12 (m, 8H), 7.33–7.37 (t, 4H), 7.47–7.49 (d, $J = 8.6$ Hz, 2H), 7.78–7.80 (d, $J = 8.2$ Hz, 1H), 7.85–7.93 (m, 2H), 8.31–8.33 (d, $J = 7.6$ Hz, 1H). GC-MS (m/z): 389 (M^+).

2.2.5. 3-(4-Chlorophthalazin-1-yl)-9-ethyl-9H-carbazole [23]

A mixture containing 4-(9-ethyl-9H-carbazol-3-yl)phthalazine-1(2H)-one (2.0 g, 5.9 mmol), CHCl_3 (20 mL) and phosphorus oxychloride (5 mL, 50 mmol, $\rho = 1.675$) was heated at 80 °C for 5 h. After cooling to a temperature of about 25 °C, the mixture was carefully poured into crushed ice. The water was rendered to alkaline by dilute ammonia. Crude product was collected by

extraction with ethyl acetate (EA) and purified by flash chromatography on silica gel with a mixture of petroleum ether–ethyl acetate to give 1.42 g of 3-(4-chlorophthalazin-1-yl)-9-ethyl-9H-carbazole. Yield: 67.3%. m.p.: 128–129 °C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 1.49–1.52 (t, 3H), 4.43–4.49 (m, 2H), 7.26–7.29 (t, 1H), 7.47–7.55 (m, 2H), 7.58–7.60 (d, $J = 8.4$ Hz, 1H), 7.85–7.87 (d, $J = 9.7$ Hz, 1H), 7.91–7.95 (t, 1H), 7.98–8.02 (t, 1H), 8.13–8.15 (d, $J = 7.7$ Hz, 1H), 8.23–8.25 (d, $J = 8.2$ Hz, 1H), 8.39–8.41 (d, $J = 8.2$ Hz, 1H), 8.49 (s, 1H). GC-MS (m/z): 357 (M^+).

2.2.6. 4-(4-Chlorophthalazin-1-yl)-N,N-diphenylaniline

Yield: 61%. m.p.: 196–197 °C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.08–7.11 (t, 2H), 7.19–7.23 (t, 6H), 7.29–7.33 (t, 4H), 7.60–7.62 (d, $J = 8.6$ Hz, 2H), 7.92–8.01 (m, 2H), 8.20–8.22 (d, $J = 8.6$ Hz, 1H), 8.35–8.37 (d, $J = 8.3$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 122.19, 123.79, 125.24, 125.46, 126.40, 127.14, 127.18, 128.27, 129.49, 131.13, 133.06, 133.12, 147.22, 149.48, 153.98, 159.93. GC-MS (m/z): 407 (M^+).

2.2.7. 3-(4-(9H-carbazol-9-yl)phthalazin-1-yl)-9-ethyl-9H-carbazole (HECPC) [15]

A 60% suspension of sodium hydride (0.31 g, 7 mmol) in paraffin oil was added slowly to a solution of carbazole (1.17 g, 6 mmol) in anhydrous DMF (10 mL). After stirred for 1 h at room temperature under nitrogen as a protective gas, this mixture was added dropwise to a solution of 3-(4-chlorophthalazin-1-yl)-9-ethyl-9H-carbazole (1.79 g, 5 mmol) in anhydrous DMF (10 mL), while stirring and cooling with an ice bath, the mixture was stirred at room temperature for 12 h. After reaction, the resulting mixture was poured into water and extracted with ethyl acetate. The extracts were combined, washed with brine, dried over anhydrous magnesium sulfate, and filtered. The solvent was completely removed and the residue was purified by column chromatography over silica gel to give **HECPC**. Yield: 41%. m.p.: 151–153 °C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 1.53–1.56 (t, 3H), 4.48–4.53 (q, 2H), 7.29–7.43 (m, 7H), 7.50–7.57 (m, 2H), 7.66–7.68 (d, $J = 8.4$ Hz, 1H), 7.71–7.73 (d, $J = 8.2$ Hz, 1H), 7.77–7.81 (t, 1H), 7.92–7.96 (t, 1H), 8.05–8.08 (d, $J = 7.5$ Hz, 1H), 8.10–8.23 (t, 3H), 8.43–8.45 (d, $J = 8.4$ Hz, 1H), 8.70 (s, 1H). EI-MS (m/z): 489 (M^+).

2.2.8. 4-(4-(9H-carbazol-9-yl)phthalazin-1-yl)-N,N-diphenylaniline (HTPC)

Yield: 45%. m.p.: 172–174 °C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.10–7.14 (t, 2H), 7.24 (s, 2H), 7.27–7.30 (m, 5H), 7.33–7.39 (m, 8H), 7.41–7.42 (d, $J = 7.1$ Hz, 1H), 7.68–7.70 (d, $J = 8.3$ Hz, 1H), 7.76–7.81 (m, 3H), 7.93–7.96 (t, 1H), 8.19–8.21 (d, $J = 7.2$ Hz, 2H), 8.38–8.40 (d, $J = 8.4$ Hz, 1H). EI-MS (m/z): 539 (M^+).

2.2.9. Bis-cyclometalated iridium(III) complexes [24]

Two bis-cyclometalated iridium(III) complexes were synthesized in two steps using standard method. A solution of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.02 g, 0.07 mmol) and three equivalents of the main ligands (**HECPC** and **HTPC**) in 2-ethoxyethanol/water (4 mL, 3:1 v/v) was stirred at 110 °C for 24 h, then cooled to room temperature, and concentrated in vacuo. Washing the residue with ethanol gave the cyclometalated chloride-bridged dimer. After drying, the crude product was directly used for next step without further purification. A solution of cyclometalated chloride-bridged dimer (1 mmol), Na_2CO_3 (10 mmol) and five equivalents of 2-picolinic acid in dichloromethane (10 mL) was stirred at 40 °C for 12 h, then cooled, and poured into water. Extraction with dichloromethane gave an organic layer which was dried over anhydrous magnesium sulfate, and concentrated in vacuo giving a residue that was subjected to be purified by column chromatography over silica gel using dichloromethane/ethyl acetate as the eluent to afford the desired bis-cyclometalated iridium(III) complexes.

2.2.10. $\text{Ir}(\text{ECPC})_2(\text{pic})$

Yield: 42.4%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 0.75–0.81 (m, 6H), 3.72–3.77 (m, 2H), 4.10–4.15 (m, 2H), 6.79 (s, 1H), 6.88–6.90 (s, 2H), 6.99–7.01 (d, $J = 7.9$ Hz, 1H), 7.11–7.23 (m, 7H), 7.30–7.36 (m, 7H), 7.44–7.48 (t, 1H), 7.53–7.56 (t, 1H), 7.67–7.68 (d, $J = 5.1$ Hz, 1H), 7.74–7.85 (m, 5H), 8.04–8.07 (t, 2H), 8.09–8.16 (m, 7H), 9.00 (s, 2H), 9.21–9.23 (d, $J = 8.5$ Hz, 2H). ESI-MS (m/z): 1312 ($\text{M}^+ + \text{Na}^+$).

2.2.11. $\text{Ir}(\text{TPC})_2(\text{pic})$

Yield: 83.9%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 6.59–6.66 (m, 4H), 6.70–6.76 (m, 6H), 6.83–6.88 (m, 3H), 6.93–6.95 (d, $J = 7.6$ Hz, 7H), 7.08 (s, 1H), 7.16–7.20 (t, 6H), 7.24 (s, 1H), 7.28–7.32 (m, 4H), 7.44–7.52 (m, 2H), 7.54–7.58 (t, 2H), 7.63–7.69 (m, 3H), 7.79–7.81 (d, $J = 7.7$ Hz, 1H), 7.84–7.88 (t, 1H), 7.90–8.00 (m, 4H), 8.03–8.10 (m, 4H), 8.14–8.16 (d, $J = 8.9$ Hz, 1H), 8.20–8.26 (m, 2H), 8.93–8.94 (d, $J = 8.6$ Hz, 2H). EI-MS (m/z): 1389.4 (M^+).

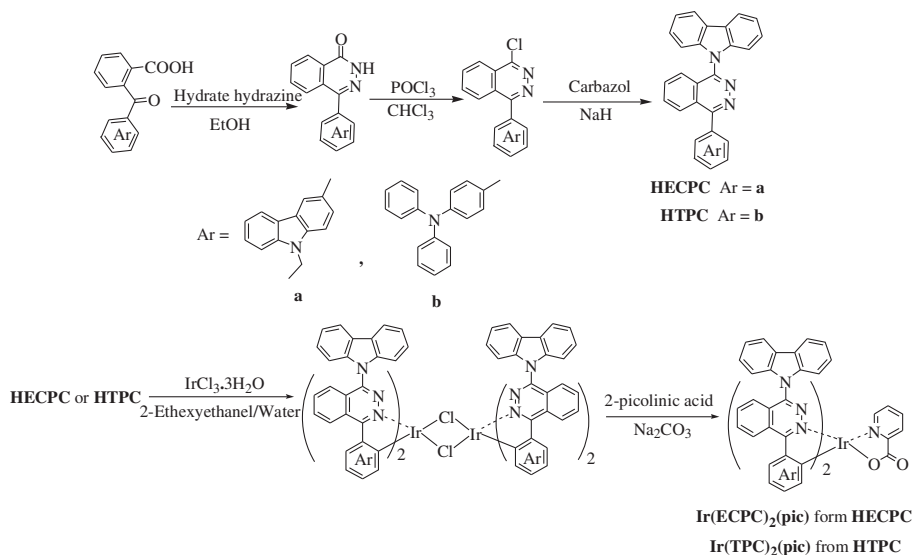
2.3. OLED fabrication and measurements

The devices based on these iridium(III) complexes with the structure of ITO/PEDOT:PSS (40 nm)/70% PVK + 30%PBD + x wt% iridium(III) complex (70 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al (120 nm) were fabricated. In the emitting layer, the doping concentrations of **Ir(ECPC) $_2$ (pic)** were 1 wt%, 2 wt%, 4 wt%, 8 wt%, of **Ir(TPC) $_2$ (pic)** were 1 wt%, 2 wt%, 4 wt%, 8 wt%, respectively; and the mass ratio of PBD was 30% in the PVK-PBD blend. ITO (Indium tin oxide) glass substrates were cleaned in turn with acetone, substrate cleaning detergent, deionized water and isopropyl alcohol, then dried for 2 h before use. Then a 40 nm thick PEDOT:PSS film was spin-coated onto the pre-cleaned ITO glass and dried at 80 °C for 8 h under vacuum. After that the mixture solution of PVK, PBD and the resulting iridium(III) complexes was spin-coated on top of the PEDOT layer using chlorobenzene as the solvent to obtain an emitting layer (70 nm); The assembly was then annealed for 20 min at 100 °C. The TPBI layer was grown by thermal sublimation under vacuum (3×10^{-6} Torr). Subsequently, a layer of CsF (1.5 nm) and a layer of Al (120 nm) were vacuum-evaporated under vacuum in 3×10^{-4} Pa on the top of the EL polymer layer. The area of efficient light-emitting device is 0.19 cm^2 . The processes were completed in the glove box except the PEDOT:PSS was spin-coated in air. Current density–voltage–luminance (J – V – L) characteristics were recorded with a Keithley 236 source meter. The EL spectra and luminance were determined by a PR705 photometer. The external quantum efficiency was calibrated in an integrating sphere (Labsphere, IS080).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes to the ligands and the iridium(III) complexes were shown in Scheme 1. The cyclometalated ligands **HECPC** and **HTPC** were prepared from 3-(4-chlorophthalazin-1-yl)-9-ethyl-9H-carbazole and 4-(4-chlorophthalazin-1-yl)-N,N-diphenylaniline, respectively. 4-(9-ethyl-9H-carbazol-3-yl)phthalazin-1(2H)-one and 4-(4-(diphenylamino)phenyl)phthalazin-1(2H)-one were treated with POCl_3 at 80 °C in CHCl_3 solution and the resulting products were treated with NaH at room temperature to afford ligands **HECPC** and **HTPC**, respectively. The iridium(III) complexes were synthesized in two steps using standard method. The cyclometalated chloride-bridged dimers were prepared according to the reported procedures and were treated with 2-picolinic acid in dichloromethane in the presence of Na_2CO_3 to yield iridium(III) complexes **Ir(ECPC) $_2$ (pic)** and **Ir(EPCC) $_2$ (pic)**. Fig. 1 gave the molecular structures of these two complexes.



Scheme 1. Synthesis of the phthalazine ligands and their iridium(III) complexes.

3.2. Photophysical, electrochemical properties, and theoretical calculations

The absorption spectra and photoluminescence (PL) spectra of the complexes in CH_2Cl_2 solutions at 298 K were shown in Fig. 2. In common with most iridium(III) complexes, the absorption spectra of **Ir(HECPC)₂(pic)** and **Ir(TPC)₂(pic)** can be divided into two regions. The intense absorption bands in the ultraviolet region areas below 400 nm were assigned to the typical spin-allowed intraligand $^1\pi-\pi^*$ transition which closely resembled the spectra of the cyclometalated ligands **HECPC** and **HTPC** (Support Information Fig. S1). On the other hand, the weak and broad absorption bands above 400 nm can be attributed to the metal to ligand charge-transfer (MLCT) transitions were clearly observed, which were not observed in the spectra of cyclometalated ligands. These data suggested that there was a substantial mixing of ligand-based $^3\pi-\pi^*$ states, spin forbidden metal to ligand charge transfer ($^3\text{MLCT}$) and higher-lying $^1\text{MLCT}$ transition induced by the spin-orbit coupling effect of iridium(III) cyclometalated complexes. The complex **Ir(HECPC)₂(pic)** with carbazole-substituted phthalazine ligand showed more distinguishable MLCT absorption features at about 530 nm, which was likely to be $^3\text{MLCT}$ based transitions [25]. Compared with **Ir(HECPC)₂(pic)**, the absorption peaks of **Ir(TPC)₂(pic)** shifted to longer wavelengths because of the enlargement of π conjugated system in the **HTPC** ligand. It can be found that the MLCT absorption bands of these two complexes both matched well with the emission spectra of host material (PVK-PBD blend $\lambda_{\text{max}} = 430$ nm). The results indicated that the Förster energy can transfer from the singlet-excited states of the host to the MLCT states of the iridium(III) complexes effectively. Upon irradiation with

420 nm light, the red emission of these two iridium(III) complexes was assigned to the $^3\text{MLCT}$ phosphorescence at the ambient temperature, which was commonplace for other similar iridium(III) cyclometalated complexes. The wavelength of maximum emission of **Ir(HECPC)₂(pic)** and **Ir(TPC)₂(pic)** were near 640 nm and 654 nm, respectively. It should be noticed that introducing triphenylamine unit instead of carbazole unit led to a red shift of 14 nm in the PL spectrum of iridium(III) complexes, which was consistent with the absorption spectra. This suggested that the carbazole moiety of this material increased the band-gap energy. PL spectra of **Ir(HECPC)₂(pic)** and **Ir(TPC)₂(pic)** in organic solvent and at low temperature were also measured (Support Information Figs. S2 and S3). A subtle blue shift of the emission maximum and the narrower peak were observed from a fluid solution at room temperature to a rigid matrix at 77 K, which was often observed for cyclometalated iridium(III) diimine MLCT and LLCT emitters [26]. The subtle blue shift and the narrower emission peak were caused by fast solvent reorganization in a fluid acetonitrile solution at room temperature, which can stabilize the CT state before emission took place. At 77 K, however, this stabilization of CT state was hampered.

The lifetime of **Ir(HECPC)₂(pic)** and **Ir(TPC)₂(pic)** showed first order as 0.25 μs and 0.21 μs in degassed toluene, respectively

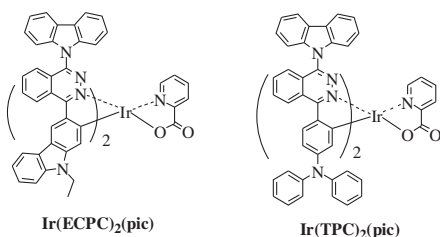


Fig. 1. Molecular structures of the complexes.

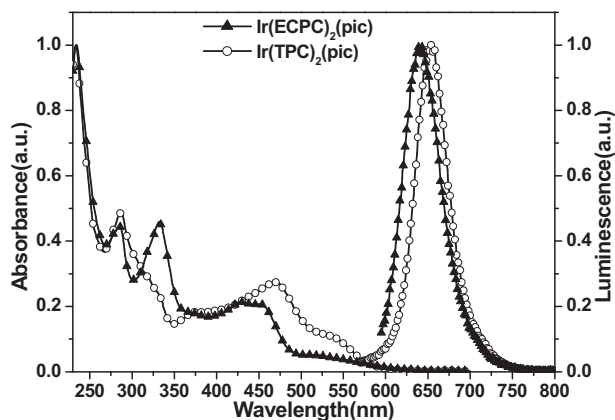


Fig. 2. UV-Vis absorption and photoluminescence spectra of **Ir(HECPC)₂(pic)** and **Ir(TPC)₂(pic)**.

(Support Information Figs. S4 and S5). Long lifetime will give rise to the emission saturation and elevate the triplet–triplet annihilation. Compared with the lifetime of the common complex $\text{Ir}(\text{ppy})_3$ (1.6 μs), these complexes had shorter lifetime. The suitable lifetime of these complexes was beneficial to improve the efficiency of OLEDs.

The electrochemical characteristics of these complexes showed that their oxidation was reversible, which was necessary information to determine their electronic energy levels (see Fig. 3). Cyclic voltammograms were recorded at 298 K and the potentials were obtained relative to an internal ferrocene reference (Fc/Fc^+). These CV scans in the 0–1.0 V (vs. Ag/AgNO_3) range showed reversible oxidation peaks. Unfortunately, the reduction behaviors were irreversible. Therefore, we were unable to directly calculation their lowest unoccupied molecular orbital (LUMO) levels. To determine the LUMO levels, we combined the CV oxidation potential with the optical energy band gap (E_g) resulting from the absorption edge in the absorption spectrum. Cyclic voltammograms of $\text{Ir}(\text{ECPC})_2(\text{pic})$ and $\text{Ir}(\text{TPC})_2(\text{pic})$ in their solution states showed that their lowest oxidative waves were at -0.47 and -0.48 V, respectively. As shown in Table 1, $\text{Ir}(\text{ECPC})_2(\text{pic})$ and $\text{Ir}(\text{TPC})_2(\text{pic})$ had the highest occupied molecular orbital (HOMO) levels of -5.17 and -5.18 eV, respectively. The higher HOMO level of $\text{Ir}(\text{ECPC})_2(\text{pic})$ indicated that the introduction of carbazole group can regulate the energy level and make the HOMO level of the object material close to the host materials. Electrochemical data estimated the lowest unoccupied molecular orbital (LUMO) levels to be -3.05 and -3.03 eV, respectively, estimated by using the oxidation potential and UV–Vis absorption spectrum edge. These frontier orbital levels were compatible to the energy levels for the hosts PBD (-6.2 eV and -2.6 eV) and PVK (-5.8 eV and -2.2 eV) so that the electronic structure requirements for the OLEDs can be satisfied.

In order to further study the photophysical and electrochemical properties of iridium(III) complexes, the HOMO and LUMO distributions of $\text{Ir}(\text{ECPC})_2(\text{pic})$ and $\text{Ir}(\text{TPC})_2(\text{pic})$ were calculated by density functional theory (DFT) (computed using the B3PW91 hybrid functional). As shown in Table 2, the HOMO primarily resided on the iridium (III) center and 9-ethyl-9H-carbazole of cyclometalated ligands, while phthalazine ring of cyclometalated ligands and pyridine ring of 2-picolinic acid almost had no composition. It can be seen that the composition of the HOMO was dramatically changed with significant d-orbital character the iridium (III) center. On the other hand, the LUMO was located almost entirely over phthalazine ring, along with minor contributions from 9-ethyl-9H-carbazole and iridium (III) center.

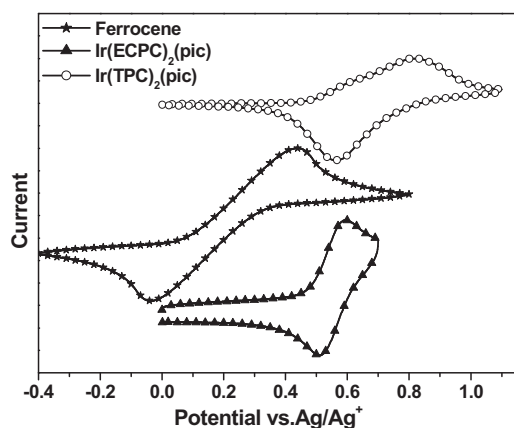


Fig. 3. Cyclic voltammograms of the iridium(III) complexes and ferrocene.

Table 1

Photophysical, thermal and electrochemical data for iridium(III) complexes.

Iridium(III) complex	Absorption ^a (nm)	Emission ^a (nm)	$E_{1/2}^{\text{oxb}}$ (V)	HOMO ^c (eV)	LUMO ^c (eV)	E_g^d (eV)
$\text{Ir}(\text{ECPC})_2(\text{pic})$	281, 331, 443	640	0.47	-5.17	-3.05	2.12
$\text{Ir}(\text{TPC})_2(\text{pic})$	286, 371, 469, 538	654	0.48	-5.18	-3.03	2.15

^a As 10^{-5} M solutions in CH_2Cl_2 .

^b As 10^{-3} M solutions in CH_2Cl_2 containing 10^{-1} M NBu_4PF_6 as electrolyte versus ferrocene/ferrocenium.

^c $\text{HOMO} = -eV(E_{1/2}^{\text{ox}}(\text{iridium(III) complex}) + 4.8 - E_{1/2}^{\text{ox}}(\text{ferrocene}))$.

^d $E_g = 1240/\lambda_{\text{abs}}$.

With respect to $\text{Ir}(\text{TPC})_2(\text{pic})$, the HOMO contributed mostly from diphenylamine, while the phthalazine and the iridium (III) center had very little composition, no significant interaction between the ligand and the metal-centered orbitals can be observed in the HOMO. Compared with $\text{Ir}(\text{ECPC})_2(\text{pic})$, the similar composition of $\text{Ir}(\text{TPC})_2(\text{pic})$ in LUMO which almost located at phthalazine ring, while diphenylamine and the iridium (III) center only had little contribution. This was another way of saying that both the HOMO and LUMO were distributed almost entirely over the cyclometalated ligands. Hence the absorption in the visible region (near 538 nm) was assignable to a transition within the filled (HOMO) and vacant (LUMO) orbitals of the cyclometalated ligands.

3.3. Electroluminescent properties

In order to study the electroluminescent properties of the complexes, the red emissive PLEDs were fabricated by adding $\text{Ir}(\text{ECPC})_2(\text{pic})$ or $\text{Ir}(\text{TPC})_2(\text{pic})$ as phosphorescent dopants into host materials PBD and PVK. The energy band diagram and molecular structures of used materials in this study with the configuration of OLEDs were shown in Fig. 4. Indium tin oxide (ITO) on a substrate of electroluminescent device was used as the anode and CsF/Al as the cathode. The PEDOT:PSS were added between the anode and the polymer to increase the hole-injection and block the electron transport to the anode. At the same time, PEDOT:PSS was spin-coated on the ITO glass which can smooth the ITO surface, reduce the probability of electrical shorts, decrease the turn-on voltage and prolong the operation lifetime of the device. PVK-PBD blend can be used as host materials, and TPBI as the hole-blocking material can improve electron injection and electron transport. The doping concentrations of $\text{Ir}(\text{ECPC})_2(\text{pic})$ or $\text{Ir}(\text{TPC})_2(\text{pic})$ were according to the host and the mass ratio of PBD was 30% in the PVK-PBD blend. The HOMO/LUMO levels of the materials used in PLEDs were described in Fig. 4. The electrode interfaces and their LUMO and HOMO energy levels best matched those of the cathode and PEDOT:PSS work functions, respectively. The PVK with high HOMO levels as electron-donating and hole-transport media, while TPBI with low LUMO levels as electron-accepting and electron-transport media for effective electron injection/transport and confinement of triplet excitons within emitting layer. The HOMO and LUMO level of $\text{Ir}(\text{ECPC})_2(\text{pic})$ or $\text{Ir}(\text{TPC})_2(\text{pic})$ was embedded between the HOMO of PVK (5.80 eV) and the LUMO of PBD (2.40 eV). Hole was injected from the anode to HOMO levels of host material and electron was injected in LUMO levels. Thus, efficient energy transfer to $\text{Ir}(\text{ECPC})_2(\text{pic})$ or $\text{Ir}(\text{TPC})_2(\text{pic})$ occurred in the emitting layer (EML). The PLED performance in luminance should be determined by the intrinsic quantum efficiency of $\text{Ir}(\text{ECPC})_2(\text{pic})$ or $\text{Ir}(\text{TPC})_2(\text{pic})$ in radiative decay. Because the HOMO level of $\text{Ir}(\text{ECPC})_2(\text{pic})$ was 0.63 eV and $\text{Ir}(\text{TPC})_2(\text{pic})$ was 0.62 eV higher than that of PVK, respectively. It behaved as an effective trapping site for holes. Meanwhile, the LUMO level of $\text{Ir}(\text{ECPC})_2(\text{pic})$ was 0.65 eV and $\text{Ir}(\text{TPC})_2(\text{pic})$ was

Table 2
Frontier molecular orbitals for iridium(III) complexes.

Molecular structure	LUMO		HOMO	
		−2.13 eV		−4.79 eV
Ir(EPCC) ₂ (pic)				
		−2.07 eV		−4.82 eV
Ir(TPC) ₂ (pic)				

0.63 eV lower than that of PBD, electrons injected from the TPBI layer into the emitting layer were mostly transported through the PBD layer and being composited in the iridium(III) phosphor. Thus, varying the concentration of Ir(EPCC)₂(pic) or Ir(TPC)₂(pic) in the EML should significantly alter the degree of charge injection in PVK-PBD-based devices. Therefore, the current density of the PVK-PBD-based devices exhibited a strong dependence on the doping concentration.

The EL spectra of the iridium(III) complexes for OLEDs were shown in Fig. 5. A weak emission at about 438 nm from PVK/PBD at the low doping concentrations was found in Fig. 5(A) and disappeared at 4 wt% doping concentrations, while no characteristic emission from the host even at the low doping concentrations in Fig. 5(B). The absence of any emission peak of host materials indicated that energy and charge transfer from the host exciton to the phosphor was efficient under electrical excitation. The maximum emission peak of Ir(EPCC)₂(pic) was 656 nm, and that of Ir(TPC)₂(pic) was 662 nm corresponding to saturated red emission. There was a shoulder at 707 nm in Ir(TPC)₂(pic)-dopant OLEDs, which can be attributed to the aggregation of the iridium(III) complex in the fabricated OLEDs. The maximum EL peak was dependent on the cyclometalated ligands. Especially, the EL spectra

of Ir(TPC)₂(pic) were red-shift by 6 nm compared to that of Ir(EPCC)₂(pic) due to the larger conjugate of HTPC ligand. Typical Commission International de L'Eclairage (CIE) coordinates of the OLEDs were presented in Fig. 6. The CIE chromaticity coordinates for Ir(EPCC)₂(pic)-dopant OLEDs and Ir(TPC)₂(pic)-dopant OLEDs at 2 wt% doping concentrations were (0.678,0.291) and (0.688,0.287), respectively. The CIE coordinates of the iridium(III) complexes were very close to the National Television System Committee of red standard with the CIE coordinate of (0.67,0.33). Due to the impact of the host, the CIE coordinates of the devices containing 1 wt% iridium(III) complexes were different from the devices at higher doping concentration. While the CIE coordinates almost had no change from 2 wt% to 8 wt% doping concentration, indicating that the devices based on Ir(EPCC)₂(pic) or Ir(TPC)₂(pic) had a good light-stability. From these results, standard red phosphorescent iridium(III) complexes were obtained.

Current density–voltage–luminance (*J–V–L*) characteristics of Ir(EPCC)₂(pic) and Ir(TPC)₂(pic) at different concentrations were shown in Fig. 7. The device performances and EL emission characteristics were summarized in Table 3. The maximum luminance of Ir(EPCC)₂(pic) and Ir(TPC)₂(pic) were found to be 1484 cd/m² at 2 wt% and 728 cd/m² at 4 wt%, respectively. The turn-on voltages of

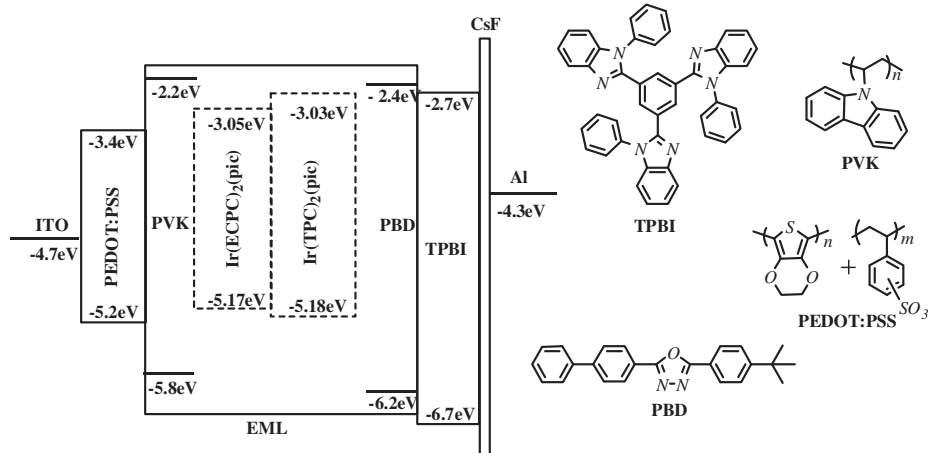


Fig. 4. Energy-level diagrams of OLEDs and molecular structures of the relevant compounds.

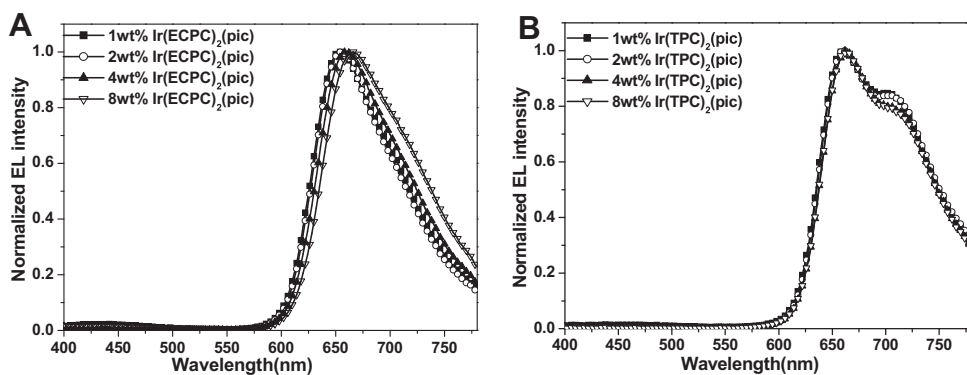


Fig. 5. Electroluminescence spectra of the devices.

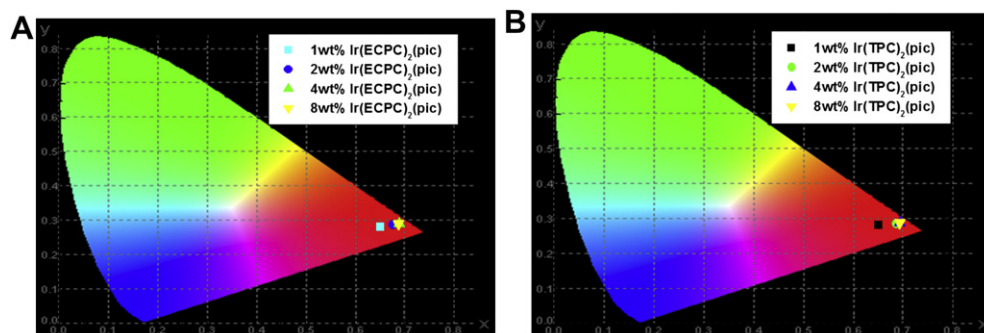


Fig. 6. CIE coordinates dependence on the luminance.

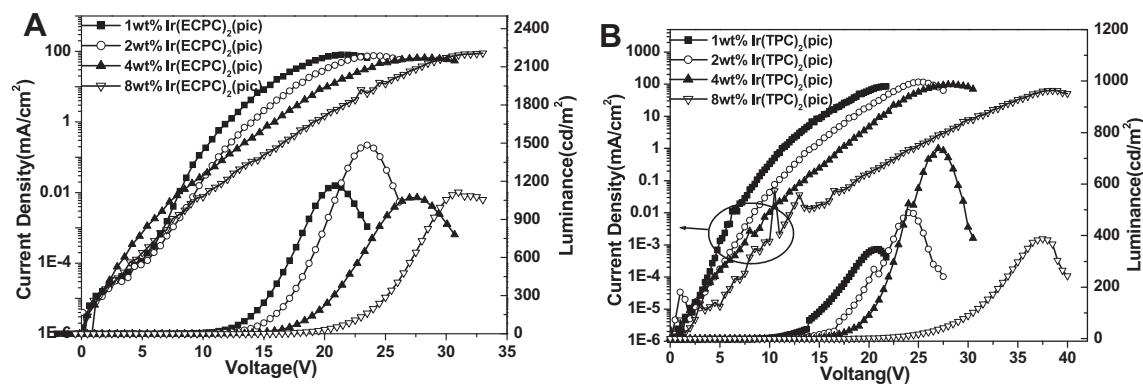


Fig. 7. Current density–voltage–luminance curves of the devices.

Table 3

Performances of the electrophosphorescent devices with different luminescent layers.

Device	$L_{\max}$ (cd/m ²)	CIE (x,y)	Turn on voltage (V)	The maximums of quantum efficiency				
				Voltage (V)	Current density (mA/cm ²)	Luminance (cd/m ²)	LE (cd/A)	EQE (%)
1 wt% Ir(EPCC) ₂ (pic)	1165	(0.652,0.285)	8.6	10.2	0.19	7.4	3.99	11.2
2 wt% Ir(EPCC) ₂ (pic)	1484	(0.678,0.291)	9.9	10.8	0.06	2.8	4.88	16.3
4 wt% Ir(EPCC) ₂ (pic)	1071	(0.691,0.293)	11.8	17.7	2.9	74.4	2.58	8.59
8 wt% Ir(EPCC) ₂ (pic)	1085	(0.689,0.294)	14.6	22.5	4.2	107	2.53	8.43
1 wt% Ir(TPC) ₂ (pic)	346	(0.652,0.283)	9.6	14.0	5.1	70.4	1.38	8.37
2 wt% Ir(TPC) ₂ (pic)	489	(0.688,0.287)	11.6	17.2	5.9	84.1	1.41	10.22
4 wt% Ir(TPC) ₂ (pic)	738	(0.695,0.289)	12.9	18.0	1.46	30.7	2.11	11.9
8 wt% Ir(TPC) ₂ (pic)	387	(0.694,0.289)	19.0	26.0	1.7	25.3	1.48	8.32

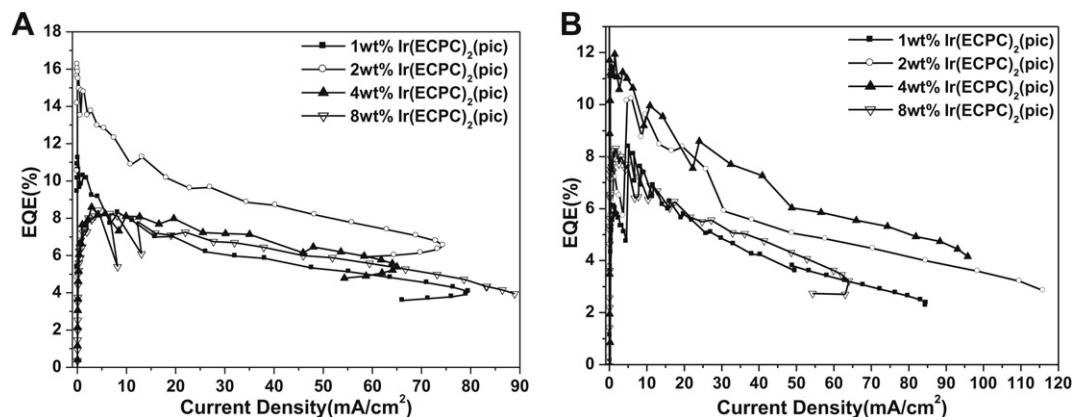


Fig. 8. External quantum efficiency–current density curves of the devices.

Ir(ECPC)₂(pic)-based devices were lower than those of **Ir(TPC)₂(pic)**-based devices at the same doping concentration. Therefore, it can be estimated that hole-transporting carbazole units in the complexes were favorable to balance charge recombination and facilitate the electrical excitation in electrophosphorescent process. The luminance of **Ir(TPC)₂(pic)** was much lower than that of **Ir(ECPC)₂(pic)**. The lower brightness of all devices (relative to the blue-emitting or green-emitting devices) was partly due to their deep red emission in a spectral region, where naked eye has poor sensitivity [27]. The external quantum efficiency (EQE) and current efficiency were plotted against current density as shown in Fig. 8. The maximum external quantum efficiency of the device based on **Ir(ECPC)₂(pic)** and **Ir(TPC)₂(pic)** were 16.3% and 11.9%, respectively. With increasing current density, the external quantum efficiency and luminance efficiency of the devices dropped rapidly, which was possibly due to the increased opportunity for triplet–triplet annihilation of the phosphorbound excitons. Therefore, it was necessary to optimize the device structure for **Ir(ECPC)₂(pic)** and **Ir(TPC)₂(pic)** in order to obtain practical applications.

4. Conclusions

Two new saturated red bis-cyclometalated iridium(III) complexes using phthalazine derivatives (**HEPCP** and **HTPC**) as cyclometalated ligands and 2-picolinic acid as ancillary ligand were synthesized and their electroluminescent properties were investigated. The **Ir(ECPC)₂(pic)**-doped OLED exhibited efficient red emission with a maximum luminance of 1484 cd/m² at 66 mA/cm² and a maximum external quantum efficiency of 16.3% at 0.06 mA/cm² when the doping concentration was 2 wt%. While the **Ir(TPC)₂(pic)**-based OLED exhibited a maximum luminance of 728 cd/m² and a maximum external quantum efficiency of 11.9%. The device luminance of **Ir(TPC)₂(pic)** was much lower than that of **Ir(ECPC)₂(pic)**. The results proved that the carbazole substituting group was introduced into bis-cyclometalated iridium(III) complexes could be better than triphenylamine in improving the device performance. The carbazole substituent group in iridium(III) complexes can tune the energy levels for a better matching and improve hole-transporting ability in devices. As far as the excellent performance and the color purity of iridium(III) complexes based on phthalazine derivatives were concerned, this class of phosphorescent materials can be used as a promising candidate for saturated red phosphorescent emitter in OLEDs. Moreover, this finding could provide a new idea in the design of new bis-cyclometalated iridium(III) complexes phosphorescent

emitters to satisfy the special requirement for saturated red PHOLEDs.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2012.11.012>.

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