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Efficient Red Phosphorescent OLEDs Using Ir(III) Complexes Based on Bezoylphenylpyridine and the Various Ancillary Ligands

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A series of red phosphorescent Ir(III) complexes 1–5 based on benzoylphenylpyridine and various ancillary ligands were synthesized and their photophysical properties were investigated. The EL efficiencies were quite sensitive to the structural features of the dopants in the emitting layers. Particularly, using complex 5 as a dopant in emitting layer, a high-efficiency orange-red OLED was fabricated, showing the maximum luminance of 16900 cd/m² at 12 V, the luminous efficiency of 12.8 cd/A, the power efficiency of 4.48 lm/W, the external quantum efficiency of 9.65% at 20 mA/cm² and CIE *x*, *y* coordinates of (0.609, 0.390) at 12 V.

Keywords: Red Phosphorescence, OLED, Iridium Complex, Benzoylphenylpyridine.

1. INTRODUCTION

Phosphorescent OLEDs are of huge interest because the high emission efficiency caused by the strong spin-orbit coupling in the presence of heavy metals leads to the mixing of singlet and triplet manifolds so that both singlet and triplet excitons can be harvested.^{1,2} The design and synthesis of efficient red emitters are intrinsically difficult because their luminance quantum yields tend to decrease with increasing emission wavelength in accordance with the energy gap law.³ Therefore, a variety of phosphorescent materials based on iridium complexes have been developed as emitting materials for the efficient phosphorescent OLEDs.^{4,5} Among those are the Ir(III) complexes with carbonylated 2-phenylpyridine ligands.⁶⁻⁹ However, their electroluminescent properties need to be improved before they can be used in flat panel displays. For example, an OLED device using (Bzppy)₂ Ir(acac) as a dopant in a CBP host showed the luminous efficiency of 7.7 cd/A and the power efficiency of 1.18 lm/W at 20 mA/cm² with the CIEx, y coordinates (x = 0.61, y = 0.38).¹⁰ To improve the EL performances of devices using this material as the emitting material, the optimization of the chemical and device structures have been carried out in this lab.

In this paper, a series of red phosphorescent Ir(III) complexes **1–5** based on benzoylphenylpyridine ligands were designed and synthesized. The electron donating methyl group and the various ancillary ligands such as acetylacetone, 1,3-diphenylpropane-1,3-dione, 2,2,6,6-tetramethylheptane-3,5-dione were introduced to tune the band gap of iridium complexes by the control of HOMO or LUMO energy level.^{11–13} These types of ligand modifications would lead the change of electronic and structural properties of the emitting materials of the devices, which are key factors affecting OLED device performances. We herein demonstrates highly efficient red OLEDs using these Ir(III) complexes.

2. EXPERIMENTAL DETAILS

2.1. Synthesis and Characterization

5-Benzoyl-2-bromopyridine,⁷ L2,¹⁴ and complex **2** $[(Bzppy)_2Ir(acac)]^{14}$ were synthesized as previously reported.

Synthesis of L1. (85% yield). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.75 (*dt*, J = 1.2, 3.3 Hz, 1 H), 8.12 (*d*, J = 8.7 Hz, 2 H), 7.92 (*d*, J = 8.7 Hz, 2 H), 7.86–7.80 (*m*, 4 H), 7.64–7.58 (*m*, 1 H), 7.54–7.48 (*m*, 2 H), 7.33–7.28 (*m*, 1 H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 196.6, 154.5, 150.2, 143.3, 138.0, 137.9, 137.1, 132.7, 130.8,

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130.3, 128. 6, 127.0, 123.1, 121.2. HRMS-EI⁺ calcd for $C_{18}H_{13}ON$: 259.0997, found: 259.0997.

Synthesis of L3. (90% yield). ¹H NMR (300 MHz, CDCl₃): ppm 9.05 (*dd*, J = 0.8 Hz, 2.3 Hz, 1 H), 8.19 (*dd*, J = 2.3 Hz, 8.3 Hz, 1 H), 8.00 (*d*, J = 8.2 Hz, 2 H), 7.87–7.84 (*m*, 3 H), 7.66–7.61 (*m*, 1 H), 7.55–7.50 (*m*, 2 H), 7.32 (*d*, J = 8.0 Hz, 2 H), 2.43 (*s*, 3 H). ¹³C NMR (500 MHz, CDCl₃): ppm 195.0, 160.6, 151.5, 140.6, 138.4, 137.3, 135.7, 133.2, 131.2, 130.2, 130.0, 128.8, 127.5, 119.8, 21.6. HRMS-EI⁺ calcd for C₁₉H₁₅ON 273.1154: found, 273.1154.

General procedure for the synthesis of 1. To a flask containing $IrCl_3 \cdot 3H_2O$ (0.30 g, 1 mmol) and L1 (0.57 g, 2.2 mmol) was added a 3:1 mixture of 2-ethoxyethanol and water (12 mL). The mixture was refluxed for 24 h and cooled to room temperature. A colored precipitate was filtered off and washed with water, methanol, and hexane. The crude product was pumped dry to give crude $(L1)_2 Ir(\mu-C1)_2 Ir(L1)_2$. Crude $(L1)_2 Ir(\mu-C1)_2 Ir(L1)_2$ was mixed with Na₂CO₃ (0.29 g, 2.7 mmol) in a twoneck flask. 2-Eethoxyethanol (10 mL) and acetylacetone (0.14 mL, 1.4 mmol) were added and the mixture was heated at 100 °C for 6 h. The solution was cooled to room temperature and the red solid was collected by filtration. The orange solid washed with water, methanol, and hexane. The crude product was purified by column chromatography using 0–50% ethyl acetate in hexane as eluent. 1 was obtained as a orange solid (0.44 g, 54%) after recrystallization from CH₂Cl₂/Methanol. ¹H NMR (300 MHz, CDCl₃): δ ppm 8.51–8.49 (m, 2 H), 7.86 (d, J = 8.1 Hz, 2 H), 7.68 (dd, J = 1.5, 7.5 Hz, 2 H), 7.63 (d, J = 8.4 Hz)2 H), 7.57-7.54 (m, 4 H), 7.49-7.44 (m, 2 H), 7.34-7.28 (m, 6 H), 7.16–7.11 (m, 2 H), 6.59 (d, J = 1.5 Hz, 2 H), 5.25 (s, 1 H), 1.80 (s, 6 H). ¹³C NMR (125 MHz, CDCl₃): ppm 197.3, 185.1, 167.5, 149.5, 148.6, 146.7, 138.4, 137.4, 136.8, 135.0, 131.7, 130.2, 127.9, 123.4, 123.4, 122.9, 119.7, 100.8, 28.9. HRMS-FAB⁺ calcd for C₄₁H₃₁IrN₂O₄: 808.1913, found: 808.1918.

Synthesis of **3**. (0.45 g, 25%). ¹H NMR (300 MHz, CDCl₃): δ ppm 9.00 (s, 2 H), 8.27 (dd, J = 2.1, 8.5 Hz, 2 H), 7.99 (d, J = 8.5 Hz, 2 H), 7.69–7.65 (m, 6 H), 7.56 (dd, J = 1.3, 8.5 Hz, 4 H), 7.34 (d, J = 7.3 Hz, 2 H), 7.22–7.13 (m, 10 H), 6.91 (td, J = 1.2, 7.3 Hz, 2 H), 6.81 (td, J = 1.3, 7.4 Hz, 2 H), 6.62 (s, 1 H), 6.41 (d, J = 7.6 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ ppm 192.6, 180.2, 171.9, 150.6, 149.9, 144.0, 141.3, 139.0, 136.8, 133.6, 132.9, 131.1, 130.5, 130.4, 129.6, 128.6, 128.4, 126.6, 125.9, 121.6, 118.7, 96.0. HRMS-FAB⁺ calcd for C₄₁H₃₁IrN₂O₄: 932.2226, found: 932.2223.

Synthesis of **4**. (0.40 g, 68%). ¹H NMR (500 MHz, CDCl₃): δ ppm 8.72 (*d*, *J* = 1.8 Hz, 2 H), 8.19 (*dd*, *J* = 1.9, 8.5 Hz, 2 H), 7.96 (*d*, *J* = 8.5 Hz, 2 H), 7.77 (*d*, *J* = 7.2 Hz, 4 H), 7.65 (*d*, *J* = 7.5 Hz, 2 H), 7.58 (*d*, *J* = 7.5 Hz, 2 H), 7.50–7.45 (*m*, 4 H), 6.88 (*t*, *J* = 7.4 Hz, 2 H), 6.77 (*t*, *J* = 7.4 Hz, 2 H), 6.44 (*d*, *J* = 7.5 Hz, 2 H), 5.46 (*s*, 1 H), 0.65 (*s*, 18 H). ¹³C NMR (75 MHz, 2 H),

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CDCl₃): δ ppm 194.9, 193.0, 172.0, 151.7, 150.5, 143.9, 138.7, 137.1, 133.8, 133.3, 131.0, 130.2, 130.0, 129.0, 125.7, 121.1, 118.2, 90.5, 41.2, 27.8. HRMS-FAB⁺ calcd for C₄₁H₃₁IrN₂O₄: 892.2852, found: 892.2847.

Synthesis of **5**. (0.69 g, 41%). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.83 (*d*, *J* = 2.0 Hz, 2 H), 8.27 (*dd*, *J* = 2.0 Hz, 8.5 Hz, 2 H), 7.93 (*d*, *J* = 8.6 Hz, 2 H), 7.82–7.79 (*m*, 4 H), 7.63–7.57 (*m*, 2 H), 7.55–7.47 (*m*, 6 H), 6.68 (*dd*, *J* = 1.6 Hz, 7.9 Hz, 2 H), 6.10 (*s*, 2 H), 5.28 (*s*, 1 H), 2.08 (*s*, 6 H), 1.55 (*s*, 6 H). ¹³C NMR (500 MHz, CDCl₃): δ ppm 193.1, 185.1, 172.4, 151.1, 150.7, 141.3, 140.9, 138.6, 137.3, 134.5, 133.0, 130.1, 129.9, 128.9, 125.8, 122.9, 118.0, 100.9, 28.9, 22.1. HRMS-FAB⁺ calcd for C₄₃H₃₅IrN₂O₄ 836.2226: found, 836.2228.

2.2. Device Fabrication and Measurements

OLEDs using red dopants in the emitting layers were fabricated by vacuum $(5.0 \times 10^{-7} \text{ torr})$ thermal evaporation onto pre-cleaned ITO coated glass substrates. The structure was as follows: ITO/2-TNATA (60 nm)/NPB (20 nm)/CBP: 8% Ir(III) complexes (30 nm)/BCP (10 nm)/Alq₃ (20 nm)/Liq (2 nm)/Al. All of the optical and electrical properties of OLEDs such as the current density, luminance, luminous efficiency and CIE coordinate characteristics were measured with Keithley 236, LS-50B, and MINOLTA CS-100A, respectively.

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3. RESULTS AND DISCUSSION

Scheme 1 shows the structure and synthetic route for the Ir(III) complexes 1–5. The ligands were synthesized in moderate yields via the Stille and Suzuki cross coupling reactions. The Ir(III)-complexes were obtained by cyclometalation of the ligands with $IrCl_3$ and subsequent reaction with acetylacetone, 1,3-diphenylpropane-1,3-dione, 2,2,6,6-tetramethylheptane-3,5-dione.

Figure 1 shows the UV-vis absorption and photoluminescense spectra of these phosphors in dilute dichloromethane solution. A summary of photophysical data of the red emitters were given in Table I. For all complexes, the absorption band below 350 nm can be assigned to the spinallowed ${}^{1}\pi - \pi^{*}$ transitions of the cyclometalated ligands. Also, in the absorption spectra of all complexes, there was a weak but well-resolved peak near 400 nm with lower extinction coefficients, which can be interpreted as arising from a spin-orbit coupling, together with an admixture of ¹MLCT and ³MLCT states.⁶ The Ir(III) complexes 1-5 show absorption peak over 450 nm region at 474, 523, 513, 528, and 517 nm, respectively. It means that ${}^{3}MLCT/{}^{3}\pi-\pi^{*}$ transition occurs in these complexes due to strong spin-orbit coupling from Ir(III). The difference of the spectra between L2 and corresponding iridium complexes (2, 3, and 4) implied that ligand has been coordinated successfully with iridium ion. In PL spectra at 278 K, the maximum emission peaks for complexes 1-5 were located from 596 to 630 nm in the red region of the



Scheme 1. Synthetic route to Ir(III) complexes 1–5. *Conditions*: (i) Pd(PPh₃)₄, LiCl, Toluene; (ii) IrCl₃ · H₂O, H₂O, 2-ethoxyethanol; (iii) Na₂CO₃, 2-ethoxyethanol; (iv) Pd(PPh₃)₄, LiCl, Toluene.



Figure 1. (a) The absorption and (b) emission spectra of Ir(III) complexes (1–5).

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Compound	1	2	3	4	5
UV [nm] ^a	285,	289,	285,	283,	283,
	474	330,	304,	320,	330,
		523	513	528	517
PL $[nm]^a$	596	619	617	630	618
PL $[nm]^b$	570	587	578	586	585
FWHM	84	76	93	94	84
HOMO [eV] ^c	-5.59	-5.56	-5.54	-5.47	-5.72
LUMO [eV]	-3.23	-3.34	-3.33	-3.11	-3.45
E	2.36	2.22	2.21	2.36	2.27
E_T	2.17	2.11	2.14	2.11	2.12
$\Phi^{[\%]^d}$	0.06	0.29	0.31	0.22	0.25

Notes: ^{*a*}Measured in CH₂Cl₂ (1 × 10⁻⁵ M at 278 K); ^{*b*}Measured in 2-Me THF (1 × 10⁻⁵ M at 77 K); ^{*c*}The energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki, AC-2); ^{*d*}Degassed CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] ($\Phi_p = 0.40$), $\lambda_{ex} = 470$ nm.

visible spectrum. Compared with complex 2, complex 1 showed a 16 nm blue shift of the maximum peak in the emission spectra, while the maximum emission peak of complex 4 red-shifted by 11 nm. This observation means that HOMO/LUMO energy levels are very sensitive to the subtle change of substituents in ligands, due to the differences in electron donating/withdrawing properties, the conjugation effects and field strength of ligand.^{12, 13} To determine the triplet energy levels, the PL of 1-5 were measured at 77 K. As shown in Table I, triplet energies of 1-5 (2.11~2.17 eV) were lower than that of host material (CBP: $T_1 = 2.60$), which indicated that energy transfer from host (CBP) to red Ir-complexes 1-5 would be effective. The emission quantum yields of complexes 1-5 were 0.06, 0.29, 0.31, 0.22, and 0.25 respectively, as determined with $Ir(ppy)_3$ (0.40), used as a reference. Interestingly, the position electron-withdrawing benzovl group in ligand of iridium complexes affected greatly the quantum yields ($\Phi = 0.06$ for **1** *ver* $\Phi = 0.29$ for **2**).

The HOMO energy levels were measured with an AC-2 photoelectron spectrometer and the LUMO energy levels calculated by subtracting the corresponding optical band gap energies from the HOMO values. The HOMO and LUMO energy levels for complexes 1-5 varied from -5.47 to -5.72 eV and -3.11 to -3.45 eV, respectively.

To explore the electroluminescent properties of these molecules, devices were fabricated with a structure of ITO/2-TNATA (60 nm)/NPB (20 nm)/CBP: 8% red Ir(III) complexes 1–5 (30 nm)/BCP (10 nm)/Alq₃ (20 nm)/Liq (2 nm)/Al and their electroluminescent performance characteristics of devices are summarized in Table II. As shown in Figure 2, the EL spectra of devices A–E were red emissions with the maximum peaks at 587–614 nm, respectively. Interestingly, the maximum emission peaks of 1–5 in devices A–E were blue-shifted as compared to those in CH₂Cl₂ solution. Iridium complexes 1–5 were surrounded with CBP host in devices A–E, while those were solvated with CH₂Cl₂ in solution states. These differences in solvation between devices and CH₂Cl₂ solution states would

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Table II.	EL performance characteristic of the devices A–E.											
Device	Dopant	EL (nm)	$V_{ m on}^a~({ m V})$	$L^b (cd/m^2)$	$LE^{c/d}$ (cd/A)	$PE^{c/d}$ (lm/W)	$EQE^{c/d}$ (%)	CIE(x, y)				
A	1	587	4.0	4501	10.4/5.32	8.32/1.76	5.02/2.54	(0.557, 0.438)				
В	2	606	4.0	5994	16.7/11.0	11.3/3.10	10.5/6.55	(0.617, 0.383)				
С	3	598	4.5	5805	12.8/8.80	9.26/2.87	6.57/4.33	(0.595, 0.402)				
D	4	614	3.5	7088	8.52/7.43	7.36/2.71	7.16/5.54	(0.633, 0.364)				
Е	5	606	4.0	16900	16.3/12.8	11.9/4.48	13.0/9.65	(0.609, 0.390)				

Notes: "Turn-on voltage at 1 cd/m2; "Maximum luminance; CMaximum values; "At 20 mA/cm2; "CIE values are measured at 12 V.

contribute the blue-shifts effect in EL spectra compared to PL spectra of 1–5. Among devices A–E, device D using complex 4 showed the deepest red emissions in the EL spectrum, which is well compatible with the trends of PL studies of 1–5 in CH₂Cl₂ solution. The CIE coordinates of device D were (0.633, 0.364) with the luminous efficiency of 7.43 cd/A, the external quantum efficiency (EQE) of 5.54% at 20 mA/cm².

The current density-voltage-luminance (J-V-L) and luminous efficiency (LE) characteristics of devices **A**-**E** are shown in Figure 3. The turn-on voltages for devices **A**-**E** were 4.0, 4.0, 4.5, 3.5, and 4.0 V, respectively, which indicated that the carrier injection into the emitting layer of device **D** was more effective than in devices **A**, **B**, **C** and **E**. Compared to the other complexes, complex **4** has the lowest HOMO energy level. Thus the direct hole-trapping process from NPB to dopant in device **D** is more effective than those in the other devices. This would lead to the low turn-on voltage of device **D**, compared to the other devices.

Among devices A-E, device E showed the extraordinary luminance and displayed excellent EL performances with a LE, PE, and EQE of 12.8 cd/A, 4.48 lm/W and 9.65% at 20 mA/cm², respectively. Hence, compared to device **B** using complex **2**, device **E** using complex **5** with the additional methyl group in ligand possessed improved EL efficiencies. Interestingly, upon the changes of ancillary ligands of iridium complexes from acetylacetone to 1,3-diphenylpropane-1,3-dione and 2,2,6,6-tetramethylheptane-3,5-dione, the EL efficiencies of devices using them as dopants were decreased greatly. For example, compared to device **B**, the EQE of devices **C** and **D** at



Figure 2. EL spectra of devices A–E.

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Figure 3. (a) J-V-L curve and (b) LE versus current density of devices **A**–**E**.

20 mA/cm² were reduced by 33.9 and 15.4%, respectively. Also, the position electron-withdrawing benzoyl group in ligand of iridium complexes affected greatly the external quantum efficiencies of devices using them as dopants (EQE = 2.54% for device **A** vs. EQE = 6.55%for device **B**). These observations reflect the complicated aspects on the nature of electroluminescences in phosphorescent dopant/host emitting systems in the amorphorus solid states. Presumably, the changes of electronic and structural properties of the emitting materials by the modification of ligands of iridium complexes would affect the physical properties of those such as the quantum yields, HOMO/LUMO energy levels and the carrier mobilities, which play important roles in OLED device performances.

4. CONCLUSION

Red phosphorescent Ir(III) complexes 1-5 based on benzoylphenylpyridine derivative units and the various

ancillary ligands such as pentan-1,3-dione, 1,3-diphenylpropane-1,3-dione and 2,2,6,6-tetramethylheptane-3,5dione were synthesized and their electroluminescent properties were investigated. Multilayered OLEDs employing the benzoylphenylpyridine derivatives as the dopant materials were found to have highly efficient EL performance. Also, this study suggests that the subtle structural modification of ligands of iridium complexes would lead the great improvement of the EL performances of OLED devices using them.

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