Iridium(III) Complexes Bearing Quinoxaline Ligands with Efficient Red Luminescence Properties

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Newly designed cyclometalated iridium(III) complexes bearing 2,3-diphenylquinoxalines, which were shown to be highly efficient and pure-red emitting materials for electrophosphorescent organic light-emitting diodes (OLEDs), were synthesized and characterized. Excellent quantum efficiencies for photoluminescence within the range of 50–79% were attained in dichloromethane solution at room temperature. Luminescence peak wavelengths of the complexes were within the preferred range of 653–671 nm in thin films. The most vivid red electrophosphorescence with CIE chromaticity coordinates $x = 0.70$ and $y = 0.28$, which are the closest to the ultimate limit of pure red among reported OLEDs, was achieved with the acetylacetonatoiridium complex bearing 2,3-diphenylquinoxaline.

ortho-Metalated complexes have attracted much attention for use in organic light-emitting diodes (OLEDs) because they are strong electroluminescent emitters.[1] Especially, iridium(III) complexes bearing *o*-pyridine-arene or *o*-pyridine-heterocycle derivatives[2,3] have been reported to show highly efficient phosphorescence due to emission from the triplet metal to ligand charge transfer (^{3}MLCT) excited state and triplet ligand centered (^{3}LC) excited state.[1] Quinoxalines are considered to be building blocks for functional materials, and so, homo- and co-polymers containing a quinoxaline unit have been investigated.[4–9] Red emission complexes with larger quantum yields have been studied towards the development of highly efficient red emissive OLEDs.[10–14] A phosphorescent organoiridium compound, bis(2-(2′-benzothienyl)-pyridinato-*N*,C3′)iridium(acetylacetonate) ([Ir(btp)$_2$(acac)]), has been reported to give red photoluminescence (PL) with a PL quantum yield of 0.21.[2] The orange-red iridium complex bearing dibenzo[*f*,*h*]quinoxaline (dbq) has been reported to give a PL quantum yield of 0.53 in dichloromethane and chromaticity of ($x = 0.62$, $y = 0.38$) on electroluminescence.[10] Since 2,3-diphenylquinoxalines[14] possess a higher energy highest occupied molecular orbital (HOMO) and lower energy lowest unoccupied molecular orbital (LUMO) due to their π orbital and susceptibility to reduction, iridium(III) complexes with 2,3-diphenylquinoxaline ligands should exhibit pure red emission.[11–15] We now report the synthesis and characterization of acetylacetonatoiridium(III) complexes with 2,3-diphenylquinoxalines.

Results and Discussion

Synthesis of Acetylacetonatoiridium(III) Complexes. Acetylacetonatoiridium(III) complex **3** was synthesized as shown in Scheme 1.[16] 2,3-Diphenylquinoxaline[5] reacted with $IrCl_3 \cdot nH_2O$ in a mixed solvent of 2-ethoxyethanol and H_2O (v/v = 3:1) at 100 °C. Filtration of the solid gave the iridium chloride-bridged dimer **2** as a main product with small amounts of *fac*- and/or *mer*-tris(2,3-diphenylquinoxalinato)-iridium(III). Due to insolubility of **2**, excess ligand and other iridium complexes were readily removed by washing with ethanol. Although two coordination sites are available with the quinoxaline ligand, only one nitrogen atom of the quinoxaline coordinated under the reaction conditions. Then, **2** reacted with acetylacetone in the presence of Na_2CO_3 to give the corresponding acetylacetonatoiridium(III) complex **3**, which was identified by ^{1}H and ^{13}C NMR, and elemental analysis.

UV–Vis and Emission Spectra. In the UV–vis spectra of the acetylacetonatoiridium(III) complexes **3a**–**3d**, a new absorption appeared at 470–480 nm, which was assigned to MLCT (Fig. 1 and Table 1).[2] Other absorption maxima around 230–400 nm may be ligand transitions (π–π^* and n–π^* transition), as compared with the absorptions of the corresponding free ligands **1a**–**1d**.[6] No emission was observed with **1a**–**1d** when excited at $\lambda = 390$ nm. The emission of the fluoro derivative **3b** was 10–20 nm blue-shifted from the other complexes **3a**, **3c**, and **3d** (Fig. 2). It should be noted that the complexes **3** showed relatively high quantum yields, which were determined to be 0.50–0.79 on the basis of quinine sulfate/0.1 M H_2SO_4 solution. These findings also suggest that emission depends on the MLCT excited state. In thin film states, the absorption maxima of the MLCT were nearly the same (Fig. 3). However, these absorption maxima for **3** were 15 nm red-shift-

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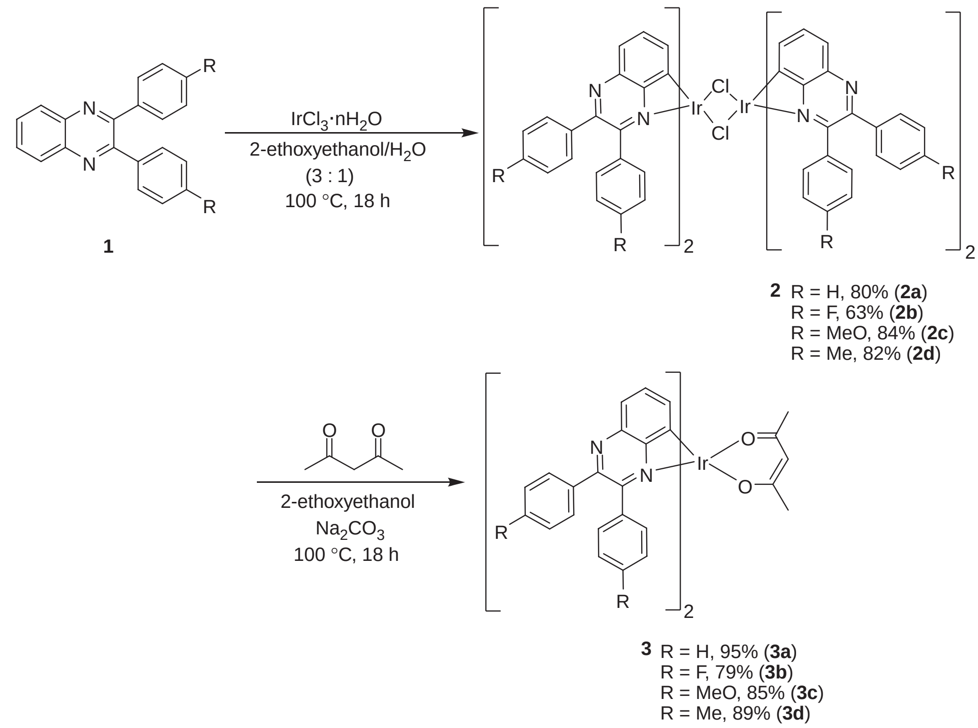

2 R = H, 80% (**2a**)
R = F, 63% (**2b**)
R = MeO, 84% (**2c**)
R = Me, 82% (**2d**)

3 R = H, 95% (**3a**)
R = F, 79% (**3b**)
R = MeO, 85% (**3c**)
R = Me, 89% (**3d**)

Scheme 1. Synthesis of iridium(III) complexes **2** and **3**.

Table 1. UV–Vis Spectra and Luminescent Properties for Acetylacetonatoiridium Complexes **3a**–**3d**[a)]

Complex	Solution[b)]			Thin film[d)]	
	UV–vis spectra $\lambda_{\max}$/nm (log ε)	Emission $\lambda_{\max}$/nm[c)]	Φ	UV–vis spectra $\lambda_{\max}$/nm	Emission $\lambda_{\max}$/nm[e)]
3a	233 (5.43), 257 (5.15), 281 (5.11), 306 (4.93), 325 (4.79), 378 (4.41), 488 (3.93)	670	0.50	277, 374, 483	671
3b	232 (5.37), 257 (5.08), 279 (5.03), 304 (4.91), 322 (4.79), 360 (4.35), 471 (3.99)	647	0.71	277, 377, 473	653
3c	232 (5.36), 254 (5.15), 280 (5.03), 380 (4.53), 477 (4.07)	659	0.67	278, 393, 481	664
3d	230 (5.27), 262 (5.05), 287 (4.90), 389 (4.31), 414 (4.35), 477 (4.04)	669	0.79	276, 374, 481	670

a) 298 K. b) 1.0×10^{-5} M in dichloromethane. c) Excitation at $\lambda_{\max}$ 390 nm. d) 20 nm thin film. e) Excitation at $\lambda_{\max}$ 470 nm.

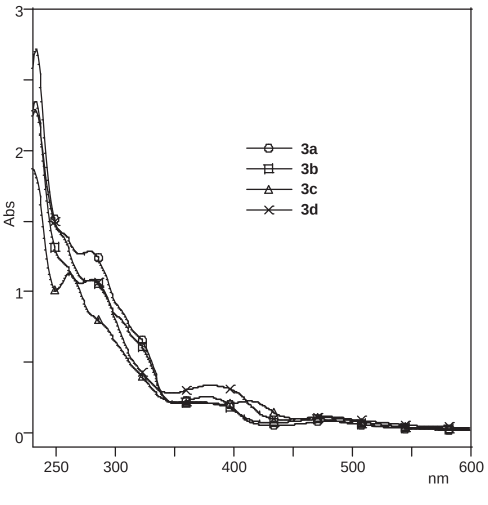

Fig. 1. UV–vis spectra of acetylacetonatoiridium(III) complexes **3a**–**3d** in dichloromethane solution.

ed as compared with those in solution states, suggesting that there is a contribution from intermolecular π interactions in solid states. The emission maxima in thin film states appeared between 653 and 671 nm, which are about 5 nm red-shifted from the solution state emission (Fig. 4). These emission processes are mainly due to the ^{3}MLCT transition. In general, the luminescence quantum yields decreased with an increase in the emission peak wavelength according to the energy gap law.[6] Therefore, these acetylacetonatoiridium(III) complexes **3a**–**3d** bearing the quinoxaline ligands appear to be promising as red luminescent materials.

OLED Performance. As described below, two types of OLEDs were fabricated with a multilayered structure by vacuum thermal evaporation on indium–tin oxide (ITO) anode prepatterned glass substrates. The organic layers between the anode and the cathode were composed of a hole-injection layer (HIL), a light-emitting layer, and an electron-injection layer (EIL). The light-emitting layer was either a doped light-emit-

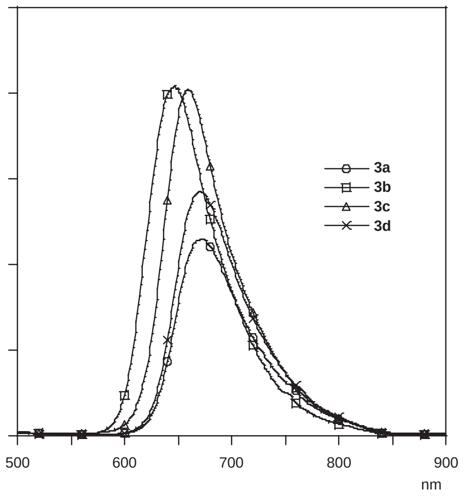

Fig. 2. Emission spectra of acetylacetonatoiridium(III) complexes **3a**–**3d** in dichloromethane solution.

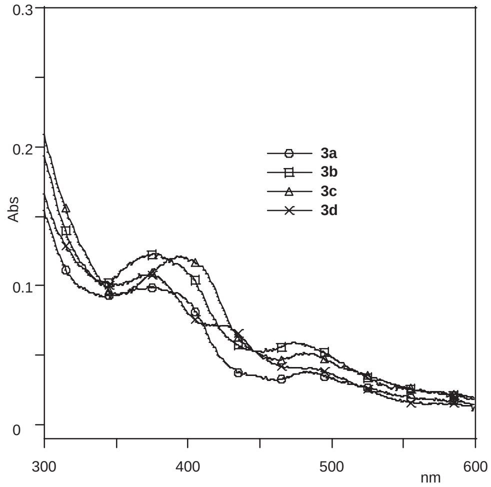

Fig. 3. UV–vis spectra of acetylacetonatoiridium(III) complexes **3a**–**3d** in 20 nm thin film states.

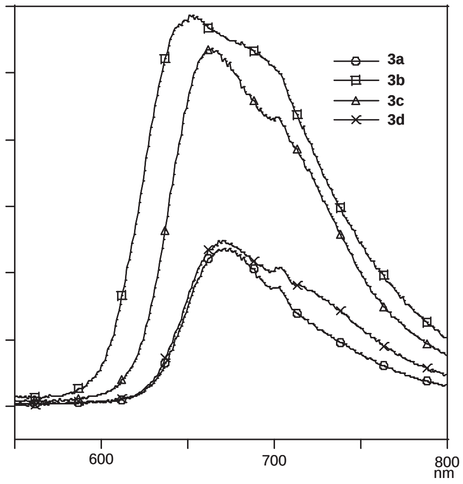

Fig. 4. Emission spectra of acetylacetonatoiridium(III) complexes **3a**–**3d** in 20 nm thin film states.

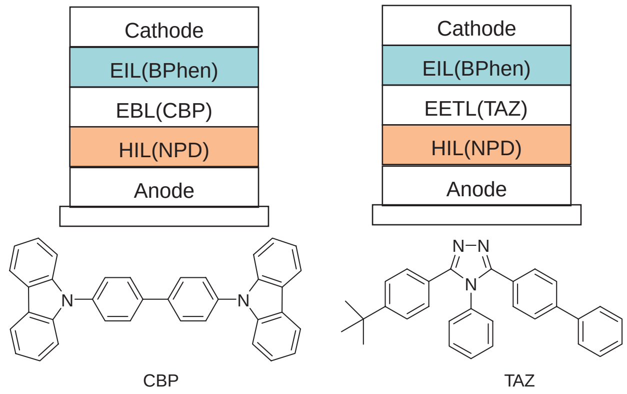

Fig. 5. The device structures and chemical structures of CBP and TAZ.

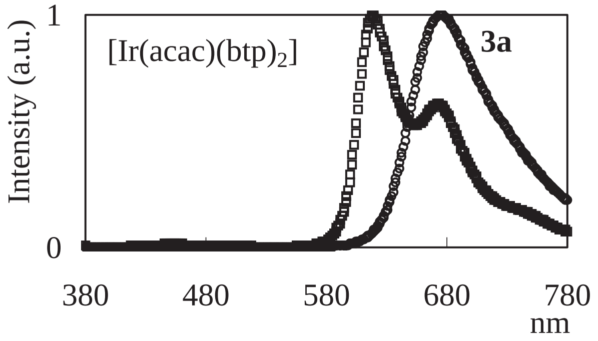

Fig. 6. Electroluminescence spectra of $[Ir(acac)(btp)_2]$ (square) and **3a** (circle) doped EBL OLEDs at room temperature.

ting bipolar layer (EBL) with 4,4′-di-9-carbazolylbiphenyl (CBP) or a doped light-emitting electron-transport layer (EETL) with 3-(4-biphenylyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) as shown in Fig. 5. The acetylacetonatoiridium(III) complex **3a** was doped into the light-emitting layer at a doping concentration of 9 wt %. The cathode was 0.5 nm thick lithium fluoride for efficient electron injection and 150 nm thick aluminum. The materials for organic layers were 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPD) for HIL (thickness: 60 nm), CBP for EBL (35 nm), TAZ for EETL (35 nm), and 4,7-diphenyl-1,10-phenanthroline (BPhen) for EIL (60 nm).

The electroluminescence spectra for **3a** and $[Ir(acac)(btp)_2]$ (btp: benzothienylpyridine) doped devices are shown in Fig. 6. The featureless broad emission peak of **3a** suggests that the electrophosphorescence predominantly originated from the ^{3}MLCT excited state. On the contrary, the electroluminescence of a conventional red complex, $[Ir(acac)(btp)_2]$, has been reported to originate dominantly from the ^{3}LC excited state as observed in the vibronic peaks.[2,17]

In relation to pure-red luminescence, the electroluminescence peak wavelength of 675 nm for **3a** is clearly superior to the one of 616 nm for $[Ir(acac)(btp)_2]$. To the best of our knowledge, **3a** exhibited the most vivid-red electroluminescence with the 1931 CIE chromaticity coordinates of (0.70, 0.28).

Figure 7 shows a comparison of the electrophosphorescence

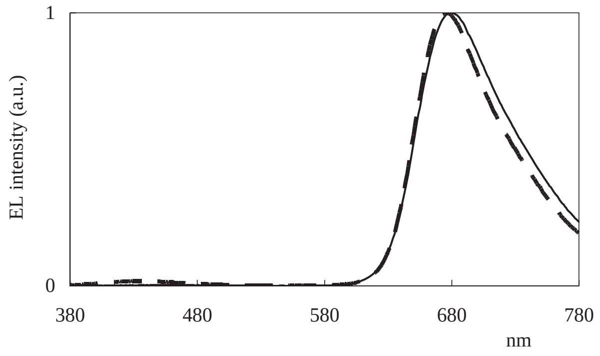

Fig. 7. Comparison of electrophosphorescence spectra for two types of **3a** doped OLEDs at luminance of 600 cd m^{-2}. Fine curve: the light-emitting electron-transport layer (EETL) OLED, dashed curve: the light-emitting bipolar layer (EBL) OLED.

spectra for two types of OLEDs of **3a** at luminance of 600 cd m^{-2}. The spectrum of EBL OLED had a peak at 675 nm, while the EETL OLED afforded the purest-red electrophosphorescence spectrum with a maximum at 680 nm and a full width at half maximum of 89 nm. A small peak at around 437 nm was observed in the EBL OLED with CBP under high luminance. The small peak corresponds to the PL peak for CBP. On the contrary, no spurious radiation was observed in the EETL OLED. In OLEDs, holes and electrons are injected into a light-emitting layer, and recombination of charges generates excited states. Excited energy of the host is transferred to the dopant, and light is mainly emitted from the dopant. However, the rate of such energy transfer is limited. Thus, emission from the host becomes possible as the charge recombination rate increases. When leakage of the charges from a light-emitting layer is substantial, spurious radiation due to recombination in the adjacent layers is also possible.

In the EBL OLED, the HOMO levels for the organic layers are 5.7 eV (NPD), 6.3 eV (CBP), and 6.4 eV (BPhen), respectively, and the HOMO offset between CBP and BPhen is only 0.1 eV. Therefore, substantial leakage of holes from CBP to BPhen is possible. In contrast, the EETL had larger HOMO offsets (0.2 eV) between TAZ and BPhen because the HOMO level for TAZ is 6.6 eV. Therefore, leakage of holes from a light-emitting layer to BPhen is more difficult in the EETL OLED than the EBL OLED. This may be one reason for the higher color purity of the EETL OLED.

In the EBL OLED, the LUMO levels for the organic layers are 2.6 eV (NPD), 3.2 eV (CBP), and 3.0 eV (BPhen), respectively. Since the LUMO offset between CBP and BPhen is 0.2 eV, electron injection from BPhen to CBP is efficient, and recombination of charges occurs predominantly on CBP. Thus, spurious emission from CBP is possible with high luminance. On the contrary, electron injection from BPhen to TAZ is more difficult in the EETL OLED since the LUMO offset between TAZ and BPhen is 0.4 eV. Direct electron injection from BPhen to the dopant or substantial carrier trap on the dopant may become significant in the EETL OLED because of the high doping concentration of 9 wt % for the OLEDs. In this case, the excited states of the dopant are directly generated on the dopant. As a result, efficient emission without spurious radiation becomes possible. This may be another reason for the higher color purity for the EETL OLED with TAZ.

Conclusion

We synthesized and characterized acetylacetonatoiridium(III) complexes **3**. Complexes **3** showed red luminescence between 647 and 670 nm in dichloromethane solution. A pure-red OLED was produced by using **3a** with 2,3-diphenylquinoxaline. The new organoiridium compound is promising as a pure-red emitting material, for use in various applications, such as surgical illumination with enhanced color reproducibility.

Experimental

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and are uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 plus. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Varian MERCURY 300 spectrometer. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. UV–vis spectra were obtained by using a Hitachi U-3500 spectrophotometer at 1.0×10^{-5} M concentration in dichloromethane at 298 K. Emission spectra were taken on a Shimadzu RF-5300PC spectrofluorophotometer with a sample concentration of 1.0×10^{-5} M in dichloromethane at 298 K. Thin films (20 nm) were prepared by sublimation at 4×10^{-2} Pa. Emission spectra of the thin films on glass were taken on a Shimadzu RF-5300PC spectrofluorophotometer at 298 K. Emission quantum yields in solution were estimated by using a solution with a concentration of 1.0×10^{-5} M concentration of (−)-quinine sulfate/0.1 M H_2SO_4 aq as a reference. Electroluminescence spectra were measured with Konica-Minolta CS-1000A spectroradiometer.

Synthesis of [{Ir(Hqx)$_2$}$_2$(μ-Cl)$_2$] (2a). IrCl$_3$$\cdot$$nH_2$O (10.0 mmol) and 2,3-diphenylquinoxaline (**1a**, 5.647 g, 20.0 mmol) were stirred in a mixed solvent of 2-ethoxyethanol/water (v/v = 3:1, 200 mL) at 100 °C for 18 h under argon. After the solvent was removed under reduced pressure, ethanol (100 mL) and dichloromethane (50 mL) were added to the resulting residue. The precipitate was collected and dried to give 6.283 g (80% yield) of **2a** as a brown solid. Mp: >300 °C; IR (KBr): 3116, 3047, 2968, 2921, 2862, 1577, 1483, 1444, 1426, 1388, 1350, 1320, 1236, 1127, 1069, 805, 758, 697, 636 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.66 (d, J = 8.3 Hz, 1H), 6.18 (t, J = 8.3 Hz, 1H), 6.45 (t, J = 8.3 Hz, 1H), 6.70 (td, J = 1.5, 8.3 Hz, 1H), 6.87 (t, J = 8.3 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.65–7.71 (m, 4H), 8.03–8.12 (br, 2H), 8.42 (d, J = 8.3 Hz, 1H); ^{13}C NMR (CDCl$_3$): 121.2, 126.3, 127.8, 128.1, 128.6, 128.8, 129.1, 129.7, 130.9, 134.8, 138.2, 139.9, 140.4, 146.5, 150.0, 151.9, 163.3 ppm; Anal. Calcd for $C_{80}H_{52}Cl_2N_8Ir_2 \cdot H_2O$: C, 60.10; H, 3.40; N, 7.01%. Found: C, 60.00; H, 3.51; N, 6.90%.

Synthesis of [{Ir(4-Fqx)$_2$}$_2$(μ-Cl)$_2$] (2b). IrCl$_3$$\cdot$$nH_2$O (5.0 mmol) and 2,3-bis(4-fluorophenyl)quinoxaline (**1b**, 3.183 g, 10.0 mmol) were stirred in a mixed solvent of 2-ethoxyethanol/water (v/v = 3:1, 100 mL) at 100 °C for 18 h under argon. After the solvent was removed under reduced pressure, ethanol (100 mL) was added to the resulting residue. The precipitate was collected and dried to give 2.713 g (63% yield) of **2b** as a orange solid. Mp: >300 °C; IR (KBr): 3120, 3060, 2968, 1871, 1584, 1560, 1507, 1484, 1457, 1387, 1353, 1313, 1259, 1234, 1195, 1158, 1126, 1096, 1066, 1015, 842, 802, 758, 733, 611, 566, 530, 521 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.29 (dd, $J = 8.6$, 2.3 Hz, 1H), 6.26 (ddd, $J = 8.6$, 6.9, 2.3 Hz, 1H), 6.68 (ddd, $J = 8.6$, 6.9, 2.3 Hz, 1H), 6.91 (dd, $J = 8.6$, 5.7 Hz, 1H), 7.32 (ddd, $J = 8.6$, 6.9, 1.1 Hz, 1H), 7.35–7.46 (br, 2H), 7.70 (dd, $J = 8.6$, 1.1 Hz, 1H), 7.97–8.18 (br, 2H), 8.25 (d, $J = 8.6$ Hz, 1H); ^{13}C NMR (CDCl$_3$): 109.8 ($J_{\text{13C–19F}} = 22$ Hz), 115.9 ($J_{\text{13C–19F}} = 22$ Hz), 117.0 ($J_{\text{13C–19F}} = 22$ Hz), 120.7 ($J_{\text{13C–19F}} = 18$ Hz), 125.6, 129.1 ($J_{\text{13C–19F}} = 4.3$ Hz), 130.6 ($J_{\text{13C–19F}} = 7.7$ Hz), 131.0 ($J_{\text{13C–19F}} = 9.4$ Hz), 132.5 ($J_{\text{13C–19F}} = 8.3$ Hz), 135.6 ($J_{\text{13C–19F}} = 4.3$ Hz), 138.2, 139.9, 142.3 ($J_{\text{13C–19F}} = 2.0$ Hz), 150.5, 151.3 ($J_{\text{13C–19F}} = 7.5$ Hz), 160.5 ($J_{\text{13C–19F}} = 240$ Hz), 162.2, 163.9 ($J_{\text{13C–19F}} = 234$ Hz) ppm; Anal. Calcd for $C_{80}H_{44}Cl_2F_8N_8Ir_2 \cdot 0.5CH_2Cl_2$: C, 54.72; H, 2.57; N, 6.34%. Found: C, 54.66; H, 2.84; N, 6.30%.

Synthesis of [{Ir(4-MeOqx)$_2$}$_2$(μ-Cl)$_2$] (2c). IrCl$_3 \cdot n$H$_2$O (5.0 mmol) and 2,3-bis(4-methoxylphenyl)quinoxaline (**1c**, 3.104 g, 10.0 mmol) were stirred in a mixed solvent of 2-ethoxyethanol/water (v/v = 3:1, 100 mL) at 100 °C for 18 h under argon. After the solvent was removed under reduced pressure, ethanol (100 mL) was added to the resulting residue. The precipitate was collected and dried to give 3.740 g (82% yield) of **2c** as a red solid. Mp: >300 °C; IR (KBr): 3070, 2932, 2834, 1606, 1580, 1507, 1457, 1384, 1353, 1302, 1254, 1222, 1174, 1132, 1031, 837, 758, 615, 548 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 3.99 (s, 6H, CH$_3$O), 5.21 (d, $J = 2.6$ Hz, 1H), 6.07 (dd, $J = 8.7$, 2.6 Hz, 1H), 6.65 (dd, $J = 8.7$, 7.5 Hz, 1H), 6.91 (d, $J = 8.7$ Hz, 1H), 7.20 (dd, $J = 8.7$, 7.5 Hz, 1H), 7.21–7.26 (br, 2H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.98–8.08 (br, 2H), 8.41 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (CDCl$_3$): 54.3 (CH$_3$O), 55.5 (CH$_3$O), 109.0, 113.7, 115.1, 118.3, 126.3, 127.8, 128.5, 129.5, 130.5, 132.6, 137.9, 139.3, 140.0, 151.2, 152.7, 158.1, 160.7, 163.0 ppm; Anal. Calcd for $C_{88}H_{68}Cl_2N_8O_8Ir_2 \cdot H_2O$: C, 57.48; H, 3.84; N, 6.09%. Found: C, 57.44; H, 3.91; N, 5.95%.

Synthesis of [{Ir(4-Meqx)$_2$}$_2$(μ-Cl)$_2$] (2d). IrCl$_3 \cdot n$H$_2$O (5.0 mmol) and 2,3-bis(4-methylphenyl)quinoxaline (**1d**, 3.104 g, 10.0 mmol) were stirred in a mixed solvent of 2-ethoxyethanol/water (v/v = 3:1, 100 mL) at 100 °C for 18 h under argon. After the solvent was removed under reduced pressure, ethanol (100 mL) was added to the resulting residue. The precipitate was collected and dried to give 3.572 g (84% yield) of **2d** as a brown solid. Mp: >300 °C; IR (KBr): 3026, 2950, 2918, 2857, 1586, 1509, 1483, 1457, 1388, 1353, 1317, 1235, 1209, 1183, 1140, 1073, 1042, 1020, 980, 828, 809, 756, 730, 613, 512 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.57 (s, 6H, CH$_3$), 5.47 (d, $J = 1.3$ Hz, 1H), 6.28 (dd, $J = 8.4$, 1.3 Hz, 1H), 6.65 (ddd, $J = 8.4$, 6.9, 1.3 Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 7.24 (ddd, $J = 8.4$, 6.9, 1.3 Hz, 1H), 7.42–7.57 (br, 2H), 7.65 (dd, $J = 8.4$, 1.3 Hz, 1H), 7.88–8.03 (br, 2H), 8.35 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl$_3$): 21.2 (CH$_3$), 21.8 (CH$_3$), 122.3, 126.4, 128.3, 128.5, 128.7, 128.9, 129.6, 135.4, 137.3, 137.9, 138.0, 139.5, 140.3, 143.9, 150.5, 151.8, 163.3 ppm.

Synthesis of [Ir(Hqx)$_2$(acac)] (3a). [Ir(Hqx)$_2$(μ-Cl)$_2$] (**2a**, 108.0 mg, 0.07 mmol), acetyl acetone (20 µL, 0.19 mmol), and Na$_2$CO$_3$ (206.4 mg, 1.95 mmol) were stirred in 2-ethoxyethanol (5 mL) at 100 °C for 18 h under argon. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane and washed with water. The organic layer was separated, dried over MgSO$_4$, and evaporated to dryness under reduced pressure. The residue was separated by column chromatography on silica gel using ethyl acetate as an eluent. The obtained solid was washed with ether (5 mL) to give 110.9 mg (95% yield) of **3a** as a black solid. Mp: >300 °C; IR (KBr): 3042, 2986, 2926, 2866, 1577, 1517, 1444, 1425, 1395, 1350, 1319, 1260, 1126, 1068, 1027, 807, 761, 733, 696, 637 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 1.62 (s, 6H, CH$_3$), 4.69 (s, 1H, CH), 6.43 (dd, $J = 8.2$, 1.5 Hz, 2H), 6.52 (td, $J = 8.2$, 1.5 Hz, 2H), 6.61 (ddd, $J = 8.2$, 7.2, 1.5 Hz, 2H), 7.08 (dd, $J = 8.2$, 1.5 Hz, 2H), 7.50 (ddd, $J = 8.2$, 7.2, 1.5 Hz, 2H), 7.61–7.68 (m, 8H), 8.00–8.05 (m, 4H), 8.12 (dd, $J = 8.2$, 1.5 Hz, 2H), 8.42 (dd, $J = 8.2$, 1.5 Hz, 2H); ^{13}C NMR (CDCl$_3$): 28.3 (CH$_3$), 99.9 (CH), 120.6, 125.8, 128.2, 128.7, 128.9, 129.0, 129.6, 130.0, 130.4, 130.8, 136.9, 139.7, 139.9, 141.5, 146.1, 153.2, 154.3, 163.5, 185.7 (CO) ppm; Anal. Calcd for $C_{45}H_{33}IrN_4O_2 \cdot 0.5C_6H_{14}$: C, 64.27; H, 4.49; N, 6.25%. Found: C, 64.42; H, 4.50; N, 6.23%.

Synthesis of [Ir(4-Fqx)$_2$(acac)] (3b). [Ir(4-Fqx)$_2$(μ-Cl)$_2$] (**2b**, 117.3 mg, 0.07 mmol), acetyl acetone (20 µL, 0.19 mmol), and Na$_2$CO$_3$ (206.4 mg, 1.95 mmol) were stirred in 2-ethoxyethanol (5 mL) at 100 °C for 18 h under argon. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane and washed with water. The organic layer was separated, dried over MgSO$_4$, and evaporated to dryness under reduced pressure. The residue was separated by column chromatography on silica gel using ethyl acetate as an eluent. The obtained solid was washed with ether (5 mL) to give 100.5 mg (79% yield) of **3b** as a black solid. Mp: >300 °C; IR (KBr): 3065, 2959, 2921, 1581, 1560, 1508, 1389, 1354, 1311, 1236, 1190, 1158, 1124, 1065, 841, 805, 762, 734, 612, 523 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 1.63 (s, 6H, CH$_3$), 4.71 (s, 1H, CH), 6.05 (dd, $J = 9.1$, 2.2 Hz, 2H), 6.39 (ddd, $J = 9.1$, 6.8, 2.2 Hz, 2H), 7.09 (dd, $J = 9.1$, 5.7 Hz, 2H), 7.30–7.35 (br, 4H), 7.53 (ddd, $J = 9.1$, 6.8, 2.2 Hz, 2H), 7.68 (ddd, $J = 9.1$, 6.8, 1.2 Hz, 2H), 8.00 (br, 6H), 8.11 (dd, $J = 6.8$, 1.2 Hz, 2H), 8.20 (dd, $J = 6.8$, 1.2 Hz, 2H); ^{13}C NMR (CDCl$_3$): 28.3 (CH$_3$), 100.2 (CH), 108.9 ($J_{\text{13C–19F}} = 23$ Hz), 116.2 ($J_{\text{13C–19F}} = 23$ Hz), 122.5 ($J_{\text{13C–19F}} = 18$ Hz), 125.2, 129.2 ($J_{\text{13C–19F}} = 23$ Hz), 130.7, 131.3, 131.8 ($J_{\text{13C–19F}} = 8.9$ Hz), 135.7 ($J_{\text{13C–19F}} = 3.2$ Hz), 139.7, 141.3, 142.0, 156.4 ($J_{\text{13C–19F}} = 7.2$ Hz), 161.5 ($J_{\text{13C–19F}} = 271$ Hz), 162.4, 163.6 ($J_{\text{13C–19F}} = 250$ Hz), 185.8 (CO) ppm; Anal. Calcd for $C_{45}H_{29}IrN_4O_2F_4 \cdot 0.5CH_2Cl_2$: C, 56.43; H, 3.12; N, 5.79%. Found: C, 56.32; H, 3.09; N, 5.73%.

Synthesis of [Ir(4-MeOqx)$_2$(acac)] (3c). [Ir(4-MeOqx)$_2$(μ-Cl)$_2$] (**2c**, 115.6 mg, 0.07 mmol), acetyl acetone (20 µL, 0.19 mmol), and Na$_2$CO$_3$ (206.4 mg, 1.95 mmol) were stirred in 2-ethoxyethanol at 100 °C for 18 h under argon. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane and washed with water. The organic layer was separated, dried over MgSO$_4$, and evaporated to dryness under reduced pressure. The residue was separated by column chromatography on silica gel using ethyl acetate as an eluent. The obtained solid was washed with ether (5 mL) to give 117.9 mg (89% yield) of **3c** as a black solid. Mp: >300 °C; IR (KBr): 3065, 2959, 2922, 2833, 1580, 1560, 1518, 1507, 1457, 1437, 1395, 1303, 1257, 1222, 1175, 1131, 1031, 838, 765, 614 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 1.61 (s, 6H, CH$_3$), 3.94 (s, 12H, CH$_3$O), 4.70 (s, 1H, CH), 5.93 (d, $J = 2.7$ Hz, 2H), 6.24 (dd, $J = 8.6$, 2.7 Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 7.11–7.13 (m, 4H), 7.45 (ddd, $J = 8.6$, 6.8, 1.1 Hz, 2H), 7.57 (ddd, $J = 8.6$, 6.8, 1.1 Hz, 2H), 7.95–7.99 (br, 4H), 8.05 (dd, $J = 8.6$, 1.7 Hz, 2H), 8.23 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl$_3$): 28.3 (CH$_3$), 54.7 (CH$_3$O), 55.5 (CH$_3$O), 100.0 (CH), 107.6, 114.4, 120.9, 125.5, 128.2, 128.7, 129.8, 130.7, 131.5, 132.6, 139.1, 139.4, 141.3, 152.6, 156.7, 158.7, 160.6, 163.2, 185.5 ppm; Anal. Calcd for $C_{49}H_{41}IrN_4O_6$: C, 60.42; H, 4.24; N, 5.75%. Found: C, 60.13; H, 4.41; N, 5.60%.

Synthesis of [Ir(4-Meqx)$_2$(acac)] (3d). [Ir(4-Meqx)$_2$(μ-Cl)$_2$] (**2d**, 115.6 mg, 0.07 mmol), acetyl acetone (20 µL, 0.19 mmol), and Na_2CO_3 (206.4 mg, 1.95 mmol) were stirred in 2-ethoxyethanol at 100 °C for 18 h under argon. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane and washed with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was separated by column chromatography on silica gel using ethyl acetate as an eluent. The obtained solid was washed with ether (5 mL) to give 106.4 mg (86% yield) of **3d** as a black solid. Mp: >300 °C; IR (KBr): 3028, 2927, 2857, 1583, 1560, 1522, 1391, 1352, 1316, 1261, 1183, 1140, 1072, 810, 767, 732, 612, 513 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.59 (s, 6H, CH_3), 2.51 (s, 12H, CH_3), 4.67 (s, 1H, CH), 6.28 (d, $J = 1.1$ Hz, 2H), 6.46 (dd, $J = 8.6$, 1.7 Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 7.40–7.59 (m, 6H), 7.61 (ddd, $J = 8.6$, 6.8, 1.1 Hz, 2H), 7.90–7.93 (br, 4H), 8.09 (dd, $J = 8.6$, 1.7 Hz, 2H), 8.21 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$): 21.5 (CH_3), 21.7 (CH_3), 28.3 (CH_3), 99.9 (CH), 121.9, 125.7, 128.6, 128.7, 129.6, 129.8, 130.0, 137.3, 137.5, 138.4, 139.5, 139.6, 141.5, 143.5, 153.2, 154.6, 163.5, 185.5 (CO) ppm.

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