



Synthesis of a novel tris-cyclometalated iridium(III) complex containing triarylamine unit and its application in OLEDs

Yuan Fang^a, Sujun Hu^b, Yuezhong Meng^a, Junbiao Peng^b, Biao Wang^{a,*}

^aState Key Laboratory of Optoelectronic Materials and Technologies, Institute of Optoelectronic and Functional Composite Materials, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

^bInstitute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, People's Republic of China

ARTICLE INFO

Article history:

Received 5 January 2009

Received in revised form 30 July 2009

Accepted 3 August 2009

Available online 9 August 2009

Keywords:

Phosphorescence

Tris-cyclometalated iridium(III) complex

Cyclometalating ligand

Triarylamine

Organic light-emitting diodes

ABSTRACT

The synthesis of the tris-cyclometalated iridium(III) complex $[\text{Ir}(\text{DCP})_3]$ (HDCP = 1-(N,N-diphenyl-amino)-4-(4-chlorophenyl)-phthalazine) from hydrated iridium(III) chloride and the ligand HDCP under mild reaction conditions was described. The photophysical, electrochemical and electrophosphorescent properties of this complex were investigated. Organic light-emitting diodes (OLEDs) using the complex as a dopant and a blend of poly(vinylcarbazole) (PVK) with 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD) as a host exhibited bright red emission at 620 nm with the Commission Internationale de l'Eclairage (CIE) coordinate of (0.67, 0.32). A maximum external quantum efficiency of 13.6% photos/electron with a luminous efficiency of 7.4 cd/A at a current density of 0.73 mA/cm², and a maximum luminance of 2941 cd/m² at 99 mA/cm² were obtained in the device at 4 wt% doping concentration.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Phosphorescent heavy metal complexes play a very important role in organic light-emitting diodes (OLEDs), because they can fully utilize both singlet and triplet excitons through the strong spin–orbital coupling caused by heavy metal ions in complexes [1]. Compared with other heavy metal complexes, iridium complexes have been recognized as one of the best phosphorescent material candidates because of their intense phosphorescence at room temperature and relatively short excited state lifetime which minimize quenching of triplet emissive state [2]. Recently, various types of iridium(III) complexes have been developed [3–5], such as tris-cyclometalated complexes $\text{Ir}(\text{C}^{\wedge}\text{N})_3$, bis-cyclometalated neutral complexes $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})$ and cationic complexes $\text{Ir}((\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})^+\text{Y}^-)$ ($\text{C}^{\wedge}\text{N}$ = cyclometalating ligand, $\text{L}^{\wedge}\text{X}$ = bidentate ancillary ligand, Y^- = anion). The synthesis of $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})$ and $\text{Ir}((\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})^+\text{Y}^-)$ can be carried out under mild conditions. In contrast, the preparations of $\text{Ir}(\text{C}^{\wedge}\text{N})_3$, especially for facial isomers, generally involve treating Ir(III) organic complexes, such as $(\text{C}^{\wedge}\text{N})_2\text{Ir}(\text{O}^{\wedge}\text{O})$ ($\text{O}^{\wedge}\text{O}$ = β -diketonate anion), $(\text{C}^{\wedge}\text{N})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{C}^{\wedge}\text{N})_2$ or $\text{Ir}(\text{O}^{\wedge}\text{O})_3$, with excess cyclometalating ligands at high temperature (>200 °C) [6]. Nevertheless, tris-cyclometalated complexes as phosphor dopants of OLEDs have attracted particular attention, owing to good chemical and photochemical stability and high

emission efficiency. It has been well demonstrated that modifications of the molecular frameworks and the substituent groups on cyclometalating ligands can afford significant color tuning and efficiency improving of electrophosphorescence. Recently, we and Gao et al. have respectively reported the strong phosphorescent tris-cyclometalated iridium(III) complexes with similar ligands owning the feature of an sp^2 -hybrid N-atom adjacent to the chelating N-atom [7–10]. These results inspired us to do more research about iridium(III) complexes bearing analogous ligands.

In this article, a novel ligand 1-(N,N-diphenyl-amino)-4-(4-chlorophenyl)-phthalazine was synthesised. Triarylamine unit in the ligand should affect the hole-transporting/trapping properties, and it is also beneficial to extend the π -electron delocalization of the aromatic ligand chromophore [11]. In addition, the synthesis of tris(1-(N,N-diphenyl-amino)-4-(4-chlorophenyl)-phthalazine) iridium(III) $[\text{Ir}(\text{DCP})_3]$ is exceptional. Different from above mentioned conditions, $\text{Ir}(\text{DCP})_3$ was synthesised in one-step by reaction of the ligand with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ at 80 °C for 20 h. The synthesis and electrochemical, photophysical and electrophosphorescent properties of this complex were investigated.

2. Experimental

2.1. General information

All commercially available starting materials were purchased from Aldrich and Alfa Aesar, and used without further purification,

* Corresponding author. Tel./fax: +86 20 84115692.

E-mail address: wangbiao@mail.sysu.edu.cn (B. Wang).

unless otherwise stated. HPLC-grade dimethylformamide (DMF) was distilled from CaH_2 immediately before use. ^1H NMR spectra were measured on a Varian Inova500NB spectrometer. Elemental analyzes of carbon, hydrogen, and nitrogen were performed on a Vario EL microanalyzer. UV–Vis absorption spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu RF-5301PC fluorescence spectrophotometer. Luminescence lifetime was determined on an Edinburgh FL920 time-correlated pulsed single-photon-counting instrument. Electron ionization (EI) mass spectrum were recorded on a Shimadzu GC–MS–QP2010 PLUS mass spectrometer, and electron spray ionization (ESI) mass spectra on a Thermo LCQ DECA XP mass spectrometer. Cyclic voltammetry (CV) was carried out on a Solartron SI 1287 voltammetric analyzer at room temperature in nitrogen-purged anhydrous CH_2Cl_2 with tetrabutylammonium hexafluorophosphate as a supporting electrolyte at a scanning rate of 100 mV/s. A Pt disk, Pt wire, and SCE (saturated calomel electrode) were used as the working, counter, and reference electrodes, respectively. 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 of 4-(4-chlorophenyl)-1-(2H)-phthalazinone (**2**)

A mixture of 2-(4-chlorobenzoyl)-benzoic acid (**1**) (13 g, 50 mmol) and hydrazine hydrate (80%) (5 mL) in ethanol (120 mL) was refluxed for 16 h. After cooled, the resulting white precipitate was filtered off, washed with cold water, and dried to give **2** in a yield of 95%. m.p.: 272–274 °C. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz): δ 12.90–12.87 (s, 1H), 8.38–8.32 (m, 1H), 7.94–7.87 (m, 2H), 7.70–7.65 (m, 1H), 7.65–7.60 (m, 4H). EI-MS (m/z): 255 (90%), 256 (100%), 257 (44%), 258 (32%).

2.3. Synthesis of 1-chloro-4-(4-chlorophenyl)phthalazine (**3**)

To a 250 mL round-bottom flask, compound **2** (10.3 g, 40 mmol) and POCl_3 (5.5 mL, 60 mmol) were added all at once in 100 mL of CHCl_3 . The mixture was refluxed for 16 h. After the reaction was completed, CHCl_3 was removed under reduced pressure. The mixture was then cooled and poured into ice water. A 20% Na_2CO_3 solution was added to adjust the pH to 7. The resulting precipitate was filtered off and purified by silica gel column chromatography using dichloromethane as the eluent to give **3** in a yield of 73%. m.p.: 180–183 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.42–8.39 (d, $J = 7.88$ Hz, 1H), 8.06–8.01 (m, 2H), 7.98–7.93 (m, 1H), 7.70–7.66 (d, $J = 8.61$ Hz, 2H), 7.58–7.54 (d, $J = 8.59$ Hz, 2H). EI-MS (m/z): 273 (100%), 274 (51%), 275 (75%), 276 (34%).

2.4. Synthesis of 1-(*N,N*-diphenyl-amino)-4-(4-chlorophenyl)-phthalazine (HDCP)

A 60.5% suspension of sodium hydride (1.0 g, 25 mmol) in paraffin oil was added slowly to a solution of diphenylamine (4.23 g, 25 mmol) in anhydrous DMF (80 mL). After stirred for 1 h at room temperature under nitrogen as a protective gas, this mixture was added dropwise to a solution of compound **3** (6.88 g, 25 mmol) in anhydrous DMF (70 mL), while stirring and cooling with an ice bath, and the mixture was stirred at room temperature for 12 h. After reaction, the resulting mixture was poured into water and extracted with chloroform. 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 using chloroform as the eluent to give HDCP as a yellow solid in a yield of 76%. m.p.: 207–

208 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.02–8.00 (d, $J = 8.3$ Hz, 1H), 7.90–7.88 (d, $J = 8.4$ Hz, 1H), 7.76–7.72 (m, 3H), 7.65–7.62 (m, 1H), 7.54–7.52 (m, 2H), 7.30–7.25 (m, 4H), 7.12–7.07 (m, 6H). EI-MS (m/z): 406 (100%), 407 (27%), 408 (33%), 409 (10%).

2.5. Synthesis of tris(1-(*N,N*-diphenyl-amino)-4-(4-chlorophenyl)-phthalazine) iridium(III) [$\text{Ir}(\text{DCP})_3$]

HDCP (0.416 g, 1.02 mmol) and hydrated iridium(III) chloride (0.1 g, 0.284 mmol) were added in a mixture of 2-ethoxyethanol (12 mL) and distilled water (4 mL). The mixture was stirred at 80 °C for 20 h under nitrogen. Cooled to room temperature, the precipitate was collected by filtration and washed with water, ethanol and hexane. The crude product was purified by column chromatography over silica gel using dichloromethane as the eluent to give $\text{Ir}(\text{DCP})_3$ as a red solid in a yield of 37%. ^1H NMR (CDCl_3 , 500 MHz): δ 8.44–8.41 (d, $J = 8.9$ Hz, 1H), 7.86–7.83 (d, $J = 8.6$ Hz, 1H), 7.68–7.65 (t, $J = 8.0$ Hz, 2H), 7.50–7.46 (t, $J = 7.5$ Hz, 1H), 7.13–7.10 (d, $J = 2.1$ Hz, 1H), 6.92–6.89 (dd, $J = 8.5$, 2.2 Hz, 1H), 6.67–6.64 (m, 2H), 6.57–6.52 (m, 8H). ESI-MS (m/z): [$\text{M}^+ + \text{H}$] Calc. for $\text{C}_{78}\text{H}_{52}\text{N}_9\text{Cl}_3\text{Ir}$ 1410.30 (32.5%), 1411.30 (30%), 1412.30 (100%), 1413.30 (83%), 1414.29 (99%), 1415.30 (67.5%), 1416.30 (45%), 1417.29 (24%); Found: 1410.30 (29%), 1411.33 (52.5%), 1412.26 (100%), 1413.26 (96%), 1414.23 (99%), 1415.22 (77%), 1416.25 (41%), 1417.21 (24%). Anal. Calcd. for $\text{C}_{78}\text{H}_{51}\text{N}_9\text{Cl}_3\text{Ir}$: C, 66.31; H, 3.64; N, 8.92. Found: C, 66.18; H, 3.83; N, 8.71%.

2.6. OLED fabrication and measurements

The pre-cleaned ITO glass substrate was treated with ozone for 20 min. Then, a 45 nm thick PEDOT:PSS film was spin-coated onto the ITO glass and dried at 80 °C for 12 h under vacuum. A film of PVK and PBD, containing different amounts of $\text{Ir}(\text{DCP})_3$, was spin-coated on top of the PEDOT:PSS using chloroform as the solvent; the assembly was then dried for 3 h at 60 °C under vacuum. The TPBI layer was grown by thermal sublimation under vacuum (3×10^{-6} Torr). Subsequently, a layer of Ba (4 nm) and a layer of Al (100 nm) were vacuum-evaporated on the top of the EL polymer layer. Current–voltage characteristics were recorded with a Keithley 236 source meter. EL spectra were collected by a PR 705 photometer (Photo Research). Luminance was measured by a calibrated silicon diode and calibrated by a PR 705 photometer. The external quantum efficiencies were determined by a Si photodiode with calibration in an integrating sphere (ISO80, Labsphere).

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 outlines the synthetic routes toward the ligand and the complex. The synthesis of $\text{Ir}(\text{DCP})_3$ is surprising for its simple reaction conditions. Generally, the reactions of ligands with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ give chloride-bridged diiridium complexes ($\text{C}^{\wedge}\text{N}$) $_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{C}^{\wedge}\text{N})_2$ at 80 °C for 20 h. Specially, at the above conditions, the treatment of HDCP with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ affords the tris-cyclometalated iridium(III) complex $\text{Ir}(\text{DCP})_3$. The ^1H NMR data indicate that $\text{Ir}(\text{DCP})_3$ is formed exclusively as facial isomer, because the three ligands surrounding the iridium atom are magnetically equivalent [6,12]. Since the yield of the complex is not high, we employed electron spray ionization mass spectrometry (ESI-MS) to investigate what side product formed. The crude mixture was prepared by reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with an excess of HDCP in 2-ethoxyethanol/water mixed solvent at 80 °C for 20 h. After cooled, this crude mixture was diluted with CH_2Cl_2 , and then characterized with mass spectrometer without purification. As shown in **Fig. 1**, the

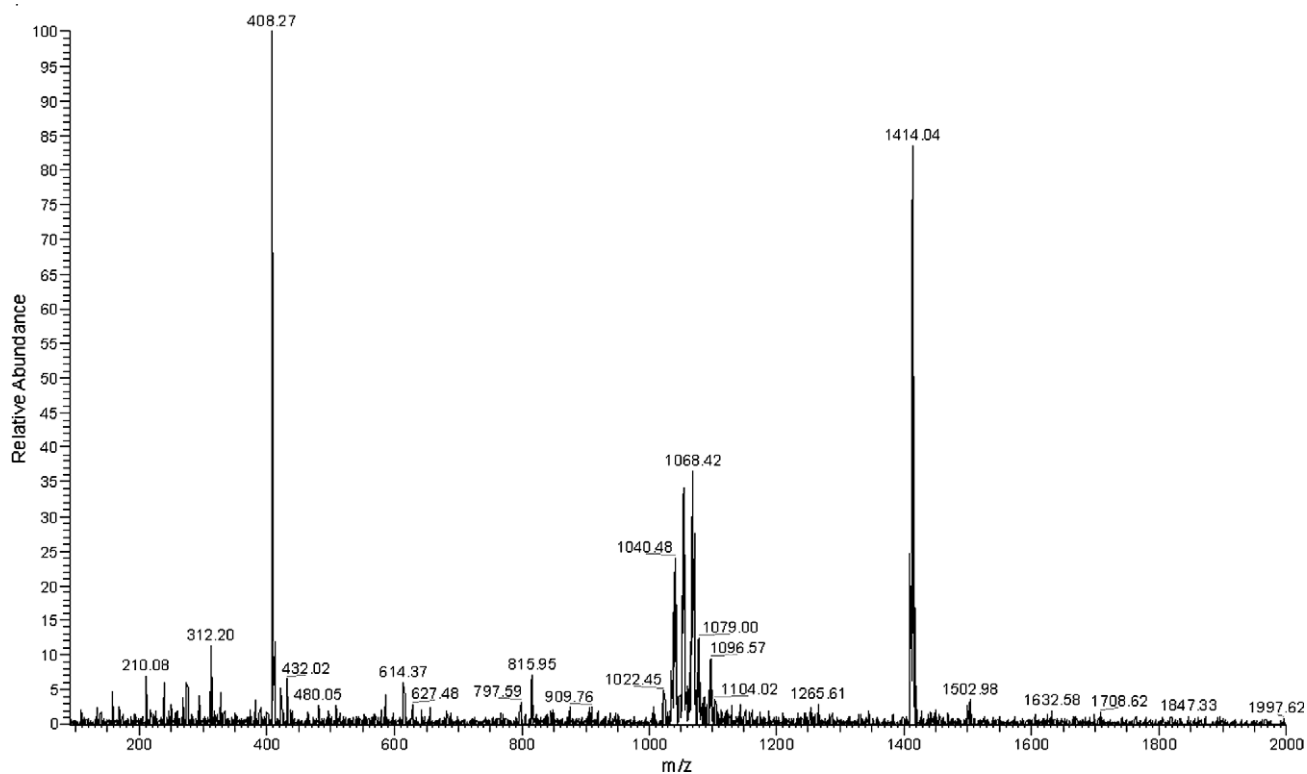


Fig. 1. ESI mass spectra of the crude mixture prepared by reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with an excess of HDCP.

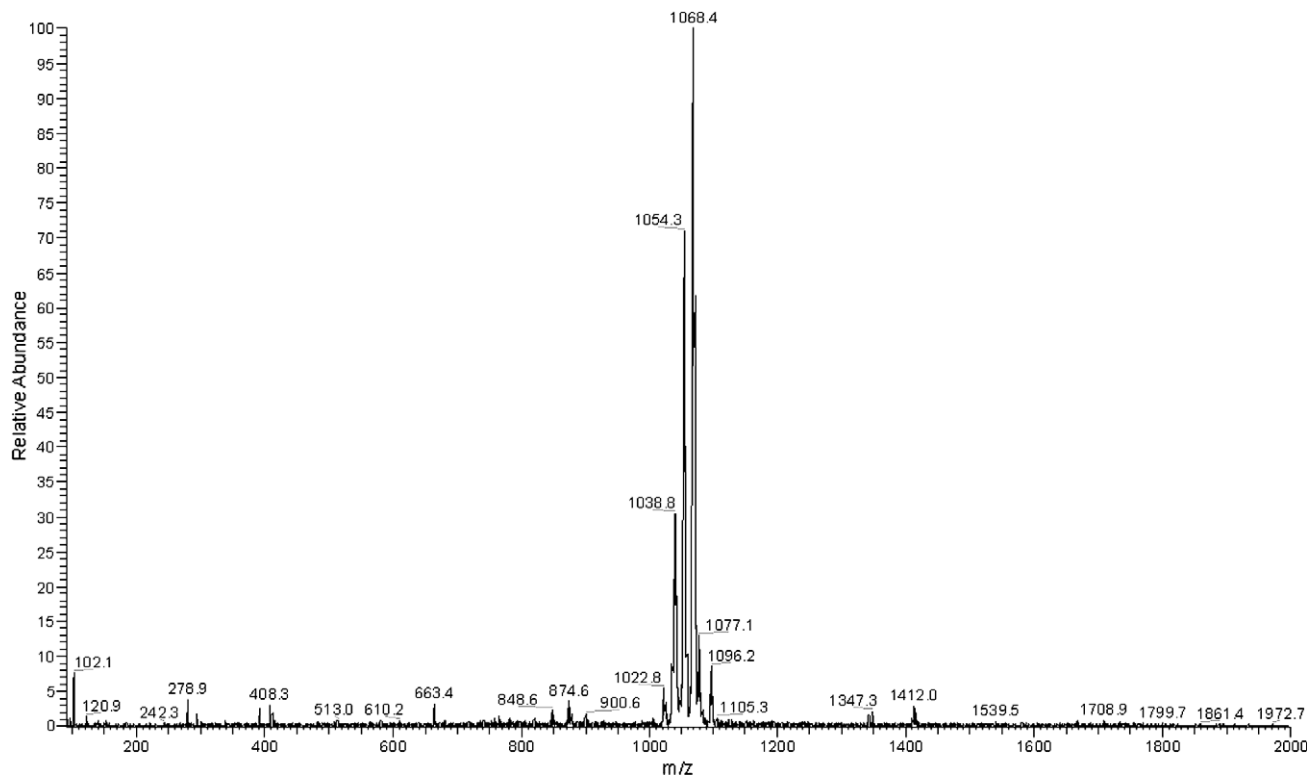


Fig. 2. ESI mass spectra of side products in reaction.

most abundant peaks are 408.3 and 1414.0, which correspond to the molecular masses of HDCP and $\text{Ir}(\text{DCP})_3$, respectively. Medium signals were obtained at 1040.5, 1054.6 and 1068.4 m/z , and the

corresponding molecule might be formulated as $\text{Ir}(\text{DCP})_2\text{Cl}$. However, due to the limitation of measurement range, we cannot obtain the signals above 2000 m/z . For comparison, we used

chromatographic column to separate side products from $\text{Ir}(\text{DCP})_3$ and HDCP, and the polarity of side products is much higher than that of $\text{Ir}(\text{DCP})_3$. Fig. 2 shows ESI mass spectra of side products. The abundant peaks have values 1038.8, 1054.3 and 1068.4 m/z , which are in accord with Fig. 1, considering the isotopes of Cl and Ir in the mass spectra.

3.2. Photophysical properties

The UV–Vis absorption and photoluminescence (PL) spectra of $\text{Ir}(\text{DCP})_3$ and HDCP in CH_2Cl_2 are shown in Fig. 3. Compared with the absorption spectra of free ligand, the intense absorption band around 290 nm are assigned to the spin-allowed $\pi-\pi^*$ transitions from the cyclometalating ligand. According to the previous report [13], the band around 395 nm can be attributed to spin-allowed metal–ligand charge transfer band ($^1\text{MLCT}$). The moderately intense and weak absorption at $\lambda > 450$ nm correspond to the formally spin-forbidden $^3\text{MLCT}$ transition. The PL spectra of $\text{Ir}(\text{DCP})_3$ show the maximum emission at 614 nm. The lifetime of $\text{Ir}(\text{DCP})_3$ was measured in degassed CH_2Cl_2 at 298 K and well fitted to a single-exponential decay. The value is 1.62 μs . By comparison with those of known tris-cyclometalated iridium(III) complexes [14], this shorter lifetime is beneficial to suppress the triplet–triplet annihilation.

3.3. Electrochemical properties

Cyclic voltammetry experiment was also carried out to investigate the electrochemical properties of $\text{Ir}(\text{DCP})_3$. The complex showed reversible oxidation processes during the anodic scan in CH_2Cl_2 , while the oxidation potential was observed to be 0.36 V which is mainly assigned to the oxidation of Ir metal cationic site ($\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}}$) [15]. However, no clear reversible reduction process was observed through many tests. The HOMO and LUMO energy levels of $\text{Ir}(\text{DCP})_3$ which are estimated with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level) and UV–Vis absorption spectrum edge are -5.16 and -3.07 eV, respectively. In order to get efficient OLEDs, the HOMO and LUMO levels of iridium(III) complex should fall within the band gap of the hosts, such as PVK (HOMO: -5.8 eV; LUMO: -2.2 eV), PBD (-6.2 , -2.6 eV) or 4,4'-N,N'-dicarbazolebiphenyl (CBP) (-6.0 , -2.9 eV) [16]. As a guest, $\text{Ir}(\text{DCP})_3$ with the lower triplet excited state energy and the narrow HOMO–LUMO energy gap has well energy level match to the above hosts.

3.4. Electroluminescent OLEDs characterization

To illustrate the electroluminescent properties of $\text{Ir}(\text{DCP})_3$, the devices using the complex as a dopant were fabricated with the following structures: ITO/PEDOT:PSS(45 nm)/x wt% $\text{Ir}(\text{DCP})_3$:PVK + 30%PBD(80 nm)/TPBI(30 nm)/Ba(4 nm)/Al(100 nm). Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonic acid) (PSS) was used as a hole-injecting material. As a good hole-transporter, PVK was blended with PBD, which is an electron-transport material, to enable the host to transport both electrons and holes [17]. 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene (TPBI) acted as both a hole-blocker and an electron-transporter. The electroluminescence (EL) spectra of OLEDs at 2 and 4 wt% doping concentrations are shown in Fig. 4. The devices emit red light with an maximum at around 620 nm and its corresponding shoulder at 670 nm. There is no residual emission from the hosts at the low doping concentrations, indicating that energy and charge transfer from the host exciton to the phosphor is efficient under electrical excitation [18]. The Commission Internationale de l'Eclairage (CIE) color coordinate is (0.67, 0.32) which is almost identical to the standard red values of (0.67, 0.33) demanded by the National Television System Committee (NTSC).

Figs. 5 and 6 present current density and luminance vs. voltage curves of $\text{Ir}(\text{DCP})_3$ -doped OLEDs at 2 and 4 wt% doping concentra-

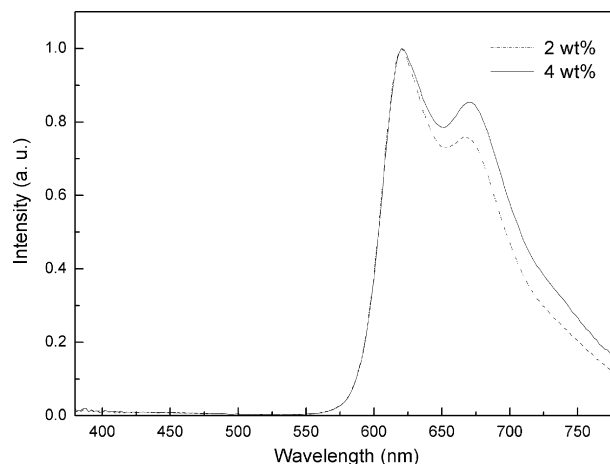


Fig. 4. EL spectra of the devices containing $\text{Ir}(\text{DCP})_3$ as a dopant at 12 V.

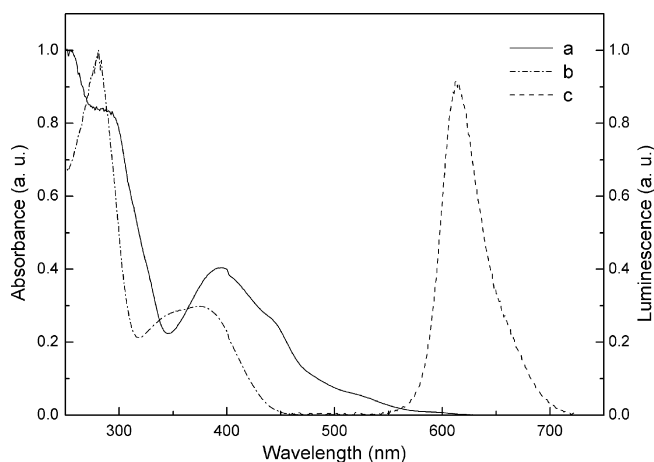


Fig. 3. UV–Vis absorption of $\text{Ir}(\text{DCP})_3$ (a) and HDCP (b), and photoluminescence spectra of $\text{Ir}(\text{DCP})_3$ (c) in CH_2Cl_2 at 293 K.

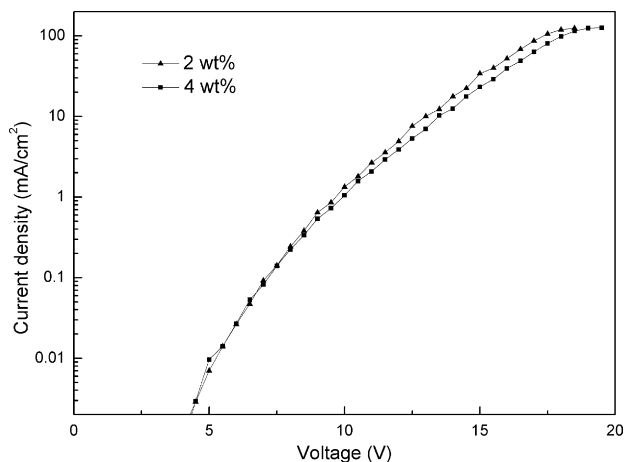


Fig. 5. Current density vs. voltage curves of devices at different doping concentrations.

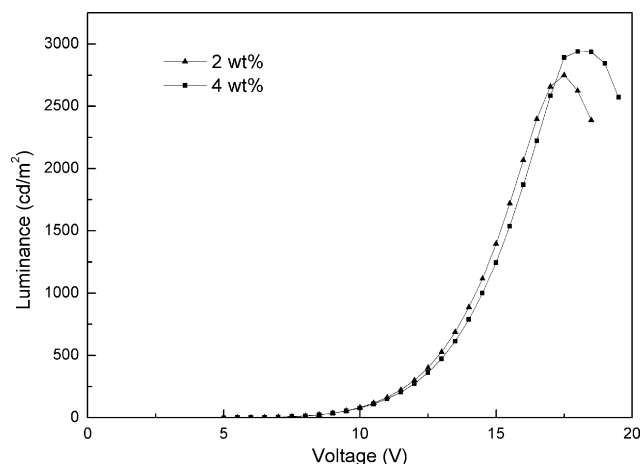


Fig. 6. Luminance vs. voltage curves of devices at different doping concentrations.

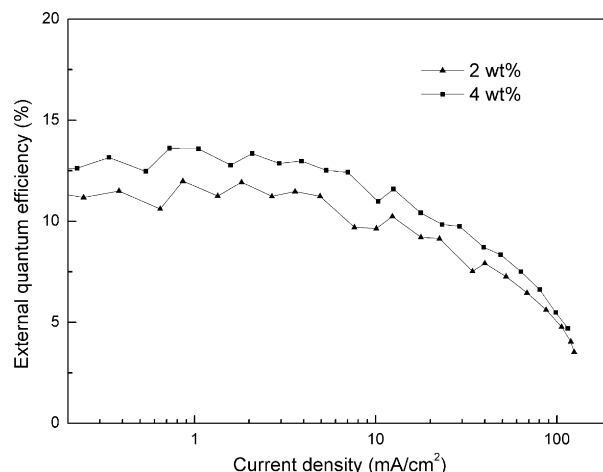
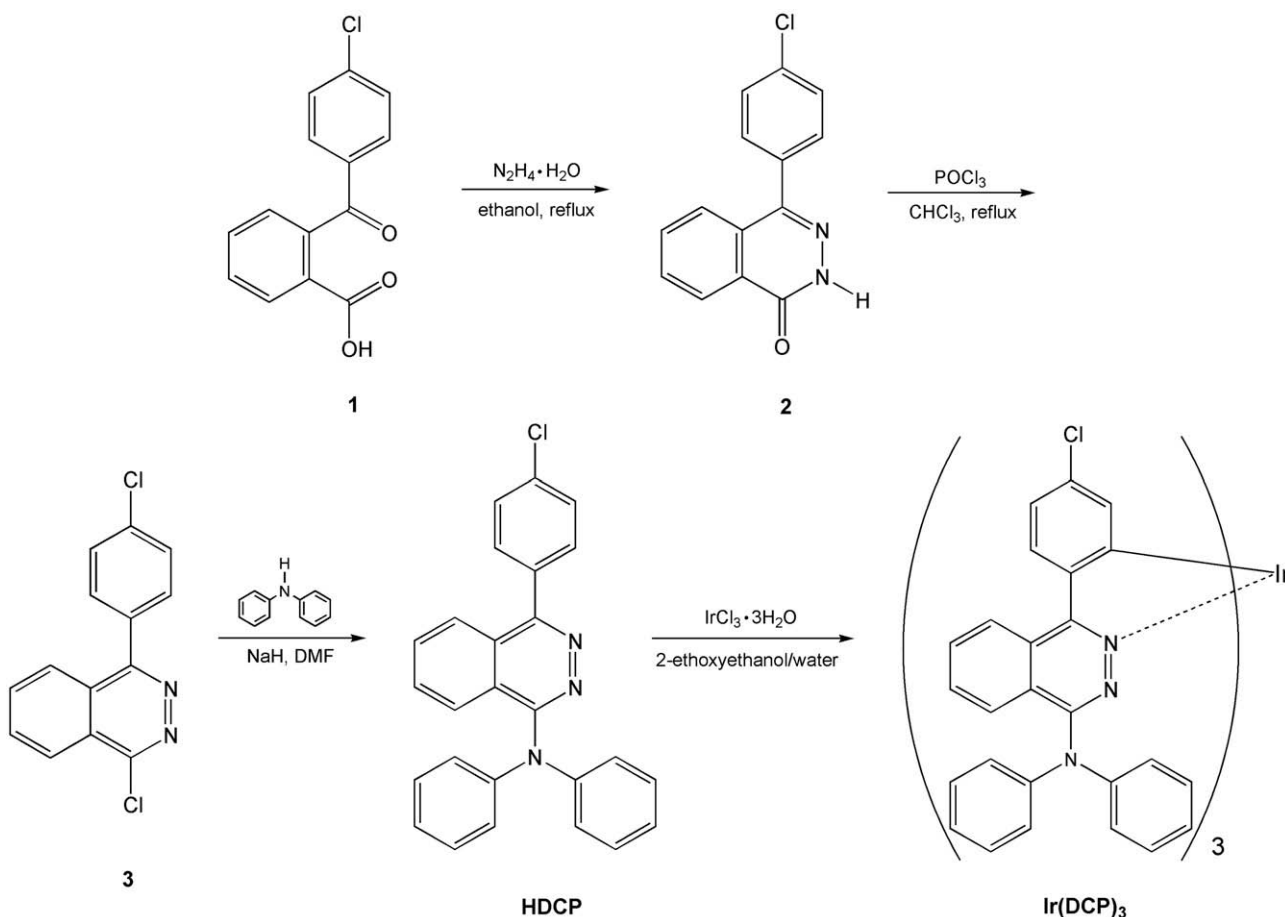


Fig. 7. External quantum efficiency vs. current density curves of devices.

tions. The device at 2 wt% doping concentration gave a maximum external quantum efficiency (η_{ext}) of 12.1% corresponding to a luminous efficiency of 6.48 cd/A at a current density of 0.86 mA/cm². When the current density increased to 17.7 mA/cm², η_{ext} decreased to 9.2% with a loss of 24.2%. At 106 mA/cm², the value of η_{ext} was 4.8% and the device showed a maximum luminance of 2750 cd/m². The efficiency started to decrease with increasing current density (Fig. 7), which can be attributed to the increasing triplet–triplet annihilation of the phosphor-bound excitons and field-

induced quenching effects [19,20]. When the doping concentration increased to 4 wt%, the maximum external quantum efficiency and luminance were enhanced correspondingly. The external quantum efficiency reached 13.6% with a luminous efficiency of 7.4 cd/A, at a practical current density of 0.73 mA/cm². The maximum luminance of 2941 cd/m² was observed at a current density of 99 mA/cm², corresponding to an external quantum efficiency of 5.5%. With the double increase in the doping concentration, the improvement of the device performance was slight. It is associated with the



Scheme 1. Synthesis of Ir(DCP)₃.

introduction of a hole-block and electron-transport layer (TPBI) which removes the necessity of increased electron injection and mobility [21].

4. Conclusions

In summary, we have synthesised the tris-cyclometalated iridium(III) complex Ir(DCP)₃ from hydrated iridium(III) chloride and the ligand 1-(N,N-diphenyl-amino)-4-(4-chlorophenyl)-phthalazine in one-step at 80 °C for 20 h. The devices based on Ir(DCP)₃ exhibited a peak electrophosphorescence wavelength of 620 nm along with a shoulder around 670 nm. For the device at doping 2 wt% concentration, a maximum external quantum efficiency of 12.1% was obtained at a current density of 0.86 mA/cm², and a maximum luminance reached 2750 cd/m² at 106 mA/cm². When the doping concentration increased to 4 wt%, the maximum external quantum efficiency and luminance rose to 13.6% and 2941 cd/m², respectively.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (10732100, 10572155), Guangdong Science and Technology Bureau (2006A11001002), and the Ministry of Education PRC Special Scientific Research Fund for Doctor Subjects in Colleges and Universities (20060558070).

References

- [1] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 75 (1999) 4.
- [2] C. Adachi, M.A. Baldo, S.R. Forrest, S. Lamansky, M.E. Thompson, R.C. Kwong, *Appl. Phys. Lett.* 78 (2001) 1622.
- [3] S. Lo, R.N. Bera, R.E. Harding, P.L. Burn, I.D.W. Samuel, *Adv. Funct. Mater.* 18 (2008) 3080.
- [4] D.M. Kang, J. Kang, J.W. Park, S.O. Jung, S. Lee, H. Park, Y. Kim, S.C. Shin, J. Kim, S. Kwon, *Adv. Mater.* 20 (2008) 2003.
- [5] L. Yang, F. Okuda, K. Kobayashi, K. Nozaki, Y. Tanabe, Y. Ishii, M. Haga, *Inorg. Chem.* 47 (2008) 7154.
- [6] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, *J. Am. Chem. Soc.* 125 (2003) 7377.
- [7] B. Tong, Q. Mei, S. Wang, Y. Fang, Y. Meng, B. Wang, *J. Mater. Chem.* 18 (2008) 1636.
- [8] Z.Q. Gao, B.X. Mi, H.L. Tam, K.W. Cheah, C.H. Chen, M.S. Wong, S.T. Lee, C.S. Lee, *Adv. Mater.* 20 (2008) 774.
- [9] B.X. Mi, P.F. Wang, Z.Q. Gao, C.S. Lee, S.T. Lee, H.L. Hong, X.M. Chen, M.S. Wong, P.F. Xia, K.W. Cheah, C.H. Chen, W. Huang, *Adv. Mater.* 21 (2009) 339.
- [10] Y. Fang, B. Tong, S. Hu, S. Wang, Y. Meng, J. Peng, B. Wang, *Org. Electron.* 10 (2009) 618.
- [11] G. Zhou, W. Wong, B. Yao, Z. Xie, L. Wang, *Angew. Chem., Int. Ed.* 46 (2007) 1149.
- [12] M.G. Colombo, T.C. Brunold, T. Riedener, H.U. Güdel, M. Förtsch, H. Bürgi, *Inorg. Chem.* 33 (1994) 545.
- [13] K.R.J. Thomas, M. Velusamy, J.T. Lin, C. Chien, Y. Tao, Y.S. Wen, Y. Hu, P. Chou, *Inorg. Chem.* 44 (2005) 5677.
- [14] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* 125 (2003) 12971.
- [15] M.K. Nazeeruddin, R.T. Wegh, Z. Zhou, C. Klein, Q. Wang, F.D. Angelis, S. Fantacci, M. Grtzel, *Inorg. Chem.* 45 (2006) 9245.
- [16] M. Thelakkat, H.W. Schmidt, *Adv. Mater.* 10 (1998) 219.
- [17] X. Yang, D. Neher, D. Hertel, T.K. Daubler, *Adv. Mater.* 16 (2004) 161.
- [18] X. Gong, J.C. Ostrowski, D. Moses, G.C. Bazan, A.J. Heeger, *Adv. Funct. Mater.* 13 (2003) 439.
- [19] M.A. Baldo, C. Adachi, S.R. Forrest, *Phys. Rev. B* 62 (2000) 10967.
- [20] J. Kalinowski, W. Stampor, J. Mezyk, M. Cocchi, D. Virgili, V. Fattori, P.D. Marco, *Phys. Rev. B* 66 (2002) 235321.
- [21] E.A. Plummer, A.V. Dijken, H.W. Hofstraat, L.D. Cola, K. Brunner, *Adv. Funct. Mater.* 15 (2005) 281.