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Synthesis of Ir(III) Complexes Containing Meta-Carbonylated Phenylpyridine Ligand for Phosphorescent Organic Light-Emitting Diodes

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The photophysical characteristics of phosphorescent Ir(III) complexes 1–3 were investigated to determine their suitability as candidates for green light-emitting materials for OLEDs. To evaluate the EL properties of using these compounds as dopant in the emitting layer, multilayered devices were designed as green-light-emitting device having the following configuration: ITO/NPB (30 nm)/Ir(III) complexe 1 (5 and 10 wt.%) doped in CBP (30 nm)/BCP (10 nm)/Alq₃ (40 nm)/Liq/Al were fabricated. An OLED device employing 1 as a dopant exhibits the performance with a maximum luminance of 46000 cd/m² at 14.0 V. The luminous efficiency, power efficiency were 17.3 cd/A, 6.97 lm/W at 20 mA/cm², respectively. Also, this device shows green emission with CIE coordinates of (0.247, 0.594) at 10.0 V.

Keywords Ir(III) complexes; *Meta*-carbonylated phenylpyridine ligand; phosphorescent OLEDs

Introduction

Organic light emitting devices (OLEDs) is gaining large success in a new display technology. A lot of efforts have been devoted to developing new materials in order to improve the efficiency of OLEDs. Electrophosphorescent OLEDs (PHOLED), in particular, present remarkable performance due to their outstanding electroluminescent properties [1]. Cyclometalated iridium(III) complexes demonstrate high phosphorescent efficiencies and relatively short lifetimes among many different phosphorescent materials. Therefore, it is considered as one of the most promising phosphorescent dyes in OLEDs [2,3]. The Ir(ppy)₃ derivatives has many advangages including easy tuning emission evergy using functionalized ppy ligand which has electron donating and withdrawing moieties, and thus various red Ir(III) complexes have been developed as electrophosphorescent emitter [4–6]. Among those are Ir(III) complexes based on the carbonylated phenyl-pyridine ligands [7–10]. For instance, orange-red emitters based on carbonylated phenyl-pyridine derivative-Ir(III)

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complexes have been reported in our study [11,12]. Furthermore, our latest work reported that by adopting 5-benzoyl-2-phenylpyridine derived Ir(III) complex with *tert*-butyl moiety in benzoyl unit [13], a highly efficient red OLED was acquired.

In this paper, a series of green phosphorescent Ir(III) complexes **1–3** based on the *meta*-carbonylated phenyl groups on the ligands were designed and synthesized. Compared to Ir(III) complex **1** with the *meta*-benzoylated phenyl-pyridine ligand, Ir(III) complex **4** with the *para*-benzoylated phenyl-pyridine ligand was studied to explore the position-effect of benzoyl-substituents. As will be described herein, the electron-withdrawing *meta*-carbonyl groups in the ligands would greatly affect the photophysical properties of the iridium complexes using them as ligands, such as quantum yield, the absorption spectrum and the emission spectrum, as well as the electroluminescent properties.

Experimental

Materials and Measurement

2-(Tributylstannyl)pyridine, 3-acetylphenylboronic acid, 3-formylphenylboronic acid, 2bromopyridine, 3-bromobenzophenone, 4-bromobenzophenone, and acetylacetone were used as received from Aldrich or TCI. All reactions were performed under nitrogen. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. ¹H NMR spectra were recorded using a Varian (Unity Inova 300Nb) spectrometer at 300 MHz. Low- and high-resolution mass spectra were recorded using either a Jeol JMS-AX505WA spectrometer in FAB mode or a Jeol JMS-600 spectrometer in EI mode. The UV-Vis absorption measurements of these Ir(III) complexes in dichloromethane (10⁻⁵ M) were acquired with a Sinco S-3100 in a quartz cuvette (1.0 cm path). The photoluminescence spectra were measured on an Amincobrowman series 2 luminescence spectrometer. The phosphorescence quantum yields were determined in CH₂Cl₂ solutions at 293 K against $Ir(ppy)_3$ as a reference ($\Phi = 0.40$) [2]. The highest occupied molecular orbital (HOMO) energy levels were determined using a low energy photoelectron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. The lowest unoccupied molecular orbital (LUMO) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

General procedure for the Synthesis of Ir^{III} complexes 1. L1 (0.68 g, 2.2 mmol) was dissolved in 2-ethoxyethanol (9 mL) in a 30 mL round-bottom flask. IrCl₃·3H₂O (0.30 g, 1.0 mmol) and water (3 mL) were then added to the flask. The mixture was stirred under nitrogen at 120 °C for 24 h and cooled to room temperature. The precipitate formed in the mixture was collected and washed with methanol, hexane, and dried in vacuum to give the corresponding cyclometalated Ir^{III}-µ-chloro-bridge dimer. In a 20 mL flask, the dimmer complex, acetylacetone (1.5 mL, 1.5 mmol), and Na₂CO₃ (0.32 mg, 3.0 mmol) were mixed with 2-ethoxyethanol (10 mL), and the mixture was heated at 100 °C for 6 h. After cooling to room temperature, the precipitation solid was collected by filtration, and washed with ethanol and hexane. The residue was dissolved in dichloromethane, and the solid was filtered off. The solution was concentrated in vacuum and the residue was purified on a silica gel column using dichloromethane and hexane as eluent. The product was obtained after recrystallization from dichloromethane/ethanol. Similar procedures were

also employed for the synthesis of other Ir(III) complexes. The yields and spectral data of all Ir(III) complexes are as follows.

Complex 1 (23% Yield). ¹H NMR (500 MHz, CDCl₃): δ ppm 8.54 (dd, J = 1.0 Hz, 6.0 Hz, 2H), 8.15 (d, J = 1.0 Hz, 2H), 7.99 (d, J = 8.5 Hz, 2H), 7.83 (td, J = 1.5, 8.0 Hz, 2H), 7.75–7.73 (m, 4H), 7.54–7.51 (m, 2H), 7.45–7.42 (m, 4H), 7.28–7.25 (m, 2H), 7.13 (dd, J = 2.0 Hz, 8.0 Hz, 2H), 6.40 (d, J = 3.0 Hz, 2H), 5.29 (s, 1H), 1.84 (s, 6H); IR (KBr): n = 3060, 3008, 1645, 1576, 1516, 1478, 1396, 1321, 1259, 1222, 1058, 1029, 956, 784, 755, 712 cm⁻¹; FAB-MS (m/z): 808 [M⁺]; HRMS-FAB⁺ calcd for C₄₁H₃₁IrN₂O₄: 808.1913, found: 808.1906.

Complex 2 (% Yield). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.49 (d, J = 5.3 Hz, 2H), 8.19 (s, 2H), 8.04 (d, J = 8.2 Hz, 2H), 7.84 (t, J = 7.8 Hz, 2H), 7.28–7.23 (m, 4H), 6.36 (d, J = 8.2 Hz, 2H), 5.25 (s, 1H), 2.44 (s, 6H), 1.80 (s, 6H); HRMS-FAB⁺ calcd for $C_{31}H_{27}IrN_2O_4$:684.1600, found: 684.1598.

Complex 3 (37% Yield). ¹H NMR (300 MHz, CDCl₃): δ ppm 9.80 (s, 2H), 8.50 (dd, J = 0.9, 5.7 Hz, 2H), 8.06–8.04 (m, 4H), 7.89 (td, J = 1.6, 7.6 Hz, 2H), 7.30 (td, J = 1.4, 6.6 Hz, 2H), 7.12 (dd, J = 1.6, 7.8 Hz, 2H), 6.45 (d, J = 7.8 Hz, 2H), 5.27 (s, 1H), 1.81 (s, 6H); HRMS-FAB⁺ calcd for C₂₉H₂₃IrN₂O₄: 656.1287, found: 656.1281.

Complex 4 (54% Yield). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.51–8.49 (m, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.68 (dd, J = 1.5, 7.5 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.57–7.54 (m, 4H), 7.49–7.44 (m, 2H), 7.34–7.28 (m, 6H), 7.16–7.11 (m, 2H), 6.59 (d, J = 1.5 Hz, 2H), 5.25 (s, 1H), 1.80 (s, 6H). IR (KBr): 3059, 3014, 1649, 1575, 1516, 1473, 1432, 1396, 1309, 1274, 950, 755, 708 cm⁻¹. HRMS-FAB⁺ calcd for C₄₁H₃₁IrN₂O₄: 808.1913, found: 808.1918.

Synthesis of L1. 3-Bromobenzophenone (1.70 g, 6.52 mmol), Pd(PPh₃)₄ (0.31 g, 0.27 mmol), and LiCl (0.69 g, 16.3 mmol) were dissolved in anhydrous toluene (25 mL). After 5 min, tributyl(2-pyridyl)tin (2.00 g, 5.43 mmol) in toluene (2 mL) was added, and the resulting mixture was stirred at 120 °C for 18 h. After cooling to room temperature, the reaction mixture was then treated with 20 mL of saturated KF solution and allowed to stir for 30 min. The solution was poured into a separation funnel and toluene was added followed by washing with water. The organic phase was dried over MgSO₄. The solvent was removed and the residue was purified by column chromatography eluting with 5–20% ethyl acetate/hexane. The product was obtained as a white solid (1.20 g, 86%). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.71 (dt, J = 1.2, 3.3 Hz, 1H), 8.40 (t, J = 1.5 Hz, 1H), 8.27 (dt, J = 1.5, 6.3 Hz, 1H), 7.87–7.82 (m, 3H), 7.79–7.77 (m, 2H), 7.63–7.58 (m, 2H), 7.53–7.48 (m, 2H), 7.27–7.45 (m, 1H); EI-MS (m/z): 259 [M⁺]; HRMS-EI⁺ calcd for C₁₈H₁₃ON 259.0997: found, 259.0998.

Synthesis of L2 (30% Yield). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.72 (dt, J = 1.4, 5.0 Hz, 1H), 8.59 (s, 1H), 8.52 (t, J = 7.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.81–7.79 (m, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.31–7.28 (m, 1H), 2.69 (s, 3H).

Synthesis of L3. A mixture of 2-bromopyridine (0.81 g, 5.13 mmol), 3-formylphenylbronic acid (0.77 g, 5.13 mmol), tetrakis(triphenylphosphine)palladium (0.24g, 0.20 mmol), toluene (20 mL), ethanol (10 mL), and 2M Na₂CO₃ (10 mL) was refluxed at 120 °C for 5 h. After reaction mixture was cooled to room temperature, it was poured into water and extracted with ethyl acetate. The combined organic layer was dried with anhydrous MgSO₄ and evaporated to dryness. The crude product was further purified by silica gel column chromatography. The product was oil with an isolated yield of 47%. ¹H NMR (300 MHz, CDCl₃): δ ppm 10.13 (s, 1H), 8.74 (d, J = 4.8 Hz, 1H), 8.52 (s, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.95 (td, J = 1.4, 7.5 Hz, 1H), 7.83–7.81 (m, 2H), 7.66 (t, J = 7.8 Hz, 1H), 7.31 (q, J = 4.5 Hz, 1H),

Synthesis of L4 (85% Yield). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.75 (dt, J = 1.2, 3.3 Hz, 1H), 8.12 (d, J = 8.7 Hz, 2H), 7.92 (d, J = 8.7 Hz, 2H), 7.86–7.80 (m, 4H), 7.64–7.58 (m, 1H), 7.54–7.48 (m, 2H), 7.33–7.28 (m, 1H). HRMS-EI⁺ calcd for C₁₈H₁₃ON: 259.0997, found: 259.0997.

Fabrication of PLED

OLED fabrication of the indium-tin-oxide (ITO) thin films coated on glass substrates were used, which were 12 Ω /sq (emitting area was 3 × 3 mm²) of the sheet resistivity and a 1000 Å of thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: acetone, methyl alcohol, distilled water, followed by storage in isopropyl alcohol for 20 min and drying with a N₂ gas gun. The substrates were treated with O₂ plasma argon environment. Organic layers were deposited by thermal evaporation from resistively heated alumina crucibles onto the substrate at a rate of 1.0 Å/s. All organic materials and metal were deposited under high vacuum (5.0×10^{-7} Torr). The OLEDs were fabricated in the following sequence: ITO / bis[N-(1-(naphthyl)-N-phenyl-amino]biphenyl (NPB) (65 nm) / 4,4′,N,N'-dicarbazolebiphenyl (CBP): Ir(III) complex 1 (5 and 8) wt.% / bathocuproine (BCP) (10 nm)/ tris-(8-hydroxyquinoline) aluminum (Alq₃) (25 nm) / lithium quinolate (Liq) (2 nm)/Al. The current density (J), luminance (L), luminous efficiency (LE), and the CIE chromaticity coordinates of the OLEDs were measured with Keithly 2400, Chroma meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

Scheme 1 shows the targeted Ir(III) complexes with the carbonylated phenylpyridine ligands and their synthetic route, respectively. Ligand L1 and L4 were synthesized using the Stille cross-coupling between tributyl(2-pyridyl)tin and 3- and 4-bromobenzophenone. The L2 and L3 ligands were prepared by Suzuki-cross coupling of 2-bromopyridine with the corresponding aromatic boronic acid. All the heteroleptic complexes were synthesized in two steps from the cyclometalation of IrCl₃.nH₂O with the corresponding ligand to initially form the chloride-bridged dimmers, followed by a treatment with acetylacetone in the presence of Na₂CO₃ to obtain the desired complexes. After conventional purification steps, such as column chromatography and recrystallization, these synthesized Ir(III) complexes (1–4) were purified further by train sublimation under reduced pressure, below 10⁻³ torr, and fully characterized with ¹H NMR and low- and high-resolution mass spectrometry.

The UV-Vis absorption and photoluminescence (PL) spectra of Ir(III) complexes (1–4) were shown in Fig. 1 and their data summarized in Table 1. The strong absorptions in the UV region between 254 nm and 350 nm with distinct vibronic features can be assigned to spin-allowed $^1\pi$ - π^* transition from the cyclometalated ligand L1-L4, and the band around 400 nm to a spin-allowed metal charge transfer (1 MLCT) band. The 3 MLCT energy bands showed with a corresponding max value of 453, 449, 451, and 474 nm, respectively. Compared to ligand L1 with a peak maximum at 246 nm, the absorption peak of L4 (290 nm) was red-shifted due to extension of the π -conjugation length by *para*-benzoylated in the phenyl-pyridine ligand. In addition, compared to the absorption spectrum of ligand L1, the peak of $^1\pi$ - π^* transition from Ir(III) complex 1 was red-shifted approximately by 16 nm. In case of lignad L4, the peak of $^1\pi$ - π^* transition from Ir(III) complex 4 shows blue-shift of approximately by 5 nm. Ir(III) complexes 1–4 showed strong PL characteristics in CH₂Cl₂ at 502, 498, 499, and 596 nm, respectively. The PL spectra maximum (wavelength) of

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Scheme 1. Synthetic route to Ir(III) complexes 1–4.

complex 1 has longer than (those) of complexes 2 and 3, owing to increasing of the π -conjugation length by benzoylated in ppy ligand. Compared to complex (ppy)₃Ir, complexs 1–3 with a *meta*-carbonyl group in the phenyl unit was blue-shifted (ca. 16–20 nm) in the PL spectrum due to the stabilization of HOMO energy by *meta*-substituted carbonyl

Table 1. Photophysical properties of Ir (III) complexes

Complexes	Absorption(293K) $\lambda_{abs}^{[a]}$ [nm]	λ _{em} ^[a] [nm]	FWHM [nm]	HOMO/ LUMO [eV]	$E_{\rm g}^{ m [b]}$ [eV]	Q.Y [c]
1	262 (7.55), 340 (2.85), 378 (2.24), 453 (0.31)	502	50	-5.65/-2.92	2.73	0.66
2	262 (7.14), 295 (4.19), 328 (3.15), 369 (1.59), 449 (0.21)	498	50	-5.65/-2.95	2.70	0.56
3	262 (6.73), 296 (3.85), 333 (2.95), 372 (1.80), 451 (0.32)	499	48	-5.69/-2.99	2.70	0.66
4	254 (4.23), 285 (4.75), 474 (0.27)	596	84	-5.59/-3.23	2.36	0.06

^[a]Measured in CH₂Cl₂ at a concentration of 10^{-5} M and molar extinction coefficient (ε) values (10^4 M⁻¹ cm⁻¹) are shown in parentheses. ^[b]Band-gap energies estimated from the red edge of absorption spectra and emission spectra. ^[c]Degassed CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] ($\Phi_p = 0.40$), $\lambda_{ex} = 400$ nm.

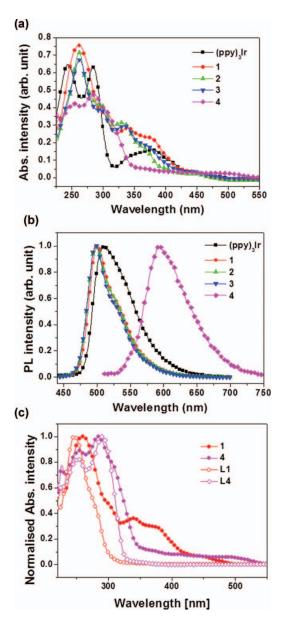


Figure 1. (a) The absorption and (b) emission spectra of complexes **1–4**. (c) Absorption spectra of L1, L4, and complexes **1** and **4**.

groups on phenyl unit in ppy ligand, which control the HOMO energy level of iridium complexes. On the other hand, complex 4 with a *para*-benzoyl group in the phenyl unit was red-shifted (*ca.* 78 nm) in the PL spectrum as compared with (ppy)₃Ir. In complex 4, the *para*-substituted benzoyl group less stabilizes the HOMO energy level than *meta*-substituted carbonyl groups on phenyl unit in ppy ligand due to the difference mesomeric and inductive ability of position effect with phenyl moiety in ppy ligand. This would contribute the red-shift of the PL spectrum of complex 4 as compared with (ppy)₃Ir. The emission quantum yields of Ir(III) complexes 1–3, measured in dichloromethane, were

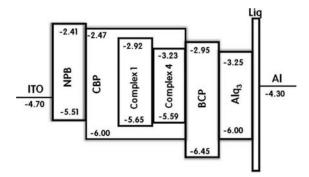


Figure 2. Energy diagram of devices A and B.

0.66, 0.56, and 0.66, respectively, by using Ir(ppy)₃ (0.40) used as the reference², and the corresponding value of complex **4** is only 0.06. Interestingly, Ir(III) complexes **1–3**, bearing on the *meta*-carbonylated in the phenyl unit, had quantum yields higher than that of Ir(ppy)₃, suggesting that these materials will have highly efficient electroluminescent properties in OLED devices.

The HOMO and LUMO energy levels of Ir(III) complexes **1–4** are shown in Table 1. The respective HOMO energy levels of Ir(III) complexes **1–4** were measured at -5.65, -5.65, -5.69, and -5.59 eV by a low-energy photoelectron spectrometer (Riken-Keiki AC-2). The optical energy band gaps (E_g) of Ir(III) complexes **1–4** were 2.73, 2.70, 2.70, 2.36 eV, respectively, as determined from the absorption spectra and emission spectra. Compared to complex **1–3** with a *meta*-carbonyl group in the phenyl unit, complex **4** was narrower energy band gap approximately by 0.36 eV. The LUMO energy levels calculated by subtraction of the optical energy band gap from the HOMO levels were -2.92, -2.95, -2.99, and -3.23 eV, respectively.

Complex 1 was selected for electroluminescent measurement because of suitable emission wavelength for green phosphorescent OLEDs. Multilayer devices were fabricated as follows: ITO/NPB (65 nm)/Ir(III) complex 1 (5 and 8) wt.% of dopant doped in CBP (30 nm)/BCP (10 nm)/Alq₃ (25 nm)/Liq (2 nm)/Al (100 nm). Also, as a control device, an OLED device using complex 4 was fabricated with the same device configuration. The energy diagram for devices is shown in Fig. 2. The electroluminescent properties of the devices of A1, A2 and B are summarized in Table 2. As shown in Fig. 3, the EL spectra

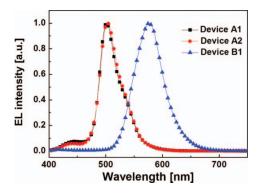


Figure 3. EL spectra of devices A and B.

 Table 2. EL properties of devices

				1			
Device	Dopant [%]	$V_{ m on}^{ m [a]} [{ m V}]$	$L^{ m [b]} [{ m cd/m}^2]$	$\mathrm{LE}^{[\mathrm{c}]/[\mathrm{d}]}\left[\mathrm{cd/A} ight]$	$ ext{PE}^{[c]/[d]}$ [lm/W]	$\mathrm{EL}^{[\mathrm{e}]}$ [nm]	$CIE^{[e]}(x,y)$
A1	1 (5%)	4.5	29170	99.8/69.8	4.40/3.40	503	0.243,0.577
A2	1 (8%)	5.5	46000	17.6/17.3	6.986.97	503	0.247,0.594
В	4 (8%)	4.0	22700	12.8/10.9	9.53/4.06	576	0.600,0.399

[a]Turn-on voltage at 1 cd/m². [b]At 14 V. [c]Maximum values. [d]At 20 mA/cm². [e]At 10 V.

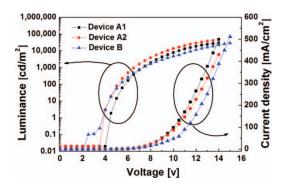


Figure 4. J-V-L curves of OLED the devices devices A and B.

of devices **A1** and **A2** using complex **1** depicted green emissions with the maximum peak at 503 nm and CIE coordinates were (0.243, 0.577) and (0.247, 0.594), respectively. On the other hand, for device **B** using complex **4**, the CIE coordinates is (0.600, 0.399) and the EL spectrum exhibited orange emission with the maximum peak at 596 nm. This trend of the CIE coordinates was well compatible with the PL spectra of iridium complexes

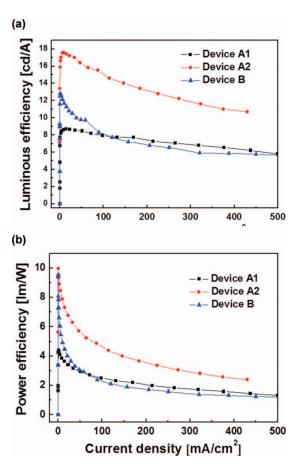


Figure 5. (a) Luminous efficiencies and (b) power efficiencies of OLED the devices devices A and B.

1 and 4. The current density-voltage-luminance (*J-V-L*) characteristics of devices A1, A2 and B are shown in Fig. 4. The maximum luminance of devices A1 and A2 were 29170 and 46000 cd/m² at 14.0 V, respectively. At this operating voltage, device A2 showed the highest luminance and displayed excellent EL performances with a maximum luminous efficiency (LE) and power efficiency (PE) of 17.9 cd/A and 9.98 lm/W (17.3 cd/A and 6.97 lm/W at 20mA/cm²), respectively (Fig. 5). The device B exhibited a maximum luminous efficiency and power efficiency of 12.8 cd/A and 9.53 lm/W (10.9 cd/A and 4.06 lm/W at 20mA/cm²), respectively. The Ir(III) complex 1–8 wt.% doped device had EL performances of two fold higher than that of (III) complex 1--5 wt.% doped device. The higher quantum yield of complex 1 than complex 4 would partially contribute the improved EL efficiencies of device A2 as compared with device B.

Conclusions

A series of the *meta*-carbonylated phenyl groups on the ligands of phosphorescent Ir(III) complexes were synthesized and their photophysical and electroluminescent properties were investigated. An OLED device employing **1** as a dopant exhibits the performance with a maximum luminance of 46000 cd/m² at 14.0 V. The luminous efficiency, power efficiency were 17.3 cd/A, 6.97 lm/W at 20 mA/cm², respectively. Also, this device shows green emission with CIE coordinates of (0.247, 0.594) at 10.0 V. This study clearly suggests that *meta*-carbonylated phenylpyridine derivatives have excellent properties suitable for green emitting materials for OLEDs.

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