Highly Soluble Green-Emitting Ir(III) Complexes with 9-(6-Phenyl-pyridin-3-ylmethyl)-9*H*-Carbazole Ligands and Their Application to Polymer Light-Emitting Diodes

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> **ABSTRACT:** Highly organic soluble Ir(III) complexes with 9-(6-phenyl-pyridin-3ylmethyl)-9*H*-carbazole were simply synthesized, and the solubility of the new complex was significantly improved when compared with the conventional green-emitting $Ir(ppy)_3$. Since a carbazole group is tethered through a nonconjugated methylene spacer, the photophysical properties of new complexes are almost identical with those of conventional $Ir(ppy)_3$. The pure complexes were utilized to prepare electrophosphorescent polymer light-emitting diodes (PLEDs). The device performances were observed to be relatively better or comparable with those of $Ir(ppy)_3$ based poly(Nvinylcarbazole) systems. The integration of rigid hole-transporting carbazole and phosphorescent complex provides a new route to design highly efficient solution-processable complex for electrophosphorescent PLED applications. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 7419–7428, 2008

> **Keywords:** absorption; crystal structures; electrophosphorescence; host-guest systems; iridium(III) complex; luminescence; miscibility; photoluminescence; solubility; triplet energy transfer

INTRODUCTION

Recently, semiconducting organic materials have attracted considerable interest as good candidate materials in electronics and optoelectronics.^{1–5} Among their many application fields, electroluminescence (EL) devices using small molar mass organic materials have become the most popular technology that have already been employed in practical applications such as flat-panel or flexible display devices. $^{6-15}$

Among the many different kinds of light-emitting organic materials available, phosphorescent materials are particularly promising, because both singlet and triplet excitons can generate unique light emission with a theoretical internal quantum efficiency of 100%.^{16–18} In particular, cyclometallated Ir(III) complexes show high phosphorescent efficiencies and are one of the most promising classes of phosphorescent dyes used in organic light-emitting diodes (OLEDs), because they exhibited relatively high phosphorescent efficiencies and are facile to modify the ligand structure for color tuning.^{19–21} These highly efficient

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phosphorescent OLEDs are often fabricated by sequential vapor deposition of several organic layers. However, the vacuum-deposition process and device fabrication are relatively complicated and costly. Along with advancement in processing solutions for the formulation of OLEDs, we have to investigate new highly soluble materials. The known Ir(III) complexes in general are excellent candidates for highly efficient EL devices; however, it is very difficult to process them into a homogeneous solution. Although a number of studies on electrophosphorescent polymer light-emitting diodes (PLEDs) in the green spectral region have been reported, the Ir(III) complex used in those studies exhibits an inherent poor solubility in organic solvent and poor miscibility in a polymer host.²² These demerits result in phase separation and poor EL device performance after longterm operation. An extensively used technique for enhancing the solubility of Ir(III) complexes is to attach long alkyl moieties mainly or to introduce them into dendrimers.²³ A dendritic architecture provides improvement of the solubility and siteisolation effect by employing a various peripheral groups around the emission center.²⁴ However, the chemical moieties placed at the periphery to improve the solubility imposes the dielectric properties so as to reduce the current density mostly.

In addition to the aforementioned methods, very promising Ir(III) complex containing the tetraphenylsilyl group has been reported to exhibit excellent luminous efficiency of around 32.8% using a conventional polymer-based [poly(*N*-vinyl carbazole), PVK] OLED. The design and synthesis of a highly phosphorescent triscyclometallated homoleptic Ir(III) complex [Ir(TPSppy)₃] (TPSppy, 2-(4'-(triphenylsilyl)biphenyl-3-yl)pyridine) with a silanebased dendritic substituent were demonstrated. It was also suggested that the aryl silane was quite effective to emit UV light for improving device efficiency compared with long alkyl substituent.²⁵

In this work, we report the very simple two-step synthesis for preparing a carbazolyl ligand in high yield (overall yield > 72–93%), and photophysical and EL properties of the new triscyclometallated homoleptic Ir(III) complexes, Ir(Czppy)₃ and Ir(BCzppy)₃, coordinated by 9-(6-phenyl-pyridin-3ylmethyl)-9*H*-carbazole. The complexes were designed to mix well with essential polymer host of polyvinylcarbazole for PLEDs. We could get a highly homogeneous photoluminescent (PL) and EL spectral behaviors of the sample bearing new Ir complex dye. The emission centers in Ir(Czppy)₃, **5a**, and Ir(BCzppy)₃, **5b**, was observed to be fairly isolated, and their properties were not affected by the presence of carbazolyl group. A significant improvement in the solubility of the iridium complex was observed only on introducing the carbazolyl moiety into the conventional ligand. Also, it can be expected that the carbazole moiety will help to improve the miscibility in the wide band-gap polymer host of PVK when elaborating PLED.

EXPERIMENTAL

Materials

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and ACROS Co. and used without further purification, unless otherwise stated. HPLC-grade dimethylformamide (DMF) and methylene chloride were purchased from Samchun chemical and distilled from CaH_2 immediately before use. All reactions were performed under an argon atmosphere, unless otherwise stated.

Synthesis

9-(6-Chloro-pyridin-3-ylmethyl)-9H-Carbazole (2a)

Sodium hydride (1.92 g, 0.044 mol) was suspended in dried DMF (50 mL) at 0 °C. Carbazole (6.86 g, 0.041 mol) in DMF (50 mL) was added dropwise into the mother solution and stirred for 0.5 h. Then, 2-chloro-5-chloromethyl-pyridine (6.48 g, 0.04 mol) in DMF (30 mL) was also added dropwise, and the reaction mixture was kept stirring at room temperature for 3 h. Finally, the reaction mixture was precipitated into 100 mL of water and neutralized with aqueous 2 M HCl. After filtration of the solution, the crude product purified by silica-gel column chromatography (EA: chloroform = 1:20) to give a white powder in 74% yield (8.63 g, 0.029 mol).

¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 5.47 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 153.931, 148.184, 140.275, 137.133, 131.922, 126.268, 124.599, 123.339, 120.750, 119.886, 108.633, 43.555. Anal. Calcd. for C₁₈H₁₃ClN₂: C, 73.85; H, 4.48; N, 9.57. Found: C, 73.23; H, 4.67; N, 9.46.

9-(6-Phenyl-pyridin-3-ylmethyl)-9H-Carbazole (3a)

A solution of **2a** (7.02 g, 24 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 0.84 g,

Journal of Polymer Science: Part A: Polymer Chemistry DOI 10.1002/pola 0.72 mmol), toluene (60 mL) was treated with a degassed solution of K_2CO_3 (6.8 g, 48 mmol) in H_2O (24 mL) followed by addition of the solution of phenylboronic acid (3.65 g, 30 mmol) in EtOH (16 mL). The mixture was stirred at 85 °C for overnight under Ar gas. After cooling, the reaction mixture was poured into 100 mL of water and extracted with toluene. The combined organic layers were washed with brine and dried over Na_2SO_4 . Removal of the solvent under reduced pressure gave a crude product, which was purified by silica column chromatography (EA:chloroform = 1:16) to give a white powder in 93% yield (7.45 g, 22 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.36– 9.45 (m, 5H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 2H), 5.49 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 157.009, 148.316, 140.524, 138.964, 135.178, 131.263, 129.202, 128.912, 126.935, 126.199, 123.343, 120.713, 120.626, 119.706, 108.860, 44.145. Anal. Calcd. for C₂₄H₁₈N₂: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.12; H, 5.55; N, 8.41.

Iridium(III) tris(9-(6-Phenyl-pyridin-3-ylmethyl)-9H-Carbazole) [Ir(Czppy)₃] (5a)

To a mixed solvent (2-ethoxyethanol:H₂O, 3:1, 60 mL) of **3a** (4.41 g, 13.2 mmol) was added IrCl₃·3H₂O (2.12 g, 6.0 mmol), and the reaction mixture was heated to 120 °C for 24 h. The resulting solution was concentrated at 55 °C, the crude solid was collected. It was washed with 100 mL of water, 50 mL of hexane, and 50 mL of ethyl ether. The crude product was purified by silica gel column chromatography (CH₂Cl₂) to give a yellow powder (**4a**) in 71% yield (3.87 g, 2.14 mmol).

To a 2-ethoxyethanol (15 mL) solution of 4a (2.42 g, 1.34 mmol) were added 3a (0.98 g, 2.95 mmol) and excess K₂CO₃, and the reaction mixture was heated to 120 °C for 12 h. After cooling to room temperature, a dark yellowish precipitate was filtered off and washed with 200 mL of methanol and 100 mL of ether. The crude product was purified by silica gel column chromatography (hexane: $CH_2Cl_2 = 1:4$) to give a yellow powder in 55% yield (1.78 g, 1.49 mmol). ¹H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 8.0 Hz, 6H), 7.34 (t, J = 8.0Hz, 6H), 7.30 (t, J = 8.0 Hz, 6H), 7.19–9.24 (m, 6H), 7.14 (d, J = 8.0 Hz, 3H), 6.84 (d, J = 8.0 Hz, 6H), 6.58-6.74 (m, 9H), 6.45 (s, 3H), 4.81-4.96 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 165.468, 160.946, 143.841, 142.867 140.194, 136.979,

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134.083, 129.857, 129.736, 126.166, 124.093, 123.090, 120.464, 119.670, 119.608, 118.271, 108.699, 43.874. FT-IR (ATR, cm⁻¹): 3043 (-C-H stretch), 1603 (C=C stretch), 1579 (C=C stretch), 1483 (C=C stretch), 1454 (C=C stretch). Exact mass (MALDI-TOF) for [MH]⁺ calcd for $C_{72}H_{51}$ IrN₆: 1192.3804, Found: 1192.4541. Anal. Calcd. for $C_{72}H_{51}$ IrN₆: C, 72.52; H, 4.31; N, 7.05. Found: C, 72.39; H, 4.31; N, 6.98.

9-(4-(6-Chloro-pyridin-3-ylmethoxy)-butyl)-9H-Carbazole (2b)

The compound, **2b** was prepared by following the similar procedure for **2a**. Instead of carbazole, 4-carbazol-9-yl-butan-1-ol was employed (yield 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 1H), 8.10 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 2H), 4.39 (s, 2H), 4.35 (t, 2H), 3.44 (t, 2H), 1.95–2.02 (m, 2H), 1.64–1.71 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 150.693, 148.789, 140.407, 138.213, 132.878, 125.726, 124.134, 122.896, 120.442, 118.923, 108.717, 70.418, 69.514, 42.801, 27.432, 25.858. Anal. Calcd. for C₂₂H₂₁ClN₂O: C, 72.42; H, 5.80; N, 7.68. Found: C, 72.36; H, 5.91; N, 7.54.

9-(4-(6-Phenyl-pyridin-3-ylmethoxy)-butyl)-9H-Carbazole (3b)

The compound, 3b was prepared by following the similar procedure for 3a. Instead of 2a, 9-(4-(6-chloro-pyridin-3-ylmethoxy)-butyl)-9H-carbazole, 2b, was employed (yield 72%). ¹H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.14 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.66-7.71 (m, 2H), 7.51 (t, 2HJ = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H), 4.48 (s, 2H), 4.35 (t, 2H), 3.48 (t, 2H), 1.98–2.05 (m, 2H), 1.67–1.74 (m, 2H). $^{13}\mathrm{C}$ NMR (125 MHz, CDCl₃) δ 157.013, 149.118, 140.476, 139.242, 136.426, 132.230, 129.077, 127.015, 125.752, 128.872, 122.947, 120.479, 120.395, 118.926, 118.926, 108.783, 70.385, 70.319, 42.900, 27.557, 26.004. Anal. Calcd. for C₂₈H₂₆ N₂O: C, 82.73; H, 6.45; N, 6.89. Found: C, 82.82; H, 6.60; N, 6.79

Iridium(III) tris(9-(4-(6-Phenyl-pyridin-3ylmethoxy)-butyl)-9H-Carbazole) [Ir(BCzppy)₃] (5b)

The compound, **5b**, was prepared by following the similar procedure for **5a**. Instead of **3a**, 9-(4-(6-

phenyl-pyridin-3-ylmethoxy)-butyl)-9H-carbazole, 3b, was employed (yield 45%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.0 Hz, 6H), 7.41 (t, J = 8.0 Hz, 6H), 7.27–7.33 (m, 12H), 7.22 (t, J = 8.0 Hz, 6H), 6.99 (d, J = 8.0 Hz, 3H), 6.61–6.78 (m, 12H), 4.14-4.28 (m, 6H), 3.94-4.07 (m, 6H), 3.00-3.09 (m, 6H), 1.66-1.76 (m, 6H), 1.37-1.44 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 165.985, 161.132, 145.943, 143.212140.506, 137.148, 135.364, 131.944, 129.765, 125.873,123.915, 122.998, 120.640, 119.867, 119.121,118.319, 108.838, 70.166, 69.994, 42.947, 27.542, 25.967.

FT-IR (ATR, cm⁻¹): 3043 (sp² C—H stretch), 2936 (sp³ C—H stretch), 2859 (sp³ C—H stretch), 1600 (aromatic C=C stretch), 1583 (aromatic C=C stretch), 1483 (aromatic C=C stretch), 1452 (aromatic C=C stretch), 1102 (C—O stretch). Exact mass (MALDI-TOF) for [MH]⁺ calcd for $C_{84}H_{75}IrN_6O_3$: 1408.7497, Found: 1408.6020. Anal. Calcd. for $C_{84}H_{75}IrN_6O_3$: C, 71.62; H, 5.37; N, 5.97. Found: C, 71.74; H, 5.36; N, 5.77.

Characterization

¹H NMR spectra were recorded on a Varian Mercury NMR 400 Hz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. ¹³C NMR spectra were recorded using a Varian Inova-500 spectrometer. IR spectra were recorded on a JASCO FT-IR 4100 spectrometer with ATR mode. Elemental analysis was performed by using an EA1112 (Thermo Electron Corp.) elemental analyzer. MALDI-TOF analysis was performed on a Voyager-DE STR MADI-TOF (matrix; DHB) mass spectrometer. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument and Mettler TGA 50.

Crystallography

X-ray data for **5** were collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å). Preliminary orientation matrix and cell parameters were determined from three sets of ω/ϕ scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic ther-

Table 1. Crystal Data and Structure Refinement for $Ir(Czppy)_3$

Empirical formula	$C_{72}H_{51}IrN_6$		
Formula weight	1192.39		
Temperature	293 K		
Crystal system, space group	Monoclinic, $P2_1/c$		
Unit cell dimensions			
a	15.6688(2) Å		
Ь	13.7647(2) Å		
с	25.6392(3) Å		
β	$98.6930(10)^{\circ}$		
Volume	$5466.25(12)~{ m \AA}^3$		
Z, Calculated density	4, 1.449 mg/m 3		
Absorption coefficient	$2.494~\mathrm{mm}^{-1}$		
<i>F</i> (000)	2408		
Theta range for data collection	$1.6128.28^{\circ}$		
Reflections collected/unique	55,484/13,532		
	[R(int) = 0.0701]		
Completeness to theta $= 28.28$	99.6%		
Data/restraints/parameters	13,532/0/712		
Goodness-of-fit on F^2	0.972		
Final <i>R</i> indices $[I > 2 \text{sigma}(I)]$	$R_1 = 0.0407,$		
_	${ m w}R_2 = 0.0644$		
R indices (all data)	$R_1 = 0.0912,$		
	$wR_2 = 0.0773$		
	-		

mal parameters for nonhydrogen atoms with the SHELXTL program. All hydrogen atoms were calculated at idealized positions and refined with the riding models. Crystallographic data and the details of data collection are listed in Table 1.

Absorption and PL Spectroscopy

Absorption spectra of chloroform solutions were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm. PL spectra were recorded with a Hita-chi's F-7000 FL Spectrophotometer.

EL Measurement

The multilayer diodes have a structure of indium tin oxide (ITO)/poly(ethylene dioxythiophene) (PEDOT):poly(styrene sulfonate) (PSS) (40 nm)/ PVK with Ir(III) complex (40 nm)/BCP (10 nm)/ Alq₃ (40 nm)/LiF(1 nm)/Al (100 nm), respectively. The conducting PEDOT:PSS layer was spincoated onto the ITO-coated glasses in an argon atmosphere. The emitting PVK/Ir-complex layer then was spin-coated onto the thoroughly dried PEDOT layer using the solution (conc: 1.5 wt %) in monochlorobenzene.

For multilayer devices, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and tris(8-

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hydroxyquinoline) aluminum (Alq₃) layer were vacuum-deposited onto the emitting polymer layer. Finally, LiF (1 nm)/Al (100 nm) electrodes were deposited onto the Alq₃ layer. Current–density–voltage characteristics were measured with a Keithley 2400 source meter. The brightness and EL spectra of the devices were measured with Spectra Colorimeter PR-650.

Measurement of resultant EL device property and device fabrication were performed in Center for Organic Light Emitting Diode located in Seoul National University, Korea.

RESULTS AND DISCUSSION

Synthesis and Characterization

The simple synthetic rout to the Ir(III) complex containing carbazolyl substituent is depicted in Scheme 1. 2-Chloro-5-chloromethyl-pyridine, 1, was first reacted with carbazole and the new carbazole substituted ligand, **3a**, was synthesized using 9-(6-chloro-pyridin-3-ylmethyl)-9*H*-carbazole, **2a**, via the Suzuki coupling reaction in moderately good yield (>90%). Following Nonoyama reaction, IrCl₃ 3H₂O was treated with an excess of carbazolyl phenylpyridyl ligands in a mixed solvent of 2-ethoxyethanol and water (3:1 v/v) to form an iridium dimer having chloride bridges. Then, the chloride-bridged dimer, **4a**, was converted to **5a** in a weak basic condition.

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The synthetic procedure for $Ir(BCzppy)_3$, **5b**, is almost similar except for inserting the longer butylene spacer between a phenylpyridyl ligand and a carbazole unit.

Every phenyl pyridine ligand came to acquire one carbazole substitutent. The reaction yields of $Ir(Czppy)_3$ and $Ir(BCzppy)_3$ are moderately high around 43–55%. To ensure solubility, the carbazole group was attached to the main ligand through an alkylene spacer. All the intermediates and resultant compound were well characterized by ¹H and ¹³C NMR, elemental analysis, and MALDI-TOF spectroscopy.

With the newly synthesized phosphorescent iridium(III) complexes, we investigated the thermal properties by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. No discernible melting behavior up to 300 °C was observed in the DSC thermograms of the complexes. In each TGA thermogram of the complex, no significant weight loss was observed up to 400–410 °C, which is the onset temperature of the primary decomposition. It is evident that attachment of carbazole substituent to the iridium complex did not have a detrimental effect on the thermal stability of the iridium(III) complex.

We examined the solubility difference between conventional Ir(ppy)₃ and new Ir(III) complexes. Monochlorobenzene (4.5 mg) was selected and 10.0 mg of Ir(Czppy)₃ and Ir(BCzppy)₃ was dissolved in 1 g of monochlorobenzene at room temperature, respectively, while only 1 mg of $Ir(ppy)_3$ was barely soluble in hot monochlorobenzene (1 g) under sonication for 1 h. A considerable improvement in solubility could be achieved for our new Ir(III) complexes. As another example, $Ir(ppy)_3$ and new Ir(Czppy)₃ showed a maximum doping concentration of 25 wt % and 30 wt % in the PVK host, respectively. It can be explained that the common carbazolyl group in the guest and host material could improve the miscibility in the mixture.

Structure of Ir(Czppy)₃

A very interesting aspect of the newly synthesized Ir(III) complex, **5a** is the determination of its crystal structure. It is quite unusual for such a large $Ir(Czppy)_3$ to be grown as a single crystal in the solution system. $Ir(BCzppy)_3$ was not successful to grow the crystal for the structural investigation, which might be due to the presence of longer butylene spacer.



Figure 1. ORTEP diagram of $Ir(Czppy)_3$. The thermal ellipsoid for the image represents a 50% probability limit.

The molecular structure of Ir(Czppy)₃ was eventually determined by X-ray crystallography and is shown in Figure 1.²⁶ The Ir(III) center surrounded by the three cyclometallating ligands adopts a distorted octahedron configuration. The three C atoms of the three ligating groups are positioned in a facial configuration. The principal axis of the molecule lies on the pseudo C3 symmetry. The central structural parameters are categorized into two groups; the Ir-C bond lengthsranging from 2.008 to 2.024 Å—are shorter than the Ir-N bond distances spanning from 2.122 to 2.138 Å. These values are more spread out than those observed in phenylpyrazolyl-based Ir(III) triscyclometallates. 27 The bond distance of Ir—N3 (2.138(3) Å) in $Ir(Czppy)_3$ is longer than the other Ir–N lengths (Ir–N5 = 2.122(3) Å and Ir-N1 = 2.130(3) Å). The legitimate explanation is that the trans effect of the phenyl group (Ir-C49 = 2.008(4) Å) is stronger than those of the other phenyl groups (Ir-C25 = 2. 022(4) Å and Ir-C1 = 2.024(4) Å). This can be compared with fac-Ir(tpy)₃ [tpy = 2-(*p*-tolyl)pyridyl], where the corresponding Ir-N (2.132(5) Å) and Ir-C (2.024(6) A) bond lengths are identical because of the presence of the same degree of trans influence. Normally, no appreciable trans effect is observed in the facial complexes, because the atomic types in trans positions are identical in the facial environments, which leads to thermodynamically stable complexes with respect to meridional isomers.²⁷ Thus, the relatively significant difference in the related bond lengths of $Ir(Czppy)_3$ may be associated with the steric consequence originating from the bulky chelating

ligand, Czppy. The extended view of $Ir(Czppy)_3$ illustrates that both Δ and Λ isomers coexist, generating diastereoisomers in the crystal packing (see Fig. 2). Each molecule is well isolated as no discernable intermolecular contacts are present.

Photophysical Properties of Ir(ppy)₃ and Its Analogues

The absorption and PL spectra of the solution samples of $Ir(Czppy)_3$, $Ir(BCzppy)_3$, and $Ir(ppy)_3$ are shown in Figure 3. The spectral shapes were similar to that observed for $Ir(ppy)_3$, except that the spectra of Ir(Czppy)₃ and Ir(BCzppy)₃ exhibits an absorption band at 343-347 nm. The absorption bands of the spectra of two carbazolyl Ir(III) complexes below 320 nm are ascribed to the intraligand π - π ^{*} transitions originating from the Ircomplex, while the absorption at around 343 nm is due to the carbazole moieties. In a lower energy region spanning from 380 to 500 nm, we could observe weak and broad absorption band with shoulders, which can be attributed to spin-allowed and spin-forbidden metal-to-ligand charge transfer (MLCT) transitions of the Ir(III) complexes. The same feature of MLCT transition observed in two absorption spectra indicates that there was no interaction between Ir-complex and pendent carbazole. There is no additional transition at lower energy (>500 nm), which can be attributed



Figure 2. Crystal packing diagram of $Ir(Czppy)_3$.

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Figure 3. UV-vis absorption and PL spectra (conc: 1×10^{-5} M in CHCl₃) of Ir(ppy)₃, Ir(Czppy)₃, and Ir(BCzppy)₃ in the solution state. Sample: (a) Ir(ppy)₃, (b) Ir(Czppy)₃, and (c) Ir(BCzppy)₃. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to the nonconjugated tethering of phenylpyridine and carbazol group in the ligand.

The PL spectra of the Ir(III) complexes in CHCl₃ solutions are shown in Figure 3 (as a dotted line). The emission maxima of $Ir(Czppy)_3$ and Ir(BCzppy)3 was observed at 520 nm in the solution state when compared with 510 nm for $Ir(ppy)_3$. The peak emission wavelengths of $Ir(Czppy)_3$ and $Ir(BCzppy)_3$ are bathochromically shifted relative to that of $Ir(ppy)_3$ by about 10 nm. This small red shift is only due to carbazolyl substituent bound through an alkylene nonconjugated spacer. It can be considered that the identical excited and ground states were involved in the phosphorescent transition of Ir(ppy)₃, Ir(Czppy)₃, and Ir(BCzppy)₃. Tethering the carbazole substituent to Ir(III) complex unit via nonconjugated alkylene spacer does not affect the optical properties significantly.

Electrophosphorescent Properties

We fabricated PLEDs by employing $Ir(ppy)_3$, $Ir(Czppy)_3$, and $Ir(BCzppy)_3$ as green phosphorescent emitters; ITO/PEDOT:PSS (40 nm)/PVK with Ir(III) complex (40 nm)/BCP(10 nm)/Alq₃ (40 nm)/LiF(1 nm)/Al (100 nm).

PVK ($M_{\rm w} \sim 90,000$, ACROS Co.) was selected as the polymer host because of its high hole-transporting mobility, high glass transition temperature, and good film-forming property. It is quite effective since its highest occupied molecular orbital and triplet state energy levels almost coincide with those of Ir(ppy)₃, Ir(Czppy)₃, and $Ir(BCzppy)_3$.²⁸ Since $Ir(Czppy)_3$ has a higher molecular weight than $Ir(ppy)_3$, we mixed 6 wt % (device A), 12 wt % (device B), and 14 wt % (device C) of Ir(ppy)₃ Ir(Czppy)₃, and Ir(BCzppy)₃, respectively, into PVK adjusting the same equivalent of pure Ir(III) core. High-quality spin-coated Ir(Czppy)₃/PVK, Ir(BCzppy)₃/PVK, and Ir(ppy)₃/ PVK films were easily realized during device fabrication, which is consistent with the excellent compatibility of Ir(Czppy)₃, and Ir(BCzppy)₃ with PVK established earlier. A thin film of PEDOT:PSS was spin-coated on ITO as the anode for facilitating hole injection, and the PVK mixture was coated on it as an emissive layer. Subsequently, a thin film of BCP with a thickness of 10 nm was vapor deposited on the doped PVK layer as a hole-blocking material to confine exciton recombination and limit the loss of the faster moving holes to the cathode. This was followed by the sequential deposition of a 40-nm electron injection layer of tris(8-hydroxylquinoline) aluminum (Alq₃) and a LiF(1 nm)/Al electrode sequentially. The performance data of the devices are summarized in Table 2.

We could observe maximum electrophosphorescent intensities at ${\sim}516,\ 532,\ {\rm and}\ 532\ {\rm nm}$ in

Device	Turn on (V)	Maximum Luminance (cd/m ²) (Corresponding J)	Maximum Power Efficiency (lm/W) (Corresponding J)	Maximum Luminous Efficiency (cd/A) (Corresponding J)	$\begin{array}{c} {\rm Maximum} \\ {\rm External \ Quantum} \\ {\rm Efficiency \ }(\eta_{\rm ext}) \\ ({\rm Corresponding \ }J) \end{array}$
A B C	$6.0 \\ 5.5 \\ 5.5$	7988 (136.1) at 14.5 V 9332 (226.4) at 17 V 6786 (188.6) at 17 V	11.67 (0.069) at 6.5 V 15.5 (0.014) at 5.5 V 14.2 (0.038) at 6 V	24.1 (0.069) at 6.5 V 27.6 (0.045) at 6 V 27.0 (0.038) at 6 V	7.24 (0.069) at 6.5 V 7.79 (0.045) at 6 V 7.69 (0.038) at 6 V

Table 2. Measured Parameters of Electrophosphorescent Devices

Device A (6 wt % Ir(ppy)₃); device B (12 wt % Ir(Czppy)₃; device C (14 wt % Ir (BCzppy)₃). Current density, J (mA/cm²).

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Figure 4. Dependence of current density and luminance on the applied voltage. Sample: $Ir(ppy)_3$ (circle), $Ir(Czppy)_3$ (triangle), and $Ir(BCzppy)_3$ (square). Filled symbol: luminance, open symbol: current density. Inset: EL spectra of three devices at 500 cd/m² (5 mA/cm²). (a) Device A, (b) device B, (c) device C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

devices A, B, and C, respectively, yielding CIE coordinates of (0.33, 0.60), (0.38, 0.58), and (0.41, 0.55) at 500 cd/m².

The current–voltage–luminance curves of the two samples are shown in Figure 4. The turn-on voltage (electric field) of the two PLEDs were in the range of 5.5–6.0V. The maximum brightness of the LEDs was around 7988 cd/m² (at 136.1 mA/cm²) for device A, 9332 cd/m² (at 226.4 mA/cm²) for device B, and around 6786 cd/m² (at 188.6 mA/cm²) for device C. The figure in the inset shows

the EL emission spectra of three devices. They are quite similar to the PL spectra, suggesting that the same excited state species is responsible for both the PL and EL emissions.

Figure 5 displays the dependence of the luminous efficiency and external quantum efficiency (EQE) on the current density for three electrophosphorescence devices. The maximum luminous efficiencies of devices A, B, and C were determined as 24.1 cd/A (at 0.069 mA/cm², $\eta_{EQE} = 7.24\%$), 27.6 cd/A (at 0.045 mA/cm², $\eta_{EQE} = 7.79\%$), and 27.0 cd/A (at 0.038 mA/cm², $\eta_{EQE} = 7.69\%$), respectively.

In addition, the maximum power efficiency of the $Ir(Czppy)_3$ and $Ir(BCzppy)_3$ devices were 15.5 and 14.2 lm/W, whereas that of the $Ir(ppy)_3$ device was 11.67 lm/W. It should be noted that the device B, which was made of $Ir(Czppy)_3$ clearly showed a promising characteristics due to its superior solubility in an organic solvent considering the moderately high luminous efficiency and EQE. A highly pure $Ir(Czppy)_3$ obtained by crystallization has a large potential for application in highly efficient EL devices.

It is notable that the luminous efficiency (27.6 cd/A) and brightness (9332 cd/m²) of the Ir $(Czppy)_3$ device are a little higher than those of devices using conventional Ir(ppy)₃. Our material has a dramatically increased solubility over Ir(ppy)₃, thus it possesses a great processibility. Also, the very high-yielding synthesis of the title compound does not require complicated synthetic steps. Furthermore, Ir(Czppy)₃ was also crystallized into a pure compound for us to neglect the levels of unwanted impurities in the emitting



Figure 5. (A) Dependence of current density and luminous efficiency. (B) Dependence of current density and external quantum efficiency. Sample: (a) device A, (b) device B, (c) device C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

layer. The modification of the structures of the iridium complexes and the optimization of their devices are in progress.

CONCLUSIONS

We have demonstrated a facile and simple method to synthesize a new green-emitting Ir(III) complexes with excellent solubility and EL efficiency. The structures do not contain an insulating unit in itself, except an alkylene spacer. In addition, it was found that 2-chloro-5-chloromethyl-pyridine is a promising starting compound to tether various kinds of functional moieties without changing the conjugation of an original ligand. $Ir(Czppy)_3$ and Ir(BCzppy)₃ exhibited good miscibility without exhibiting any phase separation or crystallization upto 25-30 wt % of PVK. Although we did not use the additional electron transporting molecules such as 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole or 1,3-bis(5-(4-tert-butylphenyl))-1,3,4-oxadiazole, the EL device performances are observed to be quite promising. The sample made of a PVK doped with $Ir(Czppy)_3$ exhibited green electrophosphorescence with a maximum EQE of 7.79%, which is higher than that achieved in $Ir(ppy)_3$ based device with an identical device configuration.

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= 13.7647(2), c = 25.6392(3) Å, $\beta = 98.6930(10)^{\circ}$, V = 5466.25(12) Å³, Z = 4, $D_{calc} = 1.449$ g/cm³, 55,484 reflections collected, 13,532 unique ($R_{int} = 0.0701$), $R_1 = 0.0407$, w $R_2 = 0.0644$, Final Rindices [I > 2sigma(I)]. CCDC 670616.

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