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Two Novel Bipolar Ir(III) Complexes based on

9-(4-(pyridin-2-yl)phenyl)-9H-carbazole and N-heterocyclic ligand

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Abstract Two novel bipolar Ir(III) complexes named (**Czppy**)₂**Ir**(**tfmptz**) and (**Czppy**)₂**Ir**(**pptz**) were synthesized and characterized, where the Czppy is 9-(4-(pyridin-2-yl)phenyl)-9H-carbazole, tfmptz refers to 2-(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine and **Hpptz** represents 2-(1H-tetrazol-5-yl)pyridine, respectively. Their molecular structures were confirmed by ¹H NMR and photophysical were investigated. The performances in phosphorescent organic light emitting devices (PhOLEDs) were characterized by a heavy doping concentration of 20 wt% in host as emitting layer. The results suggest that the number of nitrogen atoms in ancillary has no obvious effects on their photophysical properties. Both (**Czppy**)₂**Ir**(**tfmptz**) and (**Czppy**)₂**Ir**(**pptz**) display the blue-green emission with the peaks at 492, 526 nm. The performances of complexes (**Czppy**)₂**Ir**(**tfmptz**) in PhOLEDs superior to that of the (**Czppy**)₂**Ir**(**pptz**) due to the poor thermal stability.

Key words: N-heterocyclic ligand, Photophysical properties, Electroluminescent performance

Introduction:

Phosphorescent organic light emitting devices (PhOLEDs), which the emitter can harvest the single and triplet excitons to achieve the internal quantum efficiency of 100%, have attracted huge interests

for application in large-scale display and solid-state lighting due to the outstanding advantages [1-5]. Iridium(III) complexes are the most widely investigated for phosphorescent emitting materials owing to the obvious merits, such as color tunability, short excited lifetime and high quantum yields [6-9].

However, the Ir(III) complexes tend to possess the electron-transport ability, an example of the classical green-emitting material of *fac*-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$). This may result in an imbalance transportation between hole and electron; consequently reducing the efficiency in PhOLEDs. Hence the electron-donating groups, such as carbozole, triphenylamine usually were linked with the phenylpyridine to construct bipolar ligands in order to improve the balance of the carrier transport [10, 11, 12, 13, 14]. Though this kind of bipolar Ir(III) complexes can be used to fabricate the PhOLEDs by solution-processed approach, their efficiencies are still far behind the vacuum-evaporated devices [15, 16].

In addition, Ir(III) complexes based on the N-heterocyclic ancillary ligands as emitter in PhOLED have received extensive investigations because of their good electron mobility, excellent thermal stability and flexible modification ability [1, 17, 18]. We have reported Ir(III) complexes based on the 2-phenylpyridine and 2-(5-(trifluoromethyl)-2H-1, 2,4-triazol-3-yl)pyridine (Htfmptz), donated as (ppy)₂Ir(tfmptz) [19]. Its emission is observed at 485 nm, while it is very difficult to dissolve in the common organic solution. In this paper, we designed and synthesized two novel bipolar Ir(III) complexes of (Czppy)₂Ir(tfmptz) and (Czppy)₂Ir(pptz). In order to obtain the bipolar cyclometalated ligand and improve the solubility of complex (ppy)₂Ir(tfmptz), the electron-donating carbazole was connected to the electron-withdrawing phenylpyridine. The electron-accepting ancillary 2-(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine ligands of (tfmptz) and 2-(1H-tetrazol-5-yl)pyridine (pptz) were employed. The characteristics of PhOLEDs based on these compounds are also discussed.

Synthesis of 9-(4-(pyridin-2-yl)phenyl)-9H-carbazole (Czppy)

9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole:

9-(4-bromophenyl)-9H-carbazole (3.2 g, 10 mmol), bis(pinacolato)diboron (3.3 g, 13 mmol), PdCl₂(dppf)·CH₂Cl₂ (244.8 mg, 0.3 mmol) and KOAc (3.0 g, 30 mmol) were dissolved in N,N-dimethylformamide (50 mL), and were heated to 100 $^{\circ}$ C under the nitrogen atmosphere for 6 h. The mixture was washed with great deal of distilled water after cooling to the room temperature. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. The crude product was subjected to silica gel column chromatography using a 5:1 (V/V) mixture of petroleum ether and dichloromethane as the eluent to afford the white solid (yield 75 %). ¹H NMR (600 MHz, CDCl₃, δ): 8.14 (d, 2H, J = 7.8 Hz), 8.06 - 8.03 (m, 2H), 7.61 - 7.57 (m, 2H), 7.45 - 7.43 (m, 2H), 7.40 (d, 2H, J = 8.3 Hz), 7.28 (d, 2H, J = 8.0 Hz), 1.40 (s, 12H). Anal. Calcd for C₂₄H₂₄O₂NB: C, 78.26; H, 6.52; N, 3.80. Found: C, 78.92; H, 6.306; N, 3.74.

2-bromopyridine (0.8 g, 5 mmol), 1 (2.3 g, 6 mmol), Pd(PPh₃)₄ (90 mg, 0.08mmol), Na₂CO₃ (2 mol·L⁻¹, 8 mL, 15 mmol) and tetrahydrofuran (30 mL) were heated to reflux for 24 h under nitrogen atmosphere. The water was added after cooling to the room temperature. The organic phase was purified by chromatography using a 5:1 (V/V) of petroleum ether and dichloromethane as the eluent to obtain white solid of 9-(4-(pyridin-2-yl)phenyl)-9H-carbazole (**Czppy**) (yield, 82%). ¹H NMR (600 MHz, CDCl₃, δ): 8.76 (d, 1H, J = 4.8), 8.25 - 8.22 (m, 2H), 8.16 (d, 2H , J = 7.7 Hz), 7.85 - 7.80 (m, 2H), 7.71 - 7.67 (m, 2H), 7.48 (d, 2H, J = 8.2 Hz), 7.45 - 7.41 (m, 2H), 7.32 - 7.28 (m, 3H). Anal. Calcd for C₂₃H₁₆N₂: C, 86.25; H, 5.0; N, 8.75. Found: C, 86.87; H, 4.971; N, 8.48.

Synthesis of 2-(1H-tetrazol-5-yl)pyridine (Hpttz) 2-Cyanopyridine (10.4 g, 0.1 mol), sodium azide (7.3 g, 0.12 mol), glacial acetic acid (8.0 g, 0.12mol) and butyl alcohol (40 mL) was put into a reactor. The mixture was heated to reflux for 4 day. Then adding sodium azide (1.8 g, 0.03 mol), glacial acetic acid (4.0 g, 0.06 mol) into reactor again, the reaction continues reacting 2 days in reflux. After cooling to room temperature, the mixture was poured into a large amount of water. Then driped hydrochloric acid with concentrated, until all the crystal precipitation. By filtering and vacuum drying, get white crystal, Yield 95%, ¹H NMR (600 MHz, Chloroform-*d*, δ) 13.40 (s, 1H),

8.82 (d, *J* = 4.9 Hz, 1H), 8.44 (d, *J* = 7.9 Hz, 1H), 8.01 (t, *J* = 7.7 Hz, 1H), 7.58-7.54 (m, 1H). Anal. Calcd for C₆H₅N₅: C, 48.98; H, 3.40; N, 47.62. Found: C, 48.99; H, 3.384; N, 47.35

Synthesis of complex (Czppy)₂Ir(tfmptz)

Czppy (800 mg, 2.5 mmol), $IrCl_3 \cdot H_2O$ (350 mg, 1 mmol), and 2-ethoxyethanol/H₂O (3:1, V/V, 20 mL) were was stirred for 120 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and the formed precipitate was filtered, washed by water, ethanol and diethyl ether to obtain the intermediate, assumed to be a chloro-bridged dimer.

Without further purification, a mixture of chloro-bridged dimer (530 mg, 0.3 mmol), **2-(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine (Htfmptz)**[19] (64 mg, 0.3 mmol), Na₂CO₃ (640 mg, 6 mmol), 2-ethoxyethanol (20 mL) were heated to refluxed at 140 °C for 24 h, then extracted with CH₂Cl₂ and dried over anhydrous Na₂SO₄. The crude product was subjected to silica gel column chromatography with CH₂Cl₂/ ethyl acetate (10:1, V/V). Finally, the light yellow solid was obtained (yield 62%) ¹H NMR (600 MHz, CDCl₃, δ): 8.36 (d, J = 7.9 Hz, 1H), 8.08 (t, J = 7.2 Hz, 3H), 8.04 (d, J = 7.7 Hz, 2H), 7.95 - 7.89 (m, 4H), 7.87 (d, J = 8.1 Hz, 1H), 7.70 - 7.68 (m, 1H), 7.58 - 7.53 (m, 2H), 7.48 (d, J = 5.6 Hz, 1H), 7.42 - 7.29 (m, 9H), 7.26 - 7.22 (m, 4H), 7.20 (t, J = 7.5 Hz, 2H), 6.80 (dddd, J = 47.7, 7.1, 5.7, 1.3 Hz, 2H), 6.58 (dd, J = 5.6, 2.1 Hz, 2H). Anal. Calcd: C, 62.13; H, 3.26; N, 10.74. Found: C, 60.99; H, 3.529; N, 10.01. MALDI-TOF-MS (m/z): calcd for IrC₅₄H₃₄N₈F₃, 1044.25; found, 1043.80

Synthesis of complex (Czppy)₂Ir(pptz)

1H). Anal. Calcd: C, 63.92; H, 3.51; N, 12.90 Found: C, 65.13; H, 4.75; N, 13.10. MALDI-TOF-MS (m/z): calcd for IrC₅₂H₃₄N₉, 977.29 ; found, 977.26.

The detail synthetic process has been shown in Scheme 1.

Materials and Measurements

¹H-NMR spectra were confirmed using a Switzerland Bruker DR×600. C, H and N microanalysis were carried out with an Elemental Vario EL elemental analyzer. Mass spectra were obtained on SHIMADZU matrix-assisted laser desorption/ionization time-of-flight mass pectrometer (MALDI-TOF-MASS). UV-vis absorption spectra were recording using Lambda Bio 40. The Photoluminescence (PL) spectra were measured by HORIBA FluouoMax-4 spectrophotometer. The low-temperature phosphorescence spectra at 77 K in 2-methyltetrahydrofuran (2-MeTHF) were performed on an Edinburgh F-980 spectrometer. Thermogravimetric analysis curves (TGA) were undertaken on a Netzsch TG 209F3 under dry nitrogen atmosphere heating at a rate of 10 °C/min from room temperature to 800 °C.

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 level (E_{HOMO}) was 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. The lowest unoccupied molecular orbital level (E_{LUMO}) was calculated from the equation of $E_{LUMO} = E_{HOMO} + E_g$, and E_g is obtain from the absorption and emission spectra intersection (λ_{sec}), that is $E_g = \frac{1240}{\lambda_{sec}}$.

Theoretical calculations were performed using the Gaussian 03 package. Geometry optimization

was performed by density functional theory (DFT) in B3LYP/6-31G(d) basis sets. The molecular orbitals were visualized using Gauss view 5.0.

OLED fabrication and measurements

PhOLEDs with area of $3 \times 3 \text{ mm}^2$ were fabricated by vacuum deposition onto the indium tin oxide (ITO) glass substrate. ITO glass substrate was cleaned in order with deionized water, acetone and ethanol. The electroluminescent (EL) spectra and CIE coordinates were measured by PR-655 spectrophotometer. The current density – voltage – luminance (J-V-L) characteristics of PhOLEDs and OLEDs were recorded using Keithley 2400 Source Meter and ST-900M Spot Brightness Meter. The external quantum efficiency (EQE) values were calculated according to previously reported methods [20]. All measurements were carried out at room temperature under ambient conditions.

Results and discussion

Molecular structures and thermal stability

Scheme 1 shows the chemical structures and synthetic routes of the ligands and Ir(III) complexes. Cyclometalated ligand of **Czppy** are obtained from the reaction between 2-bromopyridine and 9-(4-(4, 4, 5, 5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) -9H-carbazole. The ancillary ligands of Htfmptz and Hpptz are synthesized according to the methods in reference [19]. The electron-donating group was introduced in cyclometalated ligand to improve the hole transportation. Furthermore, the ancillary ligands of tetrazol and trizole have been proved to have the excellent electron withdrawing abilities. As a result, the bipolar Ir(III) complexes, (**Czppy**)₂**Ir**(**tfmptz**) and (**Czppy**)₂**Ir**(**pptz**), were synthesized. Their molecular structures are defined by ¹H NMR and element analyses.

Their thermal stabilities were measured by thermogravimetric analysis (TGA) under a nitrogen flow, as shown in Figure 1. Both complexes show good thermal stabilities with the decomposition temperature (T_d , the temperature at the loss weight 5%) around 388 and 334 °C, respectively. The

increase in the number of nitrogen atoms in ancillary led to a lower T_d for (Czppy)₂Ir(pptz).

Photophysical properties

Two compounds exhibit the similar absorption and emission spectra in CH₂Cl₂ solution (Figure 2a), and the relative data are summarized in Table 1. The absorption bands blow 300 nm are assigned to π - π * transitions from ligands. The weak absorption peaks in the range of 300-400 nm are attributes to the typical spin-allowed singlet metal-to-ligand charge-transfer transition (¹MLCT). The others, which can be found at about 412 nm, are mainly origin from the spin-orbit coupling triplet MLCT transitions. Their emission of (**Czppy**)₂**Ir**(**tfmptz**) and (**Czppy**)₂**Ir**(**pptz**) are observed at the 493, 526 nm.

The absorption bands and emission spectra of $(Czppy)_2Ir(tfmptz)$ appears the significant blue shift relative to the free-carbazole $(ppy)_2Ir(tfmptz)$ [19]. The geometry were optimized at B3LYP/6-31G(d) level, and the electronic properties of two compounds were calculated (in Figure 3). The HOMO orbitals extend to the electron-donating carbazole and *d*-orbitals of Ir, while the LUMO are distributed on the ancillary ligand. Therefore, the introduction of the electron-donating groups will increase the HOMO level. The HOMO and LUMO of $(Czppy)_2Ir(tfmptz)$ and $(Czppy)_2Ir(pptz)$ are located at the different groups, this may be conductive to promote bipolar charge-transporting ability [21, 22].

The energy gaps (E_g) of $(Czppy)_2Ir(tfmptz)$ and $(Czppy)_2Ir(pptz)$ are estimated by the intersection of the absorption and emission spectra in CH₂Cl₂ to be 2.84 and 2.86 eV, respectively. The low-temperature phosphorescent spectra were measured in 2-methyltetrahydrofuran (2-MeTHF) matrixes at 77 K showed fine vibronic structures (in Figure 2b). The triplet energies are calculated to about 2.55 eV. These results indicate that the small changes in ancillary ligand, that the electron-withdrawing trifluoromethyl was replaced by a nitrogen atom, have no obvious effects on the ground and excited states of Ir(III) complex.

The electrochemical properties were measured by cyclic voltammetry using ferrocene as the

internal standard (Figure 4). The oxidation potentials (E_c^{ox}) of complexes $(Czppy)_2Ir(tfmptz)$, $(Czppy)_2Ir(pptz)$ are 1.25 and 1.18 V, respectively. Relative energy levels of E_{HOMO}/E_{LUMO} are -5.67/-2.83 and -5.55/-2.69 eV by the formulas of $E_{HOMO} = -4.8 - e(E_c^{ox} - E_f^{ox})V$ and $E_{LUMO} = E_{HOMO} + E_g$. The change from the electron-withdrawing trifluoromethyl to nitrogen results in a stablized LUMO level and an increased HOMO level.

Electroluminescent Performance

The electroluminescent (EL) were characterized by fabricating devices 1 and 2, in which $(Czppy)_2Ir(tfmptz)$ and $(Czppy)_2Ir(pptz)$ were used as dopants and the synthesized TAZ-2Cz in our laboratory as host [20]. The device structure is ITO / MoO₃ (3 nm) / NPB (30 nm)/TCTA(10 nm) /TAZ-2Cz: 20 wt% (Czppy)_2Ir(tfmptz) or (Czppy)_2Ir(pptz)(20 nm)/TPBi (50 nm)/ LiF (1 nm)/ Al (100 nm) ((Czppy)_2Ir(tfmptz) in device 1 and (Czppy)_2Ir(pptz) in device 2), in which N'-bis(naphthalen)-N,N'-bis(phenyl)-benzidine (NPB) and 1, 3, 5-tris(2-nhenylbenzimidazolyl) -benzene (TPBi) can take the hole-transport layer and electron-transfer layer roles, respectively; tris(4-carbazoyl- 9-ylphenyl)amine (TCTA) is used to reduce hole injection barrier and block the electron; MoO₃ (molybdenum oxide) and LiF (lithium fluoride) serve as the hole- and electron-injecting layers. The bipolar TAZ-2Cz was chosen due to the excellent carrier transporting nature and high triplet level (2.62 eV). It is proved that the performances of TAZ-2Cz in PhOLEDs superior to the classical host of 4, 4'-N, N'-dicarbazolebiphenyl (CBP) with the same device structure. The EL characteristics of devices are displayed in Figures 5, 6 7 and the relative data are summarized in Table 2.

It is observed that the both devices emit brighter green-blue emission with maximum peaks 500/527 for device 1 and 500 nm for device 2. Compared with the PL spectra in CH₂Cl₂ solution, the EL spectra have a little red shift, while the shoulder at 527 nm becomes weaker in device 2 dopant by (**Czppy**)₂**Ir**(**pptz**) in Figure 5. This indicates that the emissions are dominated by the dopants and

the effective energy transports are achieved between host and dopants. As shown in Figure 6a, the EL spectra of device 1 remain almost unchanged under the different driving voltages from 5 to 10 V. while with the increasing of voltage from 5 to 10 V, a new weak emission peak at 433 nm was appeared in Figure 6b due to the poor stability and carrier-transport properties of (**Czppy**)₂**Ir**(**pptz**).

Both devices have the similar turn-on voltages (V_{on} , the voltage at 1 cd/m²) at 4.0 and 3.9 V. The totally different of current density - voltage - Luminance (J-V-L), current efficiency- current density- power efficiency curves ($\eta_c - J - \eta_p$) and luminance - external quantum efficiency (L-EQE) are exhibited in Figure 7. The device 1 based on (**Czppy**)₂**Ir**(**tfmptz**) with trifluoromethyl group and three nitrogen atoms in ancillary ligand achieves a good EL performance with the maximum luminance (L_{max}), maximum η_c , η_p and EQE of 17 415 cd/m², 44.5 cd/A, 27.7 lm/W, and 14.4 %, respectively. While the device 2 employing (**Czppy**)₂**Ir**(**pptz**) with four nitrogen atom without trifluoromethyl in ligand exhibits an inferior EL performance with L_{max} of 6 791 cd/m², the luminance efficiencies of 23.2 cd/A, 15.7 lm/W and EQE of 7.6 %. In addition, the device 2 displays a serious roll-off in efficiencies, as can be seen in Fig. c, due to the weak thermal stability to some extent resulted from the increase of the number of nitrogen atom in ancillary ligand.

Conclusion

In summary, we have been designed and synthesized two Ir(III) complexes (**Czppy**)₂**Ir**(**tfmptz**) and (**Czppy**)₂**Ir**(**pptz**), which have the same bipolar cyclometalated ligand and the different N-heterocyclic derivatives as ancillary ligands modified with different number of nitrogen atom. The heavy doping PhOLEDs were fabricated to study their EL performances. The similar UV-vis absorption and emission in solution were observed regardless of the different ancillary ligands. Two Ir(III) complexes exhibit the brighter green-blue emission with the double peaks at 493, 526 nm. On the other hand, the EL performance of (**Czppy**)₂**Ir**(**tfmptz**) in PhOLED with the maximum EQE of 14.4 % has the superior properties to the (**Czppy**)₂**Ir**(**pptz**).

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Scheme 1 Synthetic routes of the ligand and complexes

Figure 1 The TGA curves of (Czppy)₂Ir(tfmptz) and (Czppy)₂Ir(pptz)

- Figure 2 UV-vis absorption (a) and emission (b) spectra in CH₂Cl₂ solution at room temperature
- Figure 3 Orbitals distributions of HOMO/ LUMO for (Czppy)₂Ir(tfmptz) and (Czppy)₂Ir(pptz)
- Figure 4 Cyclic voltammetry curves of (Czppy)₂Ir(tfmptz) and (Czppy)₂Ir(pptz)
- Figure 5 EL spectra of device 1 and 2
- Figure 6 The EL spectra of device 1 and 2 at the different voltages
- Figure 7 (a) J-V-L characteristics, (b) current efficiency- current density- power efficiency curves

 $(\eta_c - J - \eta_p)$ and (c) external quantum efficiency (EQE) versus luminance for devices 1 and 2.

Scheme 1



Figure 1

Figure 2a



Figure 2b



Figure 4

Figure 5



Figure 6a



Figure 7a



Figure 7c



Table 1. Photophysical and electrochemical properties of (Czppy)₂Ir(tfmptz) and (Czppy)₂Ir(pptz)

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Comp	lavas	$\lambda_{abs}{}^{a}$	λ_{em}^{a}	E_T^{b}	T_d	HOMO/LUMO	E_g^{c}
Comp	lexes	(nm)	(nm)	(eV)	(°C)	(eV)	(eV)
(Czppy) ₂ I	r(tfmptz)	345, 372, 421	493, 526	2.55	388	-5.67/-2.83	2.84
(Czppy) ₂	Ir(pptz)	345, 372, 419	493, 526	2.55	375	-5.55/-2.69	2.86

^{*a*} Recorded in CH₂Cl₂ solution at room temperature; ^{*b*} Triplet level (T_I) calculated based on low-temperature PL spectra at 77K in 2-MeTHF solution; ^{*c*} Energy gap (E_g) was estimated from the intersection of UV-vis and emission spectra

Device	Dopant	$\lambda_{max}{}^{\mathrm{a}}$	V_{on}^{b}	L_{max}^{c}	$\eta_c{}^{\mathrm{d}}$	${\eta_p}^{ m e}$	CIE^{f}	EQE _{max} ^g
	-	(nm)	(V)	(cd/m^2)	(eV)	(eV)	(x, y)	(%)
1	(Czppy) ₂ Ir(tfmptz)	500, 527	4.0	17 415	44.5	27.7	(0.25, 0.58)	14.4
2	(Czppy) ₂ Ir(pptz)	500	3.9	6 791	23.2	15.7	(0.26, 0.56)	7.6

Table 2. EL performances of devices 1 and 2

^a the EL peaks collected at 8 V, ^b turn-on voltage at 1 cd/m², ^c the maximum luminance, ^d the maximum current efficiency, ^e the maximum power efficiency, ^f the CIE coordinate at voltage of 8 V, ^g the maximum external quantum efficiency

Highlight

The bipolar Ir(III) complexes were designed and synthesized.

The green-blue emission was observed.

The performances in PhOLEDs were characterized by the heavy dope concentration.