

Synthesis and Electroluminescence Properties of *fac*-Tris(2-phenylpyridine)-iridium Derivatives Containing Hole-Trapping Moieties

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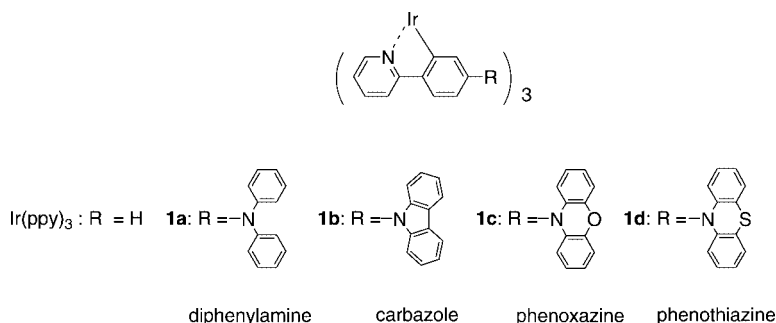
In order to investigate an effective method for carrier injection into the phosphor of organic electroluminescent (EL) devices, we synthesized *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)₃] derivatives containing hole-trapping moieties, such as diphenylamine, carbazole, and phenoxazine. Their photoluminescent maxima were observed around the maximum of Ir(ppy)₃. These values were slightly shifted depending on the hole-trapping moieties: redshifted due to diphenylamine and blueshifted due to carbazole and phenoxazine. Further, these moieties affected the oxidation potentials of Ir complexes in

cyclic voltammetry. EL devices using an Ir complex with diphenylamine exhibited high EL performance because 1,1-bis[4-(di-*p*-tolylamino)phenyl]cyclohexane (TAPC) was employed as a hole-transporting layer. The maximum external quantum efficiency (η_{ext}) was recorded as 12.2 %. This value is comparable to that observed in a device using Ir(ppy)₃. These results indicate that the diphenylamino substituent is favorable to serve as a hole-trapping moiety of Ir(ppy)₃. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Currently, organic electroluminescent (EL) devices are an active area of research because of their potential applications in flat-panel displays.^[1] The research to synthesize phosphorescent materials with heavy metals such as platinum and iridium has attracted considerable attention^[2,3] because an internal quantum efficiency of 100% can be achieved by the energy transfer from both the singlet and

triplet states to the phosphor triplet state at the emitting layer.^[4,5] *fac*-Tris(2-phenylpyridine)iridium [Ir(ppy)₃] is a well-known green emitter.^[3,6] A phosphorescent EL device using Ir(ppy)₃ demonstrated a high performance with a maximum external quantum efficiency of 19.2%.^[3c] This value was comparable to the theoretical limit of around 20% obtained from simple classical optics.^[7] However, further investigation of phosphorescent materials is still required for the research and development of phosphorescent



Scheme 1. Structures of Ir complexes 1.

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EL devices. Also, synthetic studies on various materials such as Ir,^[8,9] Pt,^[10] and other metal^[11] complexes have been conducted. These substances are used as dopants at the emitting layer. For example, the addition of an amount of ca. 6 wt.-% of Ir(ppy)₃ to the host material afforded the highest external quantum efficiency.^[3a,3b] Therefore, the combination of phosphorescent and host materials is crucial for effective injection of holes and electrons into the

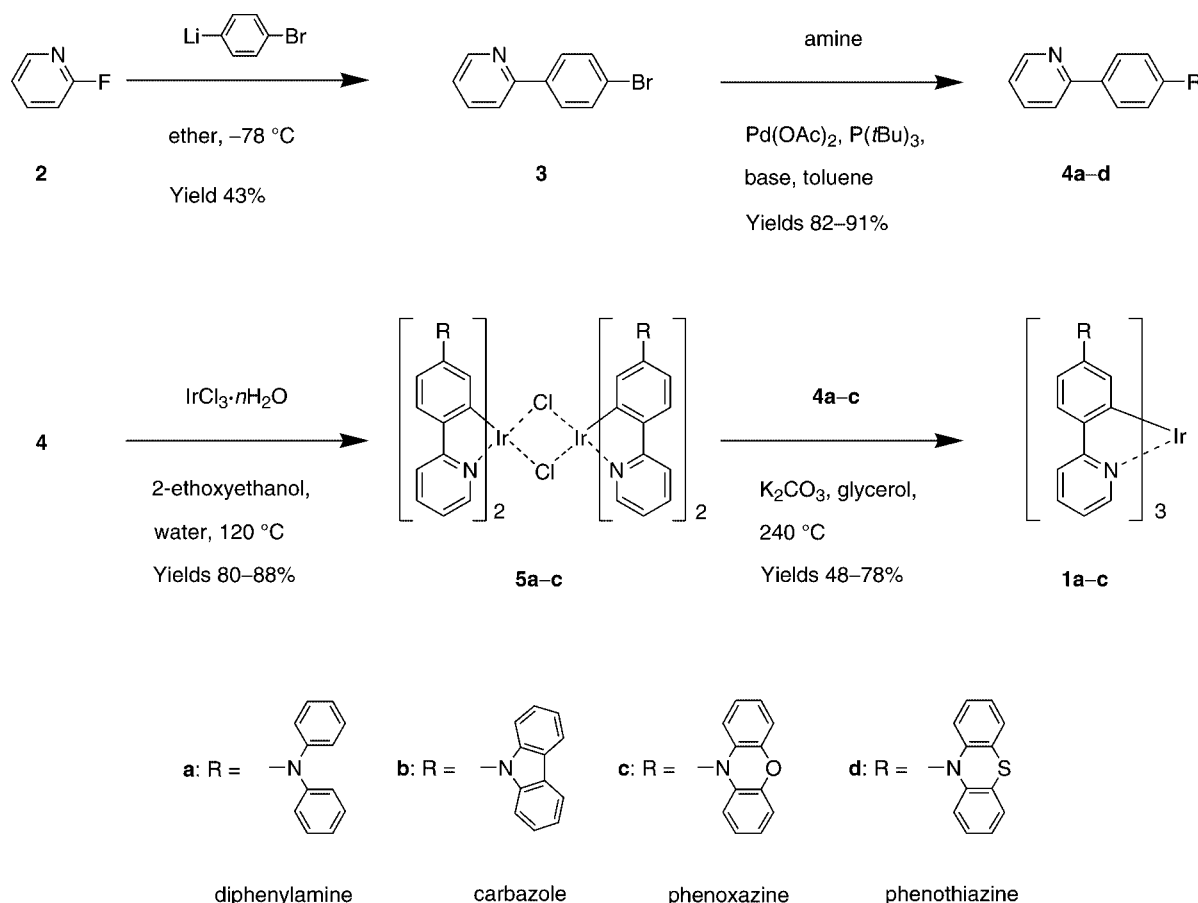
phosphor. 4,4'-Bis(carbazol-9-yl)-1,1'-biphenyl (CBP), which is an aromatic amine, is generally employed as the host material.^[2b] Thus, we synthesized Ir(ppy)₃ derivatives as new types of phosphorescent materials, which are composed of aromatic amines such as diphenylamine, carbazole, phenoxazine, and phenothiazine^[12] (see Scheme 1); these amine units act as effective hole-trapping moieties.^[13] As a compound related to **1a**, its acetylacetonate (acac) complex [Ir(ppy-NPh₂)₂(acac)] has been recently synthesized.^[14] It was reported that the phosphorescent EL performance of this complex was better than that of Ir(ppy)₂(acac). In this paper, we report the synthesis and properties of Ir complexes **1** and their applications in the study of phosphorescent EL devices.

Results and Discussion

Preparation and Properties of Ir Complexes Containing Hole-Trapping Moieties

The synthesis of the Ir complexes **1** is illustrated in Scheme 2. 2-(4-Bromophenyl)pyridine (**3**) was synthesized with a yield of 43% by the reaction of 2-fluoropyridine (**2**) with 4-bromophenyllithium;^[15] this was utilized as the key compound in the following amination reaction. The ligands

4a–d were prepared with yields of 82–91% by the Pd-catalyzed cross-coupling reaction of **3** with aromatic amines such as diphenylamine, carbazole, phenoxazine, and phenothiazine.^[16] This reaction required a selective use of an additive base. Sodium *tert*-butoxide was selected for the reaction of diphenylamine, and potassium carbonate was employed for those of rigid amines, namely, carbazole, phenoxazine, and phenothiazine. The ligands **4a–c** produced the cyclometalated Ir^{III} μ -chloro-bridged dimers **5a–c** with yields of 80–88% by treatment with IrCl₃·*n*H₂O in 2-ethoxyethanol and water at 120 °C.^[6a] However, the Ir dimer **5d** was not obtained. The Ir complexes **1a–c** were prepared with yields of 48–78% by stirring **4** and **5** in glycerol with K₂CO₃ at 240 °C.^[17] These Ir complexes were obtained in the form of orange solids for **1a** and yellow solids for **1b** and **1c**. Their melting points were above 300 °C. Structural determination was performed by using ¹H NMR, MALDI-TOF mass spectrometry, and elemental analysis. The stereochemistry of these complexes was determined to be that of facial isomers because the NMR chemical shifts observed in the three ligands were equivalent. In order to investigate the molecular structures of the Ir complexes, an X-ray crystallographic analysis of **1a** was performed. Two crystallographically independent molecules existed in this crystal. The structure of one of these molecules is shown in Figure 1. Three sets of linear C–Ir–N bonds are observed, indi-



Scheme 2. Synthesis of ligands **4** and Ir complexes **1**.

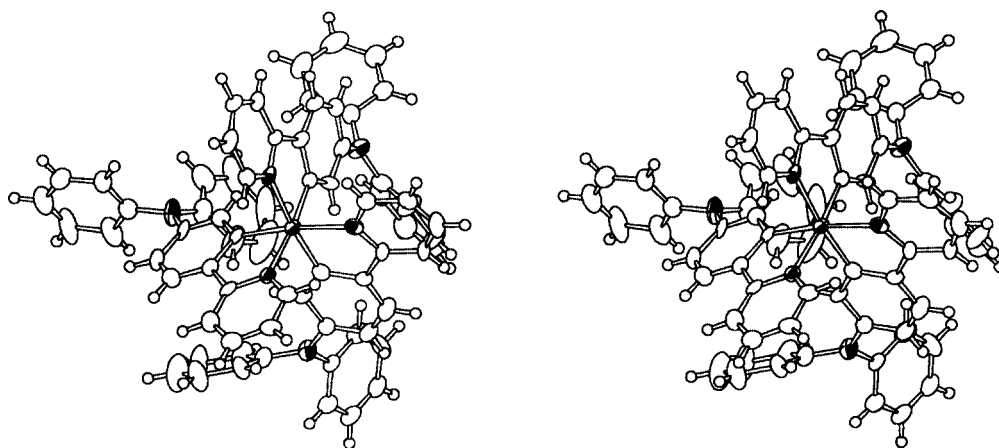


Figure 1. Molecular structure of Ir complex **1a** (stereo view). Ir and N atoms are depicted as shaded octants.

cating that complex **1a** is a facial isomer. Three diphenylamine moieties, resembling antennas, exist on the side of the Ir(ppy)₃ core.

The ligands **4** exhibited photoluminescence (PL) maxima between 400 and 540 nm in dichloromethane. The emission and absorption maxima are listed in Table 1. The Stokes shifts (Δ) for **4c–d** are greater than those for **4a–b**, indicating that the insertion of chalcogens such as O and S atoms into the carbazole moieties results in large Stokes shifts. The PL spectra of Ir complexes **1** are shown in Figure 2, and their emission and absorption maxima are listed in Table 2. The absorption maxima of the Ir complexes are redshifted as compared to those of the ligands. These maxima can be attributed to the metal–ligand charge-transfer (MLCT) excitation. The PL maxima of **1** are almost similar to that of Ir(ppy)₃, indicating the Ir(ppy)₃ cores as the source of the emission. The emission maxima marginally shifted depending on the molecular structure of the hole-trapping moiety. The maximum of **1a**, possessing a flexible amine, is redshifted from that of Ir(ppy)₃, and the maxima of **1b** and **1c**, possessing rigid amines, are blueshifted. The redshift is attributed to the resonance effect of the diphenylamino substituent, which reduced the energy gap between HOMO and LUMO. On the other hand, the π -conjugation on the rigid frameworks of carbazole and phenoxazine prevents the electron donation to the phenylpyridine (ppy) chelates. Furthermore, the emission maxima of the Ir complexes **1a** and **1b** are redshifted by ca. 100 nm from those of the ligands **4a** and **4b**, and the maximum of **1c** is similar to that of **4c** because of the large Stokes shift in the ligand. In addition, the emission maximum of **1a** is comparable to that of Ir(ppy-NPh₂)₂(acac) ($\lambda_{\text{em}} = 530$ nm).^[14] The PL quantum yields of **1a–c** were measured in dichloromethane using Ir(ppy)₃ as the standard ($\Phi_{\text{PL}} = 0.40$),^[6b] and these values are listed in Table 2. The quantum yield of **1b** is greater than those of **1a** and **1c**.

In order to investigate the redox properties of the Ir complexes **1**, cyclic voltammetry (CV) was performed in dimethylformamide (DMF) with 0.1 M *n*Bu₄NClO₄ as the supporting electrolyte. The voltammograms of **1** indicated reversible redox waves. The half-wave oxidation potentials of **1a–**

Table 1. PL and absorption maxima of ligands **4**.^[a]

Ligand	λ_{em} [nm]	λ_{abs} [nm]	Δ [nm]
4a	435	346	89
4b	406	318	88
4c	520	326	194
4d	535	320	215

[a] In CH₂Cl₂.

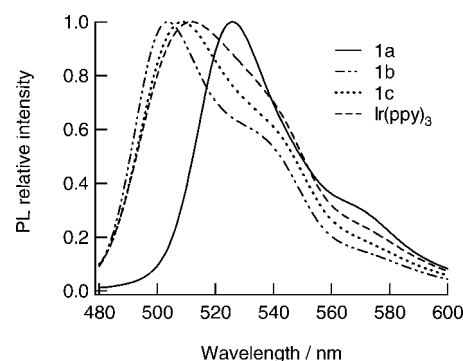


Figure 2. PL spectra of Ir complexes **1** in dichloromethane.

Table 2. PL and absorption maxima and quantum yields of Ir complexes **1**.^[a]

Complex	λ_{em} [nm]	λ_{abs} [nm]	Φ_{PL} ^[b]
1a	526	398	0.14
1b	504	378 sh	0.38
1c	509	375 sh	0.17
Ir(ppy) ₃	512	377	0.40

[a] In CH₂Cl₂. [b] Measured relative to Ir(ppy)₃, $\lambda_{\text{ex}} = 380$ nm.

c were recorded as +0.19, +0.48, and +0.23 V vs. Fc/Fc⁺, respectively.^[18] The values of **1a** and **1c** were lower than that of Ir(ppy)₃ (+0.32 V), indicating higher electron-donating abilities of **1a** and **1c**. On the other hand, the electron-donating ability of **1b** was lower than that of Ir(ppy)₃ owing to the introduction of a carbazole moiety. These results were attributed to the redox behavior of the ligands **4a–c**. The half-wave oxidation potentials of **4a** and **4c** (quasi-reversible and reversible waves) were measured to be +0.54 and

+0.30 V, respectively. The peak oxidation potential of **4b** (irreversible wave) was observed as +0.91 V. In addition, the half-wave reduction potentials of ligands **4a–c** were observed as –2.78, –2.69, and –2.64 V, respectively. Thus, the hole-trapping moieties affected the oxidation states of Ir complexes **1**.

EL Properties of Ir Complex **1a** Compared to Those of Ir(ppy)₃

An organic EL device using Ir complex **1a** as the emitter was fabricated, and its performance was investigated. The structure of ITO/TPD (50 nm)/Ir complex/CBP (20 nm)/BCP (30 nm)/LiF (1 nm)/Al (70 nm) was examined. *N,N'*-Diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), Ir complex (5 wt.-%), and CBP were em-

ployed as the hole-transporting layer, emitter, and carrier combination host, respectively. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was used as an electron-transporting and hole-blocking layer. Figure 3(a) demonstrates the luminance/current density (L/J) characteristics of the EL devices using **1a** and Ir(ppy)₃ as the emitters. The EL from **1a** was over 40000 cd m^{–2} at 14.4 V, although the emission from **1a** was weak as compared to that from Ir(ppy)₃ at the same current density. This result indicated that Ir complex **1a** as well as Ir(ppy)₃ were good emitters. The turn-on voltage was 4.8 V; this value was greater than that observed in the device with Ir(ppy)₃ (3.0 V). The external quantum efficiency (η_{ext}) of the device with **1a** also was lower than that of the device with Ir(ppy)₃ [Figure 3(b)]. Figure 3(c) shows the EL spectra. The spectrum from **1a** is similar to its PL spectrum shown in Figure 2. The EL maximum from **1a** was observed at 528 nm, which was slightly redshifted as compared to that from Ir(ppy)₃ (514 nm). In addition, a weak EL emission from TPD was observed in the wavelength region between 390 and 470 nm. This result indicated that an energy transfer occurred from the MLCT singlet state of **1a** to the singlet state of TPD by the Förster mechanism.

Scope and Limitations of Ir Complexes Containing Hole-Trapping Moieties

Because the EL emission from TPD was observed in the device with **1a**, 1,1-bis[4-(di-*p*-tolylamino)phenyl]cyclohexane (TAPC) was employed as a hole-transporting layer. The EL structure of ITO/TAPC (50 nm)/Ir complex/CBP (20 nm)/BCP (30 nm)/LiF (1 nm)/Al (70 nm) was examined. As an emitter, 5 wt.-% of **1a** was employed. Figure 4(a) shows the plots of the variation of the external quantum efficiency (η_{ext}) vs. the current density (J), indicating that the efficiency increased by replacing TPD (circles) with TAPC (triangles) as the hole-transporting layer (HTL). Thus, a maximum external quantum efficiency of 9.6% was observed at 7.4 V. The EL from **1a** was over 26000 cd m^{–2} at 14.4 V. According to the EL spectrum shown in Figure 4(b), emission from the hole-transporting layer (TAPC) was not observed. This result implied that the energy transfer from **1a** to the hole-transporting layer was suppressed because the HOMO–LUMO energy gap of TAPC is larger than that of TPD (TAPC: 3.4 eV; TPD: 3.1 eV). Further, the phosphor triplet excitons were effectively confined by the TAPC layer, thereby leading to the high EL efficiency.^[19]

An optimized amount of the Ir complex dopant was used at the emitting layer. The highest EL efficiency was observed when an amount of approximately 10 wt.-% of **1a** was doped. The molar ratio of the optimized amount was slightly higher as compared to that used for Ir(ppy)₃. The luminance (L) of **1a** was observed as 51900 cd m^{–2} at 13.0 V. This resulted in the maximum external quantum efficiency (η_{ext}) of 12.2% [Figure 4(a)]. This value is comparable to those observed in devices using Ir(ppy)₃ [η_{ext} = 11.5%, Figure 3(b)] and Ir(ppy-NPh₂)₂(acac) (η_{ext} = 11.8%).^[14] Table 3

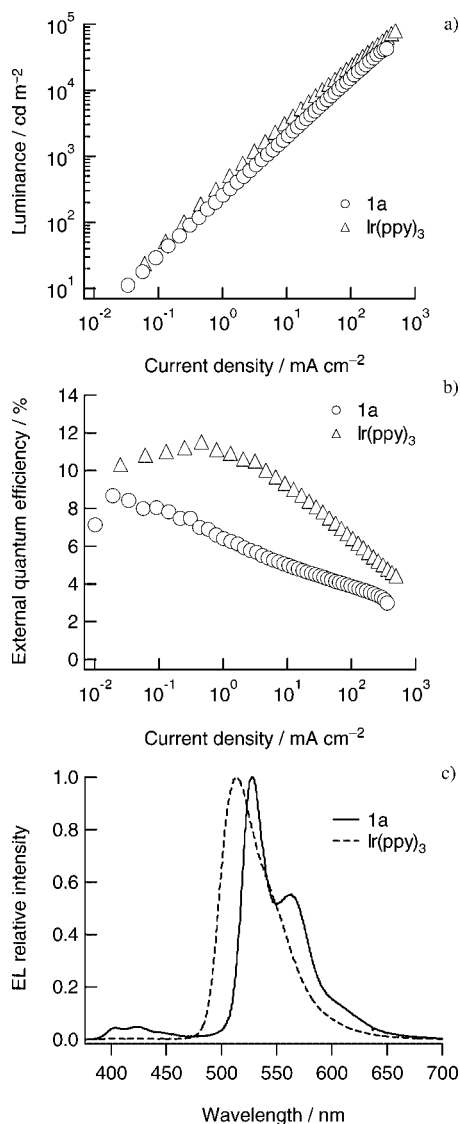


Figure 3. EL characteristics of ITO/TPD (50 nm)/Ir complex (5 wt.-%)/CBP (20 nm)/BCP (30 nm)/LiF (1 nm)/Al (70 nm). Ir complex = **1a** (circles), Ir(ppy)₃ (triangles). (a) Luminance (L)/current density (J) plots. (b) External quantum efficiency (η_{ext})/current density (J) plots. (c) EL spectra.

Table 3. EL properties of devices using Ir complexes **1**.^[a]

Complex	wt.-% [%]	Turn-on voltage [V]	η_{ext} [%/V]	L [$\text{cd}\cdot\text{m}^{-2}$, V]	η_p [$\text{lm}\cdot\text{W}^{-1}$, V]	λ_{max} [nm]	CIE (x, y)
1a	10	4.0	12.2, 6.6	51900, 13.0	24.8, 6.0	528	0.33, 0.64
1b	12	3.6	9.1, 4.8	14600, 13.6	22.5, 4.4	506	0.24, 0.64
1c	11	3.8	8.7, 6.4	31000, 13.0	15.2, 6.4	513	0.26, 0.64

[a] Device structure: ITO/TAPC (50 nm)/Ir complex/CBP (20 nm)/BCP (30 nm)/LiF (1 nm)/Al (70 nm).

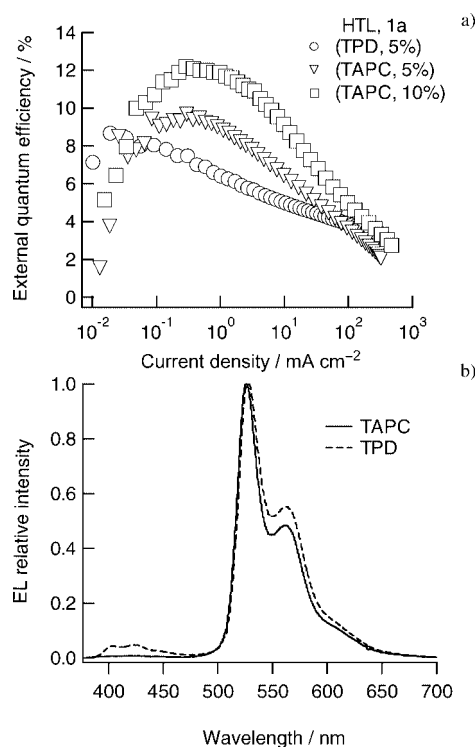


Figure 4. EL characteristics of ITO/HTL (50 nm)/**1a**/CBP (20 nm)/BCP (30 nm)/LiF (1 nm)/Al (70 nm). (a) External quantum efficiency (η_{ext})/current density (J) plots. HTL/**1a** with TPD (5 wt.-%, circles), TAPC (5 wt.-%, triangles), TAPC (10 wt.-%, squares). (b) EL spectra.

summarizes the EL performances of devices with Ir complexes **1a–c**. The luminance increased in the following order: **1b**, **1c**, and **1a**. This may be attributed to their redox behavior as explained in the CV study. The EL efficiency of **1a** is higher than those of **1b** and **1c**. These results indicate that the diphenylamine moiety with a branched structure is acceptable as the hole-trapping moiety of Ir(ppy)₃.

Conclusions

We prepared *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)₃] derivatives containing hole-trapping moieties such as diphenylamine (**1a**), carbazole (**1b**), and phenoxazine (**1c**). Their PL maxima were observed around the maximum of Ir(ppy)₃. These values were marginally shifted depending on the hole-trapping moieties: redshifted for **1a** and blueshifted for **1b** and **1c**. The electron-donating ability of Ir(ppy)₃ was increased due to the diphenylamine and phenoxazine moieties, and the oxidation state became more unstable due to

the carbazole unit. Organic EL devices using Ir complex **1a** as the emitter exhibited stronger luminance than devices that used **1b** and **1c**. Particularly, high EL efficiency was observed when TAPC was used as the hole-transporting layer. The maximum external quantum efficiency from the device was comparable to that observed in a device that used Ir(ppy)₃. Therefore, the introduction of a branched aromatic amine into phosphor is effective for the research and development of new phosphorescent materials.

Experimental Section

General: Iridium trichloride *n*-hydrate (IrCl₃·*n*H₂O) was purchased from Soekawa Chemicals. Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. IR, UV/Vis, and PL spectra were obtained with JASCO FT/IR-5300, V-550, and FP-6300 spectrometers, respectively. Mass spectra were determined with a Hitachi M-2000S mass spectrometer (EI) operating at 70 eV by a direct inlet system and a Voyager-DE STR mass spectrometer (MALDI-TOF) using dithranol as a matrix. Elemental analyses were performed with a Perkin-Elmer 2400II analyzer. ¹H and ¹³C NMR spectra were recorded with Varian GEMINI spectrometers (300 and 50 MHz) and a Bruker AVANCE 600 spectrometer (600 and 150 MHz) with tetramethylsilane as an internal standard.

Preparation of 2-(4-Bromophenyl)pyridine (3): *n*BuLi in hexane (1.60 M, 16.0 mL, 25.6 mmol) was added dropwise to a suspension of 1,4-dibromobenzene (5.90 g, 25.0 mmol) in dry diethyl ether (40 mL) at –78 °C under nitrogen. 2-Fluoropyridine (**2**) (1.72 mL, 20.0 mmol) was added after stirring for 30 min. The mixture was stirred at –78 °C for 1 h and at room temperature for 1 h. The reaction mixture was poured into water (50 mL), and diethyl ether (50 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (50 mL × 2). The combined organic solutions were extracted with a 5% HCl solution (200 mL × 3), and the aqueous layer was adjusted to an alkaline pH with KOH (63 g). The aqueous layer was extracted with diethyl ether (200 mL × 3). The organic solution was dried with MgSO₄ and concentrated. The residue was sublimed at 65–70 °C under 10⁻² Torr to afford compound **3** (2.02 g, 43%) as colorless needles. M.p. 60–62 °C. IR (KBr): $\tilde{\nu}$ = 3052, 3007, 1586, 1462, 1433, 1391, 1154, 1100, 1071, 1005, 841, 774 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 7.23–7.28 (m, 1 H), 7.60 (dt, *J* = 8.8, 2.2 Hz, 2 H), 7.68–7.79 (m, 2 H), 7.88 (dt, *J* = 8.8, 2.2 Hz, 2 H), 8.69 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1 H) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 120.3, 122.4, 123.4, 128.4, 131.8, 136.9, 138.2, 149.7, 156.2 ppm. MS (EI): *m/z* (%) = 235 (100) [M⁺], 233 (99) [M⁺], 154 (84). C₁₁H₈BrN (234.09): calcd. C 56.44, H 3.44, N 5.98; found C 56.47, H 3.55, N 5.89.

Preparation of Ligands 4a–d: A solution of Pd(OAc)₂ (28 mg, 0.12 mmol) and *t*Bu₃P (90 mg, 0.44 mmol) in toluene (4 mL) was

added to a suspension of compound **3** (0.94 g, 4.0 mmol), diphenylamine (0.68 g, 4.0 mmol), and *t*BuONa (0.47 g, 4.9 mmol) in toluene (4 mL) under nitrogen. The mixture was refluxed for 3 h. After cooling, the reaction mixture was poured into water (10 mL), and ethyl acetate (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL $\times$ 2). The combined organic solutions were dried with Na₂SO₄ and concentrated. The residue was chromatographed on alumina gel (hexane/CH₂Cl₂, 2:1) to give ligand **4a** (1.17 g, 91%) as pale yellow needles. M.p. 177–177.5 °C (from ethanol). IR (KBr): $\tilde{\nu}$ = 3057, 1586, 1491, 1466, 1433, 1325, 1279, 787, 756, 698, 515 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 7.05 (tt, *J* = 7.3, 1.4 Hz, 2 H), 7.12–7.20 (m, 7 H), 7.24–7.31 (m, 4 H), 7.65–7.74 (m, 2 H), 7.87 (dt, *J* = 8.8, 2.4 Hz, 2 H), 8.65 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1 H) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 117.8, 119.8, 121.4, 123.2, 124.7, 127.7, 129.3, 133.1, 136.6, 147.5, 148.7, 149.6, 157.1 ppm. MS (EI): *m/z* (%) = 322 (100) [M⁺]. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 346 (4.42), 308 (4.23) nm. C₂₃H₁₈N₂ (322.40): calcd. C 85.68, H 5.63, N 8.69; found C 85.63, H 5.80, N 8.56. Similar reaction conditions were applied to the synthesis of ligands **4b–d**. These were carried out using K₂CO₃ (3 equiv.) as a base instead of *t*BuONa. The reaction mixtures were refluxed for 24 h. **4b**: Yield 87% (0.56 g). Pale yellow crystals (from ethanol). M.p. 179–180.5 °C. IR (KBr): $\tilde{\nu}$ = 1603, 1516, 1453, 1366, 1335, 1318, 1235, 779, 750, 725 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 7.27–7.33 (m, 3 H), 7.40–7.51 (m, 4 H), 7.69 (dt, *J* = 8.8, 2.2 Hz, 2 H), 7.81–7.83 (m, 2 H), 8.16 (d, *J* = 7.8 Hz, 2 H), 8.23 (dt, *J* = 8.8, 2.2 Hz, 2 H), 8.76 (dt, *J* = 4.9, 1.1 Hz, 1 H) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 109.8, 120.1, 120.3, 120.5, 122.4, 123.5, 126.0, 127.2, 128.4, 136.9, 138.3, 138.4, 140.7, 149.8, 156.5 ppm. MS (EI): *m/z* (%) = 320 (100) [M⁺]. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 318 (4.25), 292 (4.30), 240 (4.68) nm. C₂₃H₁₆N₂ (320.39): calcd. C 86.22, H 5.03, N 8.74; found C 86.01, H 5.19, N 8.62. **4c**: Yield 84% (0.86 g). Pale yellow crystals (from methanol). M.p. 173–174.5 °C. IR (KBr): $\tilde{\nu}$ = 1589, 1491, 1341, 1273, 743, 729 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 6.01 (dd, *J* = 7.8, 1.5 Hz, 2 H), 6.57–6.72 (m, 6 H), 7.27–7.31 (m, 1 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 7.80 (m, 2 H), 8.21 (d, *J* = 8.7 Hz, 2 H), 8.74 (d, *J* = 4.7 Hz, 1 H) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 113.3, 115.4, 120.7, 121.4, 122.5, 123.2, 129.6, 131.1, 134.2, 137.1, 139.4, 139.6, 143.9, 149.7, 156.4 ppm. MS (EI): *m/z* (%) = 336 (100) [M⁺], 182 (69). UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 326 (3.95), 276 (4.21), 240 (4.75) nm. C₂₃H₁₆N₂O (336.39): calcd. C 82.12, H 4.79, N 8.33; found C 82.28, H 4.82, N 8.32. **4d**: Yield 82% (0.42 g). Pale yellow crystals (from ethanol). M.p. 174–175.5 °C. IR (KBr): $\tilde{\nu}$ = 1589, 1464, 1437, 1310, 1260, 1244, 1046, 920, 783, 743 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 6.34 (dd, *J* = 7.7, 1.9 Hz, 2 H), 6.80–6.90 (m, 4 H), 7.05 (dd, *J* = 6.9, 2.1 Hz, 2 H), 7.25–7.30 (m, 1 H), 7.49 (dt, *J* = 8.7, 2.2 Hz, 2 H), 7.77–7.81 (m, 2 H), 8.20 (dt, *J* = 8.7, 2.2 Hz, 2 H), 8.74 (dt, *J* = 4.7, 1.4 Hz, 1 H) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 116.6, 120.6, 120.9, 122.4, 122.7, 126.8, 126.9, 129.2, 130.5, 136.9, 139.0, 141.9, 144.0, 149.8, 156.5 ppm. MS (EI): *m/z* (%) = 352 (100) [M⁺]. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 320 (3.87), 257 (4.74) nm. C₂₃H₁₆N₂S (352.45): calcd. C 78.38, H 4.58, N 7.95; found C 78.32, H 4.53, N 7.89.

Preparation of Ir Dimers 5a–c: A mixture of ligand **4a** (0.65 g, 2.0 mmol) and IrCl₃·*n*H₂O (0.36 g, 1.0 mmol) in a solution of 2-ethoxyethanol (12 mL) and water (4 mL) was stirred under nitrogen at 120 °C for 24 h. After cooling, the precipitate was filtered and washed with methanol, diethyl ether, and hexane to afford Ir dimer **5a** (0.69 g, 80%) as yellow solid. M.p. > 300 °C. ¹H NMR (CDCl₃, 300 MHz): δ = 5.48 (d, *J* = 2.2 Hz, 4 H), 6.21 (t, *J* = 6.5 Hz, 4 H), 6.45 (dd, *J* = 8.5, 2.2 Hz, 4 H), 6.85–6.94 (m, 24 H), 7.09 (t, *J* = 7.8 Hz, 16 H), 7.22–7.28 (m, 8 H), 7.43 (d, *J* = 7.7 Hz, 4 H), 8.89

(d, *J* = 6.5 Hz, 4 H) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 114.3, 117.3, 120.4, 122.7, 122.9, 123.8, 125.4, 128.8, 135.4, 137.2, 146.1, 147.3, 147.7, 151.0, 167.4 ppm. MALDI-TOF MS: *m/z* = 1741.40 [M⁺ + 1], 1705.41 [M⁺ – Cl], 870.19 [M⁺/2], 835.22 [M⁺/2 – Cl]. C₉₂H₆₈Cl₂Ir₂N₈ (1740.9): calcd. C 63.47, H 3.94, N 6.44; found C 63.41, H 3.83, N 6.36. Similar reaction conditions were applied to the synthesis of Ir dimers **5b** and **5c**. **5b**: Yield 85% (0.36 g). Yellow solid. M.p. > 300 °C. MALDI-TOF MS: *m/z* = 1733.37 [M⁺ + 1], 1697.40 [M⁺ – Cl], 866.22 [M⁺/2], 831.25 [M⁺/2 – Cl]. C₉₂H₆₀Cl₂Ir₂N₈ (1732.9): calcd. C 63.77, H 3.49, N 6.47; found C 63.15, H 3.43, N 6.32. **5c**: Yield 88% (0.43 g). Yellow solid. M.p. > 300 °C. MALDI-TOF MS: *m/z* = 1761.33 [M⁺ – Cl], 898.23 [M⁺/2], 863.26 [M⁺/2 – Cl]. C₉₂H₆₀Cl₂Ir₂N₈O₄ (1796.9): calcd. C 61.50, H 3.37, N 6.24; found C 60.57, H 3.25, N 6.01.

Preparation of fac-Ir Complexes 1a–c: A mixture of Ir dimer **5a** (130 mg, 0.075 mmol), ligand **4a** (49 mg, 0.15 mmol) and K₂CO₃ (106 mg, 0.77 mmol) in glycerol (5 mL) was stirred under nitrogen at 240 °C for 11 h. After cooling, water (5 mL) and dichloromethane (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (10 mL $\times$ 2). The combined organic solutions were dried with Na₂SO₄ and concentrated. The residue was chromatographed on silica gel (CH₂Cl₂) to afford *fac*-Ir complex **1a** (82 mg, 48%) as orange solid. M.p. > 300 °C (from CH₂Cl₂). ¹H NMR (CDCl₃, 600 MHz): δ = 6.24 (dd, *J* = 8.4, 2.1 Hz, 3 H), 6.58 (d, *J* = 2.1 Hz, 3 H), 6.78 (t, *J* = 6.4 Hz, 3 H), 6.83 (d, *J* = 7.7 Hz, 12 H), 6.87 (t, *J* = 7.7 Hz, 6 H), 7.09 (t, *J* = 7.7 Hz, 12 H), 7.27 (d, *J* = 8.4 Hz, 3 H), 7.52–7.55 (m, 6 H), 7.68 (d, *J* = 8.0 Hz, 3 H) ppm. ¹³C NMR (CDCl₃, 150 MHz): δ = 114.6, 117.7, 120.5, 122.2, 124.5, 124.8, 128.6, 130.2, 135.4, 137.6, 147.2, 147.6, 148.2, 161.9, 166.2 ppm. MALDI-TOF MS: *m/z* = 1156.42 [M⁺]. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 398 (4.68), 367 (4.70), 320 (4.67), 261 (4.69), 227 (4.80) nm. C₆₉H₅₁IrN₆ (1156.4): calcd. C 71.67, H 4.45, N 7.27; found C 71.65, H 4.32, N 7.33. Similar reaction conditions, stirring at 240 °C for 48 h and 24 h, were applied to the synthesis of *fac*-Ir complexes **1b** and **1c**, respectively. **1b**: Yield 78% (0.27 g). Yellow solid. M.p. > 300 °C. ¹H NMR (CDCl₃, 300 MHz): δ = 6.87 (br. m, 6 H), 6.96–7.03 (m, 18 H), 7.20 (d, *J* = 2.2 Hz, 3 H), 7.71 (td, *J* = 8.0, 1.5 Hz, 3 H), 7.76 (d, *J* = 4.7 Hz, 3 H), 7.81 (d, *J* = 8.2 Hz, 3 H), 7.94 (d, *J* = 7.1 Hz, 6 H), 7.99 (d, *J* = 8.0 Hz, 3 H) ppm. MALDI-TOF MS: *m/z* = 1150.35 [M⁺]. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 378 sh (4.40), 346 (4.70), 238 (5.18) nm. C₆₉H₄₅IrN₆ (1150.4): calcd. C 72.04, H 3.94, N 7.31; found C 72.20, H 4.03, N 7.26. **1c**: Yield 54% (0.20 g). Yellow solid. M.p. > 300 °C. ¹H NMR (CDCl₃, 300 MHz): δ = 5.69 (dd, *J* = 7.8, 1.4 Hz, 6 H), 6.01 (td, *J* = 7.8, 1.4 Hz, 6 H), 6.39 (td, *J* = 7.8, 1.4 Hz, 6 H), 6.52 (dd, *J* = 7.8, 1.4 Hz, 6 H), 6.72 (d, *J* = 2.0 Hz, 3 H), 6.76 (dd, *J* = 8.1, 2.0 Hz, 3 H), 7.02 (t, *J* = 5.9 Hz, 3 H), 7.69–7.73 (m, 6 H), 7.81 (d, *J* = 8.1 Hz, 3 H), 7.92 (d, *J* = 7.7 Hz, 3 H) ppm. MALDI-TOF MS: *m/z* = 1198.34 [M⁺]. UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 375 sh (4.23), 330 (4.52), 283 (4.85), 241 (5.20) nm. C₆₉H₄₅IrN₆O₃ (1198.4): calcd. C 69.16, H 3.78, N 7.01; found C 69.14, H 3.90, N 6.89.

X-ray Crystallographic Analysis for fac-Ir Complex 1a: A single crystal was obtained as a greenish brown platelet by recrystallization of **1a** from a mixture of dichloromethane and ethyl acetate. Crystal data for **1a**: 0.15 $\times$ 0.13 $\times$ 0.03 mm, C₆₉H₅₁IrN₆, *M* = 1156.42, monoclinic, space group *P*2₁/*n*, *a* = 13.9742(9), *b* = 17.1467(9), *c* = 44.590(3) Å, β = 98.158(3)°, *V* = 10576(1) Å³, *Z* = 8, *D*_c = 1.452 g cm⁻³, μ = 25.82 cm⁻¹, *F*(000) = 4672. A total of 21884 unique reflections for 2 θ_{max} = 55° was collected [*I* > 2 σ (*I*)] with a Rigaku MSC MercuryCCD diffractometer (Mo-*K*_α radiation, λ = 0.71070 Å, graphite monochromator) at 173 K. A numerical absorption correction was applied. The structure was solved

using the direct method (SHELXS-97)^[20] and refined by the full-matrix least-squares analysis (SHELXL-97)^[21] giving values of $R_1 = 0.088$, $R_w = 0.165$, $S = 1.26$, $\rho_{\text{max}}/\rho_{\text{min}} = 3.44/-2.31 \text{ e} \cdot \text{\AA}^{-3}$. All calculations were performed using the *teXsan* programs.^[22] CCDC-294487 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Measurements: CV was performed with a Toho Technical Research polarization unit PS-07 potentiostat/galvanostat. The CV studies of compounds **1** and **4** were carried out in DMF with 0.1 M *n*Bu₄NClO₄ using Pt and SCE electrodes. The values are expressed in potentials vs. Fc/Fc⁺.

Electroluminescence Measurements: An ITO-coated glass substrate was patterned and cleaned by scrubbing, ultrasonication, and irradiation in a UV/ozone chamber. Organic layers were deposited on the ITO at an evaporating rate of 1 nm/s. The cathode of a LiF/Al bilayer was formed by sequential deposition. The rate and thickness of the films were monitored with a quartz oscillator. The sample area was 2 × 2 mm. Current and luminance on applied voltage were measured with an HP 4145A semiconductor parameter analyzer, which was connected with a Topcon BM-3 luminance meter. The electroluminescence spectra were measured with an Ocean Optics S2000 spectrometer. The external quantum efficiency (η_{ext}) was calculated from the luminance, the current density, and the emission spectrum of each device assuming that the observed emission was the Lambertian one.

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