Dyes and Pigments 134 (2016) 148-154



Contents lists available at ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

Solution-processed blue and blue-green phosphorescent organic light-emitting devices using iridium(III) complexes based on 9-(6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hexyl)-9*H*-carbazole ligand



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A R T I C L E I N F O

Article history: Received 4 May 2016 Received in revised form 5 July 2016 Accepted 6 July 2016 Available online 7 July 2016

Keywords: Carbazole 1 2 4-trizole derivatives Pure-blue Iridium(III) Complex

ABSTRACT

We have designed and successfully synthesized a series of solution-processed iridium(III) complexes of $(Czphtz)_2Ir(N^N)$ bearing main ligand of 9-(6-(4-phenyl-1H-1,2,3 -triazol-1-yl)hexyl)-9H-carbazole, namely $(Czphtz)_2Ir(fmptz)$ (Ir1) $(Czphtz)_2Ir(pptz)$ (Ir2) and $(Czphtz)_2Ir(fpptz)$ (Ir3). The hole-transporting carbazole and electron-transporting 1, 2, 4-trizole moieties were introduced through hexyl to balance carrier transport. The solution-processed host-free and doped phosphorescent organic light-emitting devices (PhOLEDs) were fabricated. Here, in this paper, we will present the photophysical, electrochemical properties and performances in devices of three complexes. All of them exhibit excellent solubilities in common organic solvents. The pure-blue-light-emitting Ir1 with the maximum emission peak at 463 nm was attained by varying the structure of ancillary ligand and have the CIE coordinate of (0.19, 0.18) in host-free PhOLED. Our work shows that the rational structure modification of ancillary ligand is an effective approach to develop deep blue-light-emitting materials.

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1. Introduction

Phosphorescent organic light-emitting devices (PhOLEDs) attract intense interests because the emitter can harvest both singlet and triplet excitons, and in turn elevate the internal quantum efficiency to 100% [1,2]. The Ir(III) complexes are the most

promising candidate for PhOLEDs owing to the color tunability and short triplet lifetimes [3,4]. To reduce self-quenching and serious triplet-triplet annihilation (TTA), phosphorescent emitter of Ir(III) complexes must be doped into host materials [5,6]. Such doping deteriorates the interface stability between layers, the lifetime of the host and the energy-level matching. Alternatively, a variety of approaches, including introducing large sterically-hindered configurations to separate chromophoric units, have been studied to reduce TTA [7–9].

It is feasible to connect the charge-transport (hole and electron) group with the light-emitting core by using appropriate chemical bonds to provide a large sterically-hindered ligands in Ir(III) complexes [10,11]. Such charge-transport groups not only enlarge the distance between phosphorescent emitting cores to reduce TTA, but also balance the carrier-transport and injection in devices.

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Employing these materials as emitter, the host-free or heavyblending devices with high efficiencies and stability have been fabricated [12,13].

In comparison with vacuum deposition, solution processing is more promising and intriguing technology due to the applications in flexibility and large-area display [14–16]. Phosphorescent Ir(III) complexes in solution-processed red and green PhOLEDs have achieved excellent performances [17–19]. However, less attentions have been paid to solution-processed blue-light-emitting Ir(III) complexes because of high triplet energy (E_T) and large energy gap (E_g) [20,21].

Carbazole (Cz) units, which possess the high stability and holetransport properties, have been introduced into transition-metalbase complexes to improve their hole-transport ability [22,23]. Meanwhile, the 1, 2, 4-triazole is usually used to synthesized blueemitting Ir(III) complexes [3,24] and these complexes exhibit electron-transport property [25]. Recently, we designed and synthesized solution-processed pure-blue and blue-green phosphorescent Ir(III) complexes (Ir1–Ir3). Also we selected different ancillary ligands of 1, 2, 4-triazole derivatives ($N^{\circ}N$) [26]. The flexible hexyls can reduce the intermolecular interaction and facilitate the solution-process of the complexes, Cz was attached to the 1, 2, 3-triazol cyclometalated ligand by hexyls. Our work shows that the pure-blue-light-emitting Ir(III) complex can be obtained by turning the structure of $N^{\circ}N$ ancillary ligands.

2. Experimental section

2.1. General information

¹H NMR and ¹³C NMR data were recorded with Switzerland Bruker DR \times 600 NMR spectrometers. FT-IR spectra were measured with a Nicolet 7199B spectrometer in KBr pellets in the range of 4000-400 cm⁻¹. Element analysis was performed on a Vario EL microanalyzer. Thermogravimetric analysis (TGA) was undertaken using a Netzsch TG 209 under dry nitrogen atmosphere heating at a rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC Q2000 unit at a heating rate of 10 °C/ min from room temperature to 350 °C under a flow of nitrogen and cooling at rate of 20 °C/min; Glass transition temperatures (Tg) were determined from the second heating scan. UV-vis absorption spectra were recorded using Lambda Bio 40. The fluorescence spectra were examined by HORIBA FluouoMax-4 spectrophotometer in dichloromethane (CH₂Cl₂) solution. The absolute florescence quantum yields in solid film were measured by a HORIBA FluouoMax-4 equipped with an integrating sphere. The films were prepared by drop-coating, which synthesized Ir(III) complexes doped in polymethylmethacrylate (PMMA) (10 wt. %) in distilled dichloromethane (CH₂Cl₂) onto a quartz-glass plate, and were dried under vacuum at 120 °C for 2 h before photophysical measurements.

Cyclic voltammetry (CV) was carried out in CH₂Cl₂ solution with chromatographic purity at room temperature using a CHI 660E voltammetry analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) was used as the supporting electrolyte. The platinum wire is used as working electrode. The platinum electrode is the counter and a calomel electrode is the reference with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. The scan rate for CV curves is 100 mV/s. The highest occupied molecular orbital (HOMO) levels were calculated according to the equation $E_{HOMO} = -4.8 - e(E_c^{ox} - E_f^{ox})V$, where E_c^{ox} was the first oxidation peaks measured from CV curves and E_f^{ox} was the oxidation peak of ferrocene. On the other hand, the lowest unoccupied orbital (LUMO) levels were calculated based on the equation LUMO = HOMO + E_g , and E_g is from the absorption and emission

spectra.

The Ir(III) complex structure was optimized by density functional theory (DFT) using B3LYP/6-31G(d) basis sets, and LANL2DZ basis sets for Ir atom. Theoretical prediction for molecular orbital distributions was acquired based on the optimized structure.

To evaluate the electroluminescent properties of Ir1–Ir3, hostfree and doped PhOLEDs were fabricated by spin-coating technology with the configurations of ITO/PEDOT:PSS(30 nm)/Ir1-Ir3 (40 nm)/TPBi(60 nm)/LiF(0.8 nm)/AL (100 nm) and ITO/PEDOT:PSS (30 nm)/TCTA:10 wt% Ir1-Ir3 (40 nm)/TPBi (60 nm)/LiF (0.8 nm)/AL (100 nm). Prior to use, the indium tin oxide (ITO) substrates were cleaned, and then followed by O₂ plasma treatment for 8 min. Poly(ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) were spin-coated onto the cleaned ITO substrates at 2000 rpm for 60 s, and annealed for 20 min at 120 °C. For host-free PhOLEDs, the chloroform solutions (6 mg/mL) of Ir1–Ir3 were spincoated onto the uniform PEDOT:PSS layer to yield single-emitting layer of 30-40 nm. Subsequently, the substrates were annealed at 100 °C for 15 min. On the other hand, for doped devices, the EML was prepared by spin-coating 4,4',4"-tris(N-carbazolyl) -triphenylamine (TCTA) in chlorobenzene (10 mg/mL) as a host and Ir1–Ir2 in chloroform (6 mg/mL) as a dopant at the same way in the glove boxes. Next, a 40 nm thickness 2,2',2"-(1,3,5-benzinetriyl)tris(1-phenyl-1H-benzimidazole) (TPBi), acting as a high tripletenergy exciton blocking layer with electron transport properties, was deposited on the emissive layer. Finally, a very thin (0.8 nm) LiF as an electron injecting layer and a 100 nm-thick Al layer were deposited by thermal evaporation at pressures below 10^{-4} Pa.

The electroluminescent (EL) spectra were measured by PR-655 spectrophotometer. The voltage-current density (V-J) characteristics of PhOLEDs were recorded using Keithley 2400 Source Meter and ST-900M Spot Brightness Meter. All measurements were performed at room temperature.

2.2. Synthesis

All reagents were purchased from commercial sources and used as received without further purification. Solvents for synthesis were purified according to standard procedures before use.

2.2.1. Synthesis of cyclometalated ligand

9-(6-bromohexyl)-9H-carbazole (**a**)

A mixture solution of carbazole (5.0 g, 30 mmol), 1, 6dibromohexane (36.0 g, 150 mmol), tetrabutyl ammonium bromide (TBAB) (1.0 g, 3 mmol), toluene (40 mL) and KOH (25 mL, 50%) was heated to reflux for 12 h. After cooling to room temperature, the mixture was poured into the water (50 mL) and extracted with CH₂Cl₂. The organic extracts were washed with water and dried over MgSO₄. The crude product was subjected to silica gel column chromatography using a 8:1 mixture of petroleum ether and CH₂Cl₂ as the eluent. The white crystals of 9-(6-bromohexyl)-9*H*-carbazole (7.7 g) were obtained. Yield: 78%, ¹H NMR (600 MHz, CDCl) δ 8.11(dt, 2H, *J* = 7.8 Hz, 1.2 Hz), 7.47–7.44(m, 2H), 7.40(d, 2H, *J* = 8.4 Hz), 7.24–7.21(m, 2H), 4.31(t, 2H, *J* = 7.2 Hz), 3.35(t, 2H, *J* = 7.2 Hz), 1.92–1.78(m, 2H), 1.50–1.37(m, 2H).

9-(6-azidohexyl)-9H-carbazole (**b**)

Compound **a**, Sodium azide (NaN₃) (2.0 g, 30.8 mmol) and dimethylformamide (DMF, 20 mL) were reacted at 80 °C for 10 h. The solution was washed with water, extracted in ethyl acetate and dried over MgSO₄. The residue was purified using column chromatography on silica gel with *n*-hexane/ethyl acetate (10:1) so as to give 9-(6-azidohexyl)-9*H*-carbazole (**b**) (1.6 g, 89%).

9-(6-(4-phenyl-1H-1, 2, 3-triazol-1-yl)hexyl)-9H-carbazole (Czphtz)

Ethynylbenzene (102 mg, 1 mmol), compound **b** (280 mg, 1 mmol), tert-butanol (t-BuOH) (2 mL), water (2 mL), sodium

ascorbate (1 M, 0.1 mL, 0.1 mmol) and CuSO₄·5H₂O (2.5 mg, 0.01 mmol) were reacted at room temperature for 24 h. Then, the solution was washed with water and extracted with ethyl acetate. The combined organic layers were dried over MgSO₄. The crude materials was purified by column chromatography (*n*-hexane/ethyl acetate = 1:1) to yield of 9-(6-(4-phenyl-1*H*-1, 2, 3-triazol-1-yl) hexyl)-9*H*-carbazole (**Czphtz**) as white solid. (82%) ¹H NMR (600 MHz, CDCl) δ 8.10(d, 2H, *J* = 7.8 Hz), 7.81(d, 2H, *J* = 7.2 Hz), 7.62(s, 1H), 7.47–7.41(m, 4H), 7.38(d, 2H, *J* = 8.4 Hz), 7.33(t, 1H, *J* = 6.6 Hz), 7.23(t, 2H, *J* = 7.8 Hz), 4.32–4.30(m, 4H), 1.92–1.86(m, 4H), 1.44–1.34(m, 4H).

2.2.2. Synthesis of the ancillary ligand

The detailed information for the synthesis process of the ancillary ligand of 2-(5-(4-fluorophenyl)-2*H*-1,2,4-triazol-3-yl) pyridine (Hfpptz), and 2-(5- (trifluoromethyl)-2*H*-1,2,4-triazol-3-yl)pyridine (Htfmptz) can be found in Ref. [3].

The similar method was employed to obtain the ancillary ligand of 2-(5-phenyl-2*H*-1,2,4-triazol-3-yl)pyridine (Hpptz). Yield: 91%. The ¹H NMR data of Hpptz: ¹H NMR (600 MHz, CDCl) δ 12.11(s, 1H), 8.71(d, 1H, *J* = 4.2 Hz), 8.31(d, 1H, *J* = 7.8 Hz), 8.21(d, 2H, *J* = 7.2 Hz), 7.91–7.88(m, 1H), 7.48(t, 2H, *J* = 8.4 Hz), 7.44–7.40(m, 2H). Anal. Calcd for C₁₃H₁₀N₄ (%): C, 70.26; H, 4.54; N, 25.21; found: C, 70.10; H, 4.62; N, 25.13.

2.2.3. Synthesis of $(Czphtz)_2 Ir(\mu-Cl)_2 Ir(Czphtz)_2$

A mixture of main ligand Czphtz, iridium chloridetrihydrate, 2ethoxyethanol, and water was refluxed under argon for 24 h. After cooling to room temperature, the precipitate was collected by the filtration and washed with water, ethanol and *n*-hexane. Then, the product was dried in vacuum for 12 h. The yellow-green (Czphtz)₂lr(μ -Cl)₂lr(Czphtz)₂ was obtained and used in the next reaction without further purification. Yield: 58%.

2.2.4. Synthesis of (Czphtz)₂Ir(N^N) complexes

Iridium(III)bis-(9-(6-(4-phenyl-1H-1,2,3-triazol-1-yl)hexyl)-9Hcarbazole)2-(5-(trifluoromethyl)-2H-1,2,4-triazol-3-yl)pyridine (Czphtz)₂Ir(tfmptz) (Ir1)

(Czphtz)₂Ir(µ-Cl)₂Ir(Czphtz)₂ (0.2 g, 0.1 mmol), tfmptz (0.05 g, 0.25 mmol), K₂CO₃ (0.1 g, 0.7 mmol) and 2-ethoxyethanol (20 mL)

were heated to 140 °C under nitrogen for 24 h. After cooling to room temperature, enough water was added and then filtered. The residue was purified by column chromatography (n-hexane/ dichloromethane = 1:5) to obtain yellow powder of (Czphtz)₂Ir(tfmptz) (Ir1) (97 mg, 34%).¹H NMR (600 MHz, CDCl) δ 8.10 (dt, 1H, I = 1.2, 7.8 Hz), 8.09(dt, 3H, I = 3.0, 1.2 Hz), 8.08(dt, 2H, *I* = 3.6, 0.6 Hz), 7.79–7.77 (m, 1H), 7.51–7.47(m, 1H), 7.45–7.40(m, 6H), 7.34(t, 4H, I = 8.4 Hz), 7.23-7.19(m, 4H), 7.14-7.12(m, 1H), 6.82-6.78(m, 3H), 6.70-6.67(m, 1H), 6.67-6.65(m, 2H), 4.24(t, 2H, I = 7.2 Hz), 4.20 - 4.18(m, 2H), 4.02 - 3.92(m, 2H), 3.85 - 3.71(m, 2H), 1.82-1.75(m, 2H), 1.74-1.69(m, 2H), 1.63-1.55(m, 4H), 1.30-1.24(m, 4H), 1.24-1.17(m, 2H), 1.16-1.09(m, 2H), 1.07-1.00(m, 2H),0.92-0.82(m, 2H). ¹³C NMR (600 MHz, CDCl): δ 167.46, 160.34, 159.83, 154.79, 153.23, 151.79, 146.98, 143.30, 140.42, 139.11, 135.79, 130.81, 129.86, 128.59, 126.73, 125.69, 123.19, 121.72, 121.37, 120.44, 111.62, 53.78, 45.55, 32.14, 31.58, 29.32, 28.69. Anal. Calcd for C₆₀H₅₄N₁₂F₃Ir: C, 60.45; H, 4.534; N, 14.10. Found: C, 61.80; H, 4.81; N, 13.56.

Iridium(III)bis-(9-(6-(4-phenyl-1H-1,2,3-triazol-1-yl)hexyl)-9Hcarbazole)2-(5-phenyl-2H-1,2,4-triazol-3-yl)pyridine (Czphtz)₂lr(pptz) (Ir2)

(Czphtz)₂Ir(pptz) (Ir2) was obtained as yellow solid from (Czphtz)₂Ir(μ -Cl)₂Ir(Czphtz)₂ and Hpptz ligand, in a yield of 34%. ¹H NMR (600 MHz, CDCl) δ 8.10 (d, 3H, *J* = 8.4 Hz), 8.07–8.04(m, 5H), 7.41–7.37(m, 6H), 7.29–7.27(m, 4H), 7.21–7.17(m, 6H), 6.78(t, 1H, *J* = 7.2 Hz), 6.73–6.69(m, 2H), 6.66(t, 2H, *J* = 7.2 Hz), 6.33(d, 1H, *J* = 7.2 Hz), 6.15(d, 1H, *J* = 7.2 Hz), 4.14–4.10(m, 5H), 3.98–3.85(m, 2H), 3.68–3.52(m, 3H), 1.65–1.58(m, 4H), 1.51–1.46(m, 2H), 1.40–1.35(m, 2H), 1.25(t, 2H, *J* = 7.2 Hz), 1.12(m, 4H), 0.96–0.91(m, 6H). ¹³C NMR (600 MHz, CDCl): δ 166.85, 160.12, 153.05, 152.87, 148.04, 143.29, 140.16, 139.32, 138.82, 136.53, 135.92, 130.96, 130.08, 129.05, 128.56, 127.70, 124.54, 124.17, 123.20, 121.71, 120.87, 120.44, 111.67, 54.20, 45.68, 32.35, 31.55, 29.18, 28.70. Anal. Calcd for C₆₅H₅₉N₁₂Ir: C, 65.05; H, 4.921; N, 14.01. Found: C, 64.87; H, 5.455; N, 12.56.

Iridium(III)bis-(9-(6-(4-phenyl-1H-1,2,3-triazol-1-yl)hexyl)-9Hcarbazole)2-(5-(4-(trifluoromethyl)phenyl)-2H-1,2,4-triazol-3-yl) pyridine (Czphtz)₂Ir(fpptz) (Ir3)

The similar method to (Czphtz)₂Ir(pptz) was used to obtain complex (Czphtz)₂Ir(fpptz) (Ir3), in a yield of 35%. ¹H NMR



(Czphtz)₂Ir(tfmptz) (Ir1) (Czphtz)₂Ir(pptz) (Ir2) (Czphtz)₂Ir(fpptz)(Ir3)

Scheme 1. Synthesis of main ligand and related Iridium complexes.



Fig. 1. TGA and DSC (insert) curves for Ir1, Ir2 and Ir3.

(600 MHz, CDCl) δ 8.10–8.05(m, 5H), 7.75(s, 1H), 7.50–7.45(m, 1H), 7.41(t, 6H, J = 7.2 Hz), 7.31(d, 4H, J = 8.4 Hz), 7.23–7.18(m, 4H), 7.17–7.03(m, 1H), 6.89(t, 2H, J = 8.4 Hz), 6.82–6.77(m, 1H), 6.76–6.65(m, 4H), 6.36(d, 1H, J = 7.2 Hz), 6.18(d, 1H, J = 7.2 Hz), 4.19–4.06(m, 6H), 3.99–3.85(m, 2H), 3.78–3.50(m, 2H), 1.72–1.58(m, 5H), 1.58–1.48(m, 2H), 1.47–1.36(m, 3H), 1.29–1.25(m, 2H), 1.20–1.06(m, 4H), 1.04–0.88(m, 4H). 13 C NMR (600 MHz, CDCl): δ 160.27, 153.08, 143.28, 140.26, 139.19, 138.68, 135.80, 133.63, 131.68, 130.94, 130.21 129.13, 128.55, 125.70, 124.62, 124.21, 123.19, 122.26, 121.73, 120.56, 120.19, 117.66, 111.61, 53.00, 45.70, 32.94, 31.55, 29.29,28.74. Anal. Calcd for C₆₅H₅₈N₁₂FIr: C, 64.09; H, 4.766; N, 13.80. Found: C, 63.14; H, 4.95; N, 12.53.

3. Results and discussion

3.1. Synthesis and molecular structures

Scheme 1 illustrates the synthesis of complexes $(Czphtz)_2 Ir(N^N)$. The hole-transport carbazole were attached to the 5-phenyl-1*H*-1,2,3-triazole through hexyl to form 9-(6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hexyl)-9*H*-carbazole (Czphtz). Czphtz and Iridium trichloride hydrate in 2-ethoxyethanol solution were treated to produce the chloride-bridged dimer. Consequently, complexes of $(Czphtz)_2 Ir(N^N)$ were obtained from the reaction of the corresponding N^N ligands with chloride-bridged dimer.

3.2. Thermal stability

Thermogravimetric analysis (TGA) was used to investigate the thermal properties of Ir1–Ir3. Fig. 1 shows the TGA curves and the results are summarized results in Table 1. The TGA revealed a 5%

Table 1



Fig. 2. The absorption (dot lines) and emission (solid lines) spectra of $(Czphtz)_2 lr(N^N)$ in CH_2Cl_2 solution (a) and in film (b).

weight loss (T_d) at 375, 360 and 315 °C in a N₂ atmosphere for Ir1, Ir2 and Ir3, respectively. The high T_d of synthesized iridium(III) complexes suggests that they were thermally stable under the solution-processed OLED fabrication conditions. The T_g of complex Ir1 was observed to be at 192 °C and no T_g temperatures were observed for complexes Ir2 and Ir3, as can be seen in the insert of Fig. 1.

3.3. Photophysical properties

Fig. 2 presents the UV–vis absorption and photoluminescence (PL) spectra of Ir1–Ir3 in CH₂Cl₂ and doped PMMA films at 10%. The absorption peaks in the range from 200 to 350 nm are assigned to a ligand-centered 1π - π * transition. Carbazole moieties contribute to the peaks at about 230 and 260 nm [20]. The absorption peaks

Ir(III) complexes	$\lambda_{abs}{}^a$	λ _{max} (nm)		$\Phi_{\mathrm{PL}}(\%)^{c}$	HOMO/LUMO (eV)	Eg(eV)	T_d (°C)
		Solution ^a	Film ^b				
Ir1	237, 262, 294, 331, 346, 395	463	467	13.61	-6.0/-2.9	3.1	375
Ir2	237, 263, 294, 331, 346, 402	495	497	24.21	-6.0/-3.1	2.9	360
lr3	238, 263, 295, 331, 346, 403	490	493	25.48	-5.9/-2.9	3.0	315

^a Measured in CH_2Cl_2 at concentration of 10^{-5} M.

^b Measured in PMMA at 10 wt.%.

^c Solid state quantum yields using an integration sphere were measured at 298 K in PMMA at 10 wt.%.



Fig. 3. Cyclic voltammograms for complexes Ir1-3 in CH₂Cl₂ solution.

around 290 nm are due to the ${}^{1}\pi$ - π * transitions of the triazol, and the shoulder peaks in the range of 300–350 nm result from the intramolecular charge-transfer transitions. The weak and broad absorption peaks around 400 nm are ascribed to singlet the metal-to-ligand charge-transfer (1 MLCT) and spin-forbidden 3 MLCT transitions. It is worth noting that the absorption spectra for (Czphtz)₂Ir(N·N) is overlapped with the fluorescent spectrum of Czphtz in the region of 350–430 nm, which ensures Förster-type energy transfer from the excited-singlet HCzphtz chromophore to the Ir complex core.

Complex Ir1 emits pure-blue light in CH_2Cl_2 solution with the emission maximum at ~463 nm, while complexes Ir2 and Ir3 exhibit the emission peaks at ~495 and ~490 nm in the blue-green region. The absorption and emission spectra in doped PMMA are shown in Fig. 2b and the corresponding data are listed in Table 1. Compared with the spectra in solution, the emission in thin film with the maximum emission peaks at ~467, ~497 and ~493 nm have a little red-shift due to the matrix rigidity difference. The emission color is tuned successfully by changing the ancillary ligands, and the pureblue-light room-temperature Ir(III) complexes were obtained.



Fig. 5. EL spectra of host-free and doped (insert) (a), and energy levels of materials (b).

The absolute photoluminescence quantum yields (Φ_{PL}) of complexes in films are summarized in Table 1. The blue-emitting complex Ir1 possess the lower Φ_{PL} of 13.61% with respect to Ir2 and Ir3 due to the small conjugation of tfmptz.



Fig. 4. Frontier molecular orbitals for complexes Ir1and Ir2.

Electroluminescence characteristics of the devices.	Table 2	
	Electroluminescence characteristics of the devices.	

Devices	λ_{max}^{a} (nm)	V _{turn-on} ^b (V)	L_{max} (cd/m ²)	$\eta_c^{\rm c}$ (cd/A)	CIE ^a (x, y)
Ir1	460	3.5	1776	0.6	(0.19, 0.18)
Ir2	490	4.5	1880	0.9	(0.19, 0.30)
Ir3	500	7.0	4379	5.6	(0.24, 0.49)
TCTA: 10 wt%lr1	480	5.0	1095	2.8	(0.22, 0.36)
TCTA: 10 wt%lr2	508	6.5	3231	4.7	(0.27, 0.52)
TCTA: 10 wt%lr3		4.0	968	1.1	(0.19, 0.22)

^a Recorded at a voltage of 8 V.

^b The voltage at luminescence of 1 cd/m².

^c The maximum current efficiency.

3.4. Electrochemical properties

Cyclic voltammetry (CV) was performed to investigate the electrochemical behaviors of complexes Ir1–Ir3. The HOMO energy levels determined from the oxidation potentials relative to the energy level of ferrocene are shown in Fig. 3 and Table 1.

The HOMO energy levels of all titled complexes are almost equal, which lacate in the 5.9–6.1 eV because the HOMO are mainly distribute on the π orbitals of the carbazole, as shown in Fig. 4. The LUMO level increases in the following order: Ir2<Ir1<Ir3. The structure change of *N*[^]N ancillary ligands strongly affects the LUMO level because the LUMO is completely dominated by the π -orbitals attributed to 1, 2, 4-triazole and Ir³⁺ cores involving the contributions of the Ir d-orbitals. The band gaps of Ir1, Ir2 and Ir3 are 3.1, 2.9 and 3.0 eV, respectively.

3.5. Performances in PhOLEDs

To evaluate the performances of Ir1–Ir3 complexes as phosphorescent emitters, host-free and doped PhOLEDs were fabricated with the configurations of ITO/PEDOT:PSS(30 nm)/Ir1–Ir3: or TCTA: 10 wt% Ir1–Ir3(40 nm)/TPBi(60 nm)/LiF(0.8 nm)/AL (100 nm). The EL spectra of host-free devices are nearly identical to their PL counterparts in solid film, showing that the same triplet excited states induced both the EL and PL processes. The EL spectra are displayed in the insert of Fig. 5a and the maximum emission peaks and CIE coordinates are listed in Table 2.

The host-free devices show the EL peaks at 460, 490 and 500 nm for Ir1, Ir2 and Ir3, respectively, with the CIE coordinates of (0.19, 0.18), (0.19, 0.30) and (0.24, 0.49). The EL emissions of based-Ir1, Ir2 and Ir3 are located in pure-blue regions, and blue-green regions, respectively.

The current density-voltage-luminance (J-V-L) characteristics of host-free and doped devices are shown in Fig. 6a and the detail data are summarized in Table 2. The maximum luminances (L_{max}) of the free-host PhOLEDs based on Ir1, Ir2 and Ir3 were 1776, 1880 and 4379 cd/m² and their turn-on voltages were 3.5, 4.5 and 7.0 V with the maximum current efficiency (η_c) of 0.6, 0.9 and 5.6 cd/A, respectively. The current density-current efficiency curves are characterized in Fig. 7b.

While the doped PhOLEDs with the TCTA as host have the maximum EL peaks at 480 and 508 nm for Ir1 and Ir2 in Fig. 5, and the EL peak of doped device using Ir1 as emitter has redshifts of 25 nm relative to the host-free device due to the unmatched energy level between TCTA and Ir1 (The HOMO/LUMO energy levels of compound TCTA are -5.7/-2.4 eV [27]).

The energy levels of all materials in PhOLEDs are shown in Fig. 5b. The L_{max} of doped PhOLEDs using Ir1, Ir2 and Ir3 as guest were 1095, 3231 and 968 cd/m² with the η_c of 2.8, 4.7 and 1.1 cd/A, respectively, as displayed in Figs. 6b and 7b. The doped PhOLEDs have the better EL performances than that of host-free ones. The

reson is that the ancillary lidans of degsined Ir(III) complexes have the small steric hindrance and cannot completely suppress the TTA.

4. Conclusions

The $(Czphtz)_2Ir(N^N)$ complexes were synthesized using the large steric hindrance 9-(6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hexyl)-9*H*-carbazole and different 1,2,3-triazol derivatives as ligands. The emission color was tuned to the blue range with the emission peak at ~460 nm and photoluminescence quantum yield of 13.61%. The host-free and doped PhOLEDs were fabricated by spin-coating. The blue and blue-green host-free devices exhibit the maximum luminance of 1776 and 1880 cd/m² with the CIE coordinates of (0.19, 0.18) and (0.19, 0.30). The synthesized Ir(III) complexes are



Fig. 6. Current density-voltage-luminance characteristics for host-free (a) and doped (b) devices.



Fig. 7. Current density versus current efficiency curves for host-free (a) and doped (b) devices.

suitable for low-cost solution processing and can be fabricated host-free devices by further design molecular structures.

Acknowledgments

This work was financially supported by the Program for New Century Excellent Talents in University (NCET-13-0927); International Science & Technology Cooperation Program of China (2012DFR50460); National Natural Science Foundation of China (61274056, 61205179, 61307030, 61307029); Shanxi Provincial Key Innovative Research Team in Science and Technology (2012041011); Natural Science Foundation of Shanxi Province (2015021070).

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