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Article

Ligand Effects on Luminescence of New Type Blue Light-Emitting Mono(2-phenylpyridinato)iridium(III) Complexes

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Newly prepared hydrido iridium(III) complexes $[Ir(ppy)(PPh_3)_2(H)L]^{0,+}$ (ppy = bidentate 2-phenylpyridinato anionic ligand; L = MeCN (**1b**), CO (**1c**), CN^- (**1d**); H being trans to the nitrogen of ppy ligand) emit blue light at the emission λ_{max} (452−457, 483−487 nm) significantly shorter than those (468, 495 nm) of the chloro complex $Ir(ppy)(PPh_3)_2(H)(Cl)$ (**1a**). Replacing ppy of **1a**−**d** with F_2ppy (2,4-difluoro-2-phenylpyridinato anion) and F_2Meppy (2,4-difluoro-2-phenyl-*m*-methylpyridinato anion) brings further blue-shifts down to the emission λ_{max} at 439−441 and 465−467 nm with CIE color coordinates being $x = 0.16$ and $y = 0.18−0.20$ to display a deep-blue photoemission. No significant blue shift is observed by replacing PPh_3 of **1a** with PPh_2Me to produce $Ir(ppy)(PPh_2Me)_2(H)(Cl)$ (**1a**PPh_2Me), which displays emission λ_{max} at 467 and 494 nm. The chloro complexes, $[Ir(ppy)(PPh_3)_2(Cl)(L)]^{0,+}$ (L = MeCN (**2b**), CO (**2c**), CN^- (**2d**)) having a chlorine ligand trans to the nitrogen of ppy also emit deep-blue light at emission λ_{max} 452−457 and 482−487 nm.

Introduction

Iridium(III) complexes containing 2-phenylpyridinato ligand (ppy, bidentate anionic ligand) have been intensively and extensively studied because they are efficient phosphorescent materials emitting lights in the region of red, green, and blue, which are tuned by modification of ppy as well as by introducing diverse ancillary ligands.[1] There are three different types of ppy-iridium complexes investigated for their photo- and electrical-luminescent properties: tris(ppy)[2] complexes (*fac*-$Ir(ppy)_3$ and *mer*-$Ir(ppy)_3$) and bis(ppy) complexes, *cis*-$Ir(ppy)_2LL'$[3] and *trans*-$Ir(ppy)_2LL'$[4] with the two ppy ligands cis and trans to each other, respectively.

In the course of searching new blue-light emitting materials, we recently began our investigation into another type of complexes containing only one ppy ligand, $Ir(ppy)(PR_3)_2LL'$ with the two phosphines trans to each other and two cis-ancillary ligands L and L′ because there are three different types of ligands ppy, axial ligand PR_3, and ancillary ligands L and L′ that could be modified to control the luminescence characteristics of the complexes. We now wish to report a new type of photoluminescent monoppy Ir(III) complexes $[Ir(C^\wedge N)(PR_3)_2LL']^{0,+}$ ($C^\wedge N$ = ppy, F_2ppy, F_2Meppy; PR_3 = PPh_3, PPh_2Me) emitting deep- and sky-blue light when L and L′ are strong field ligands such as H^-, CO, and CN^- and medium-field ligand MeCN.

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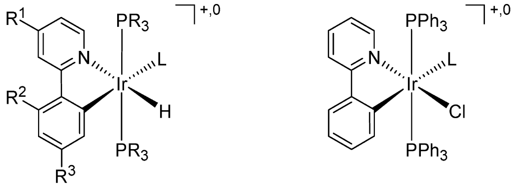

1 **2**

R^1 = H, CH_3; R^2, R^3 = H, F; L = Cl^-, CO, CN^-, NCMe; PR_3 = PPh_3, PPh_2Me

Figure 1. Chemical Structures of $[Ir(C^{\wedge}N)(L)(H)(PR_3)_2]^{0,+}$ (**1**) and $[Ir(ppy)(L)(Cl)(PPh_3)_2]^{0,+}$ (**2**).

No luminescent property has been reported for monoppy iridium(III) complexes, $Ir(ppy)(PR_3)_2LL'$, whereas synthesis of $[Ir(ppy)(PPh_3)_2(H)(CO)]^+$ and analogues were previously reported[5] with no luminescence data. Isoelectronic osmium(II) analogues were reported with photophysical properties.[6] We recently reported that stronger field ancillary ligands L and L′ cause a significant blue shift of the emission λ_{max} for bis(ppy) complexes $Ir(ppy)_2LL'$.[7]

To establish the effects of trans ligands to ppy on the luminescent property, two different series of complexes, **1** and **2**, have been synthesized in this study (below Figure 1). The two ligands, chlorine and hydrogen, have been chosen in this study since (i) both H^- and Cl^- are anionic ligands and (ii) hydride (H^-) is a strong field ligand whereas chloride (Cl^-) is weak one.

Experimental Section

^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian 200 or 300 MHz spectrometer. Nicolet 205 instrument was used to measure infrared spectra. Absorption spectra measured on an Agilent 8453 UV−vis spectrophotometer. Steady-state emission spectra were measured on a JY Horiba Fluorolog-3 spectrofluorimeter. Quantum efficiency was calculated using *fac*-$Ir(ppy)_3$ as the reference in toluene ($\Phi_{PL} = 0.40$).[8] Elemental analysis was carried out using a Carlo Erba EA1180 at the Organic Chemistry Research Center, Sogang University. Color coordinates of luminescence were measured with a Minolta CS-200 chromameter.

X-ray Crystallography. X-ray intensity data were obtained using a Bruker SMART APEX-II CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 and 295 K for **1a**PPh_2Me and **2b**, respectively. Initial unit-cell parameters were obtained from *SMART* software.[9] Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed by *SAINTPLUS*.[10] An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program *SADABS*.[11] Structures were obtained by a combination of the direct methods and difference Fourier syntheses and refined by full matrix least-squares on F^2 using *SHELXTL*.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in calculated positions. Details of crystallographic data collection for **1a**PPh_2Me and **2b** are listed in Table 1.

Synthesis. Schlenk-type glass wares were used in most of experiments for synthesis and measurements although newly prepared complexes are stable in solution to be handled in air. 2-Phenylpyridine (ppyH), PPh_3, PPh_2Me, pyridine, MeCN, AgOTf, tetrabutylammonium cyanide, $Pd(PPh_3)_4$, 2-bromopyridine, 2,4-difluorophenylyboronic acid, and 2-bromo-4-methylpyridine were purchased from Aldrich. F_2ppyH and F_2MeppyH were synthesized by Suzuki coupling reactions.[13] $IrCl_3 \cdot xH_2O$ and CO were obtained from Pressure Chemicals and Dong-A Gas Co., Korea, respectively. Iridium complexes, $[Ir(ppy)(H)(NCMe)(PPh_3)_2]^+$ (**1b**)[14] and $[Ir(COD)Cl]_2$[15] were synthesized by the literature methods. **1a**, **1a**F_2, **1a**F_2Me, and **1a**PPh_2Me have been prepared practically by the same method described below for **1a**.

Synthesis of $Ir(ppy)(H)(Cl)(PPh_3)_2$ (1a). A reaction mixture of $[Ir(COD)Cl]_2$ (0.1 g, 0.14 mmol), PPh_3 (0.15 g, 0.56 mmol), and ppyH (43 mg, 0.28 mmol) in 2-ethoxyethanol (10 mL) was refluxed under N_2 (1 atm) for six hours. After cooling down to 25 °C, the yellow precipitate was filtered off and washed with methanol (3 × 10 mL), recrystallized in $CHCl_3$/*n*-pentane, and dried under vacuum. The yield was 0.23 g and 93% based on **1a**. ^1H NMR (300 MHz; $CDCl_3$): δ 8.93 (d, $J = 5.4$ Hz, 1H), 7.38−7.32 (m, 15H), 7.16 (t, $J = 7.2$ Hz, 6H), 7.11−7.06 (m, 13H), 6.63−6.55 (m, 1H), 6.36 (d, $J = 7.8$ Hz, 2H), 5.96 (t, $J = 7.2$ Hz, 1H), −16.72 (t, $J = 16.8$ Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.51, 149.75, 148.04, 143.61, 142.44, 135.42, 134.18, 131.92, 130.17, 129.02, 127.34, 122.49, 120.57, 119.35, 117.30. ^{31}P NMR (81 MHz, $CDCl_3$): δ 10.56. (s). IR (KBr, cm^{-1}): 2130 (m, ν_{Ir-H}). Anal. Calcd for $IrC_{47}NH_{39}ClP_2$: C, 62.21; H, 4.33; N, 1.54. Found: C, 62.18; H, 4.39; N, 1.53.

$Ir(F_2ppy)(H)(Cl)(PPh_3)_2$ (1aF_2). ^1H NMR (300 MHz; $CDCl_3$): δ 9.00 (d, $J = 5.1$ Hz, 1H), 7.82 (d, $J = 8.7$ Hz, 1H), 7.41−7.35 (m, 13H), 7.21 (t, $J = 6.9$ Hz, 6H), 7.16−7.10 (m, 12H), 6.68 (t, $J = 5.7$ Hz, 1H), 6.04−5.97 (m, 1H), 5.76 (d, $J = 9.0$ Hz, 1H), −16.76 (t, $J = 16.5$ Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 162.82, 150.06, 146.82, 141.81, 136.20, 134.12, 131.78, 131.42, 131.07, 129.40, 127.50, 94.65. ^{19}F NMR (188.2 MHz, $CDCl_3$): δ −110.42 (q, $J = 9.2$ Hz, 1F), −112.75 (t, $J = 6.7$ Hz, 1F). ^{31}P NMR (81 MHz, $CDCl_3$): δ 9.02 (s). IR (KBr, cm^{-1}): 2155 (m, ν_{Ir-H}). Anal. Calcd for $IrC_{47}NH_{37}F_2ClP_2$: C, 59.84; H, 3.95; N, 1.48. Found: C, 59.80; H, 3.92; N, 1.50.

$Ir(F_2Meppy)(H)(Cl)(PPh_3)_2$ (1aF_2Me). ^1H NMR (300 MHz; $CDCl_3$): δ 8.85 (d, $J = 5.4$ Hz, 1H), 7.67 (s, 1H), 7.43−7.37 (m, 12H), 7.22 (t, $J = 7.2$ Hz, 6H), 7.16−7.11 (m, 12H), 6.55 (d, $J = 5.4$ Hz, 1H), 6.04−5.96 (m, 1H), 5.77(d, $J = 9.3$ Hz, 1H), 2.32 (s, 3H), −16.79 (t, $J = 16.5$ Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 161.89, 154.93, 149.36, 147.63, 149.36, 147.63, 134.13, 131.55, 129.32, 127.43, 125.33, 122.62, 121.87, 95.22, 21.32. ^{19}F NMR (188.2 MHz, $CDCl_3$): δ −110.90 (q, $J = 10.0$ Hz, 1F), −112.89 (t, $J = 11.5$ Hz, 1F). ^{31}P NMR (81 MHz, $CDCl_3$): δ 8.87 (s). IR (KBr, cm^{-1}): 2127 (m, ν_{Ir-H}). Anal. Calcd for $IrC_{48}NH_{39}F_2ClP_2$: C, 60.21; H, 4.11; N, 1.46. Found: C, 60.25; H, 4.16; N, 1.47.

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Table 1. Details of Crystallographic Data Collection for **1a**PPh_2Me and **2b**

	1a$PPh_2Me \cdot CHCl_3$[a]	**2b**$\cdot CHCl_3$
chemical formula	$IrC_{38}H_{36}Cl_4NP_2$	$IrC_{51}H_{42}Cl_4F_3N_2O_3P_2S$
chemical fw	902.62	1215.87
T, K	173(2)	295(2)
cryst dimensions, mm^3	0.10 × 0.08 × 0.07	0.08 × 0.05 × 0.04
cryst syst	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/c$
color of crystal	pale yellow	pale yellow
a, Å	13.4805(2)	10.4325(8)
b, Å	18.7541(3)	22.5809(16)
c, Å	14.7961(2)	21.5244(16)
α, deg	90	90
β, deg	103.0790(10)	91.132(2)
γ, deg	90	90
V, $Å^3$	3643.63(9)	5069.6(6)
Z	4	4
ρ_{calcd}, $g \cdot cm^{-1}$	1.645	1.593
μ, mm^{-1}	4.074	3.004
$F(000)$	1784	2416
θ range, deg	1.78 to 28.29	1.31 to 26.00
hkl range	$-17 \le h \le 17$	$-12 \le h \le 12$
	$-22 \le k \le 25$	$-27 \le k \le 27$
	$-16 \le l \le 19$	$-26 \le l \le 26$
no. of reflns	38 680	64 298
no. of unique data	9028	9955
completeness to theta	99.8% at 28.29 deg	99.9% at 26.00 deg
no. of data/restraints/params	9028/0/419	9955/0/590
refinements method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
R1	0.0278	0.0527
wR2	0.0513	0.1242
GOF	1.016	1.033

[a] $R1 = [\sum|F_o| - |F_c|/|F_o|]$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$; $w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 1.8667P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Ir(ppy)(H)(Cl)(PPh$_2$Me)$_2$ (1aPPh$_2$Me). ^1H NMR (300 MHz; $CDCl_3$): δ 8.59 (d, J = 5.4 Hz, 1H), 7.43−7.32 (m, 6H), 7.27−7.04 (m, 18H), 6.75 (d, J = 7.4 Hz, 1H), 6.61−6.50 (m, 2H), 1.60 (t, J = 3.8 Hz, 6H), −16.74 (t, J = 15.6 Hz, 1H). ^{31}P NMR (81 MHz, $CDCl_3$): δ −3.29. (s). IR (KBr, cm^{-1}): 2156 (m, ν_{Ir-H}). Anal. Calcd for $IrC_{37}NH_{35}ClP_2$: C, 56.73; H, 4.50; N, 1.79. Found: C, 56.71; H, 4.53; N, 1.79.

1c, 1cF_2, and **1c**F_2Me have been prepared practically by the same method described below for **1c**.

Synthesis of [Ir(ppy)(H)(CO)(PPh$_3$)$_2$](OTf) (1c). A 0.1 g (0.09 mmol) of **1b** in CH_2Cl_2 (10 mL) was stirred under CO (1 atm) at 25 °C for 12 h before *n*-pentane (30 mL) was added to precipitate white microcrystals, which were isolated by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 90 mg and 92% based on **1c**. ^1H NMR (300 MHz; CD_2Cl_2): δ 8.89 (d, J = 5.4 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.38−7.02 (m, 35H), 6.65 (t, J = 6.6 Hz, 1H), −15.38 (t, J = 12.3 Hz, 1H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 173.99, 169.98, 163.98, 153.46, 152.84, 147.10, 142.86, 138.45, 133.50, 131.33, 130.05, 128.60, 127.74, 125.91, 124.85, 122.83, 120.67, 118.56. ^{31}P NMR (81 MHz, $CDCl_3$): δ 6.15. (s). IR (KBr, cm^{-1}): 2195 (m, ν_{Ir-H}), 2042 (s, $\nu_{C'O}$), 1270, 1153 and 1031 (s, OTf^-). Anal. Calcd for $IrC_{49}NH_{39}F_3O_4SP_2$: C, 56.10; H, 3.75; N, 1.34. Found: C, 56.16; H, 3.78; N, 1.32.

[Ir(F$_2$ppy)(H)(CO)(PPh$_3$)$_2$](OTf) (1cF$_2$). ^1H NMR (300 MHz; CD_2Cl_2): δ 9.04 (d, J = 5.4 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 6.9 Hz, 6H), 7.34−7.29 (m, 12H), 7.24−7.15 (m, 14H), 6.53 (t, J = 8.1 Hz, 1H), 6.43−6.37 (m, 1H), −15.50 (t, J = 12.0 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 173.92, 161.06, 154.17, 139.20, 133.71, 132.01, 129.07, 127.41, 124.95, 124.86, 124.78, 124.45, 100.71. ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −107.31 (t, J = 11.5 Hz, 1F), −107.82 (q, J = 9.2 Hz, 1F). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 6.17. (s). IR (KBr, cm^{-1}): 2194 (m, ν_{Ir-H}), 2052 (s, $\nu_{C'o}$), 1265, 1153 and 1031 (s, OTf^-). Anal. Calcd for $IrC_{49}NH_{37}F_5O_4SP_2$: C, 54.24; H, 3.44; N, 1.29. Found: C, 54.29; H, 3.49; N, 1.30.

[Ir(F$_2$Meppy)(H)(CO)(PPh$_3$)$_2$](OTf) (1cF$_2$Me). ^1H NMR (300 MHz; CD_2Cl_2): δ 8.89 (d, J = 5.7 Hz, 1H), 7.44 (t, J = 7.2 Hz, 6H), 7.33 (t, J = 7.5 Hz, 12H), 7.24−7.18 (m, 13H), 7.10 (d, J = 5.7 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 6.41 (t, J = 10.2 Hz, 1H), 2.32 (s, 3H), −15.46 (t, J = 12.3 Hz, 1H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 173.88, 160.50, 153.34, 151.62, 133.75, 131.91, 128.99, 127.53, 125.82, 125.38, 124.89, 100.62, 21.37. ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −107.41 (t, J = 10.7 Hz, 1F), −108.29 (q, J = 9.0 Hz, 1F). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 6.12. (s). IR (KBr, cm^{-1}): 2184 (m, ν_{Ir-H}), 2052 (s, $\nu_{C'O}$), 1261, 1151 and 1031 (s, OTf^-). Anal. Calcd for $IrC_{50}NH_{39}F_5O_4SP_2$: C, 54.64; H, 3.58; N, 1.27. Found: C, 54.68; H, 3.60; N, 1.24.

1d, 1dF_2, and **1d**F_2Me have been prepared practically by the same method described below for **1d**.

Synthesis of Ir(ppy)(H)(CN)(PPh$_3$)$_2$ (1d). A reaction mixture of $[Ir(ppy)(H)(NCMe)(PPh_3)_2](OTf)$ (**1b**, 0.10 g, 0.09 mmol) and tetrabutylammonium cyanide (27 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was stirred under N_2 (1 atm) at 25 °C for three hours until the pale-yellow solution turned bright yellow. Addition of *n*-pentane (30 mL) to the resulting solution yielded yellow microcrystals, which were isolated by filtration, washed with methanol (3 × 10 mL), and dried under vacuum. The yield was 78 mg and 92% based on **1d**. ^1H NMR (300 MHz; $CDCl_3$): δ 8.83 (d, J = 5.1 Hz, 1H), 7.40−7.34 (m, 12H), 7.24−7.09 (m, 21H), 6.67 (t, J = 8.1 Hz, 2H), 6.45 (td, J = 7.8, 1.8 Hz, 1H), 6.18 (t, J = 7.2 Hz, 1H), −17.45 (t, J = 15.6 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 166.20, 159.24, 152.50, 145.73, 144.85, 135.26, 133.95, 131.92, 129.54, 129.28, 127.52, 123.10, 121.16, 120.52, 118.09. ^{31}P NMR (81 MHz, $CDCl_3$): δ 12.85. (s). IR (KBr, cm^{-1}): 2130 (m, ν_{Ir-H}), 2101 (s, ν_{CN}). Anal. Calcd for $IrC_{48}N_2H_{39}P_2$: C, 64.20; H, 4.38; N, 3.12. Found: C, 64.26; H, 4.34; N, 3.15.

$Ir(F_2ppy)(H)(CN)(PPh_3)_2$ (1dF$_2$). ^1H NMR (300 MHz; $CDCl_3$): δ 8.91 (d, J = 5.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.43−7.34 (m, 12H), 7.27−7.15 (m, 19H), 6.53 (t, J = 6.9 Hz, 1H), 6.12−6.04 (m, 1H), 6.02 (t, J = 9.0 Hz, 1H), −17.62 (t, J = 15.9 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 162.85, 152.91, 136.06, 133.88, 131.40, 129.63, 127.67, 125.86, 122.46, 122.16, 121.39, 100.11, 96.45. ^{19}F NMR (188.2 MHz, $CDCl_3$): δ −113.33 (q, J = 9.0 Hz, 1F), −114.73 (t, J = 6.7 Hz, 1F). ^{31}P NMR (81 MHz, $CDCl_3$): δ 9.33 (s). IR (KBr, cm^{-1}): 2147 (m, ν_{Ir-H}), 2106 (s, ν_{CN}). Anal. Calcd for $IrC_{48}N_2H_{37}F_2P_2$: C, 61.73; H, 3.99; N, 3.00. Found: C, 61.77; H, 4.02; N, 2.98.

$Ir(F_2Meppy)(H)(CN)(PPh_3)_2$ (1dF$_2$Me). ^1H NMR (300 MHz; $CDCl_3$): δ 8.73 (d, J = 5.1 Hz, 1H), 7.55 (s, 1H), 7.39−7.36 (m, 12H), 7.22−7.14 (m, 18H), 6.38 (d, J = 4.8 Hz, 1H), 6.09−6.01 (m, 1H), 5.99 (d, J = 9.6 Hz, 1H), 2.26 (s, 3H), −17.67 (t, J = 15.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 162.44, 152.29, 147.67, 133.95, 131.55, 129.60, 127.64, 125.92, 123.48, 122.55, 100.14, 96.42, 21.29. ^{19}F NMR (188.2 MHz, $CDCl_3$): δ −113.73 (q, J = 5.8 Hz, 1F), −114.79 (t, J = 6.7 Hz, 1F). ^{31}P NMR (81 MHz, $CDCl_3$): δ 9.16 (s). IR (KBr, cm^{-1}): 2140 (m, ν_{Ir-H}), 2104 (s, ν_{CN}). Anal. Calcd for $IrC_{49}N_2H_{39}F_2P_2$: C, 62.08; H, 4.15; N, 2.95. Found: C, 62.02; H, 4.17; N, 2.97.

Synthesis of $Ir(ppy)(Cl)_2(PPh_3)_2$ (2a). A reaction mixture of $IrCl_3 \cdot xH_2O$ (0.1 g, 0.33 mmol), PPh_3 (0.26 g, 1 mmol), and ppyH (0.16 g, 1 mmol) in 2-ethoxyethanol (30 mL) and water (10 mL) was refluxed under N_2 (1 atm) for 12 h. After cooling down to 25 °C, the yellow precipitate was filtered off and washed with methanol (10 mL) and dichloromethane (60 mL) and dried under vacuum. The yield was 0.19 g and 61% based on **2a**. ^1H NMR (300 MHz; CD_2Cl_2): δ 8.57 (d, J = 5.7 Hz, 1H), 7.43−7.37 (m, 13H), 7.30−7.17 (m, 8H), 7.14−7.04 (m, 13H), 6.79 (t, J = 7.5 Hz, 1H), 6.43 (t, J = 7.5 Hz, 1H), 6.08 (t, J = 7.5 Hz, 1H). ^{31}P NMR (81 MHz, CD_2Cl_2): δ −15.28 (s).

Synthesis of $[Ir(ppy)(Cl)(NCMe)(PPh_3)_2](OTf)$ (2b). A reaction mixture of $Ir(ppy)(Cl)_2(PPh_3)_2$ (**2a**, 0.10 g, 0.10 mmol) and AgOTf (26 mg, 0.10 mmol) in $CHCl_3$ (10 mL) in the presence of MeCN (1.0 mL) was stirred under nitrogen at 25 °C for two hours, and the white precipitate (AgCl) was removed by filtration. A 1.0 mL of MeCN was added into the filtrate solution, and the resulting solution was stirred further for two hours under N_2 before *n*-pentane (30 mL) was added to yield pale-yellow microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.11 g or 95% based on **2b**. ^1H NMR (300 MHz; $CDCl_3$): δ 8.66 (d, J = 5.7 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.30−7.22 (m, 18H), 7.18−7.13 (m, 13H), 7.10−6.96 (m, 3H), 6.85−6.76 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.51, 153.08, 145.02, 138.10, 137.57, 137.19, 134.36, 133.82, 128.09, 127.27, 125.07, 123.74, 123.54, 123.06, 118.99, 118.18, 4.10. ^{31}P NMR (81 MHz, $CDCl_3$): δ −14.77 (s). IR (KBr, cm^{-1}): 2286 (m, $\nu_{N'C_{Me}}$), 1277, 1150 and 1031 (s, OTf^-). Anal. Calcd for $IrC_{50}N_2H_{41}ClF_3O_3SP_2$: C, 54.77; H, 3.77; N, 2.55. Found: C, 54.78; H, 3.80; N, 2.58.

Synthesis of $[Ir(ppy)(Cl)(CO)(PPh_3)_2](OTf)$ (2c). A 0.1 g (0.09 mmol) of **2b** in CH_2Cl_2 (10 mL) was stirred under CO (1 atm) at 25 °C for 12 h before *n*-pentane (30 mL) was added to precipitate white microcrystals, which were isolated by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 94 mg and 95% based on **2c**. ^1H NMR (300 MHz; $CDCl_3$): δ 7.51 (d, J = 6.0 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.02−6.97 (m, 6H), 6.89−6.77 (m, 26H), 6.61 (d, J = 7.8 Hz, 1H), 6.41 (t, J = 7.8 Hz, 1H), 6.30 (t, J = 6.0 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 173.23, 165.16, 153.38, 150.91, 144.67, 139.71, 136.56, 134.32, 134.00, 133.56, 132.05, 131.56, 130.41, 128.68, 128.17, 127.08, 126.69, 126.30, 126.13, 126.03, 124.15, 120.77. ^{31}P NMR (81 MHz, $CDCl_3$): δ −13.01 (s). IR (KBr, cm^{-1}): 2056 (s, $\nu_{C'O}$), 1271, 1152 and 1031 (s, OTf^-). Anal. Calcd for $IrC_{49}NH_{38}ClF_3O_4SP_2$: C, 54.32; H, 3.53; N, 1.29. Found: C, 54.36; H, 3.50; N, 1.28.

Synthesis of $Ir(ppy)(Cl)(CN)(PPh_3)_2$ (2d). A reaction mixture of $[Ir(ppy)(Cl)(NCMe)(PPh_3)_2](OTf)$ (**2b**, 0.10 g, 0.09 mmol) and tetrabutylammonium cyanide (27 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was stirred under N_2 (1 atm) at 25 °C for three hours before the pale-yellow solution turned bright yellow. Addition of *n*-pentane (30 mL) to the resulting solution yielded yellow microcrystals, which were isolated by filtration, washed with methanol (3 × 10 mL), and dried under vacuum. The yield was 80 mg and 94% based on **2d**. ^1H NMR (300 MHz; CD_2Cl_2): δ 8.30 (d, J = 6.0 Hz, 1H), 7.43−7.37 (m, 13H), 7.32−7.20 (m, 8H), 7.13−7.08 (m, 13H), 6.89 (t, J = 7.5 Hz, 1H), 6.60 (t, J = 7.5 Hz, 1H), 5.99 (t, J = 7.5 Hz, 1H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 167.92, 155.46, 153.75, 145.09, 137.98, 136.37, 134.80, 130.59, 130.24, 129.93, 127.72, 122.88, 122.63, 122.55, 118.17. ^{31}P NMR (81 MHz, CD_2Cl_2): δ −12.58 (s). IR (KBr, cm^{-1}): 2103 (s, ν_{CN}). Anal. Calcd for $IrC_{48}N_2H_{38}ClP_2$: C, 61.83; H, 4.11; N, 3.00. Found: C, 61.856; H, 4.13; N, 3.02.

Results and Discussion

Synthesis and Charaterizations. New cationic and neutral monocyclometalated iridium(III) complexes, $[Ir(C\^{}N)(PR_3)_2LL']^{0,+}$ (**1** and **2**) have been prepared according to procedures depicted by Schemes 1 and 2, characterized by detailed NMR (^1H, ^{13}C, ^{19}F, ^{31}P), IR, and elemental analysis data, and also by X-ray diffraction data analysis for the crystals of $Ir(ppy)(PPh_2Me)_2(H)(Cl)$ (**1a**PPh$_2$Me) and $[Ir(ppy)(PPh_3)_2(Cl)(NCMe)]^+$ (**2b**). The crystal structure of **1a**PPh$_2$Me (Figure 2) unambiguously shows the Cl ligand being trans to the carbon atom of the phenyl ring of the ppy ligand, whereas Figure 3 shows the chlorine ligand being trans to the nitrogen of pyridyl ring in **2b**. The Ir−Cl distance is significantly shorter in **2b** (2.3882 Å) than in **1a**PPh$_2$Me (2.4943 Å), probably due to the higher trans effect of the carbon ligand in **1a**PPh$_2$Me, whereas the Ir−P distance is longer for **2b** (2.390 Å) than in **1a**PPh$_2$Me (2.305 Å), which may be understood by PPh_2Me being less bulky and more basic than is PPh_3.

Luminescence Properties. Ancillary Ligand (L and L′) Effects. Knowing that d orbitals of iridium are involved in the HOMO of ppy complexes such as $Ir(ppy)_3$ and $Ir(ppy)_2LL'$,[16] one could expect the HOMO energy level being lowered by strong field ligands more than by weak field ligands. Table 2 summarizes photoluminescence data for **1** and **2**. Significantly longer wavelength emission λ_{max} are measured for the two complexes **1a** and **2a** that contain a chlorine ligand trans to the carbon of the ppy ligand, whereas the emission λ_{max} is measured at much shorter wavelengths for all other complexes **1b**−**d** without the chlorine ligand and **2b**−**d** that contain a chlorine ligand trans to the nitrogen of the ppy ligand (Table 2). The weak field ligand chlorine does not seem to play a role of lowering d orbitals of iridium when it is in trans position to the strong field ligand atom carbon of ppy as in **1a** and **2a**, whereas no

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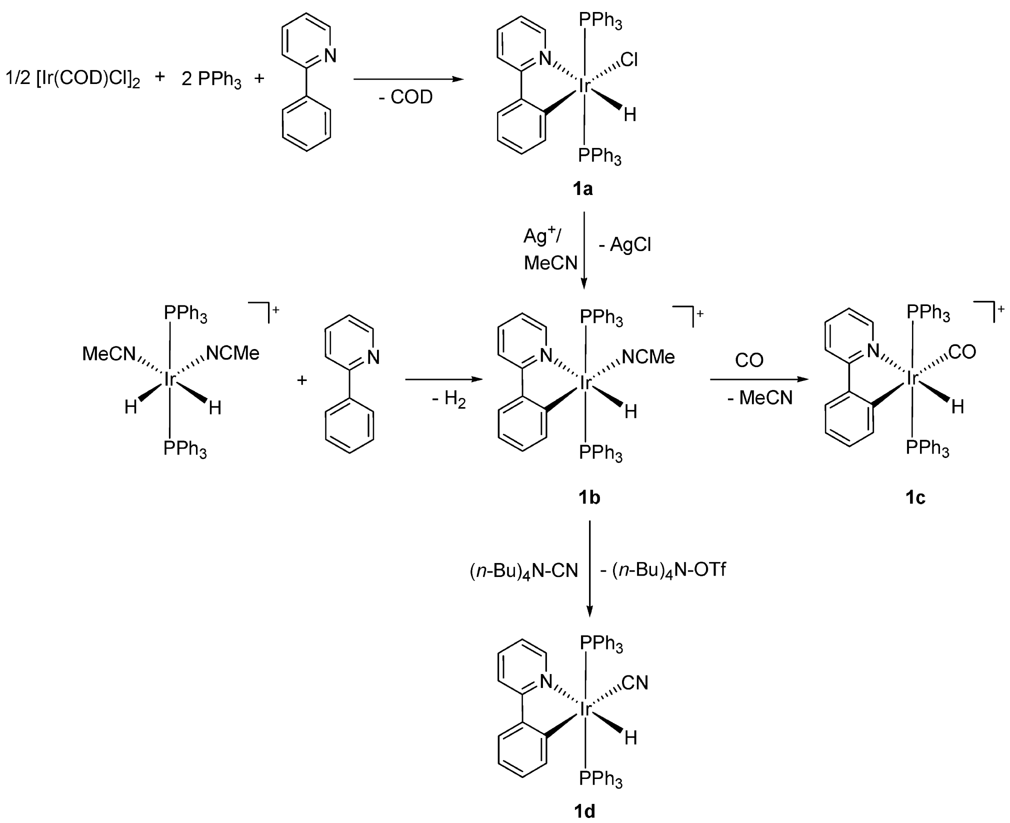
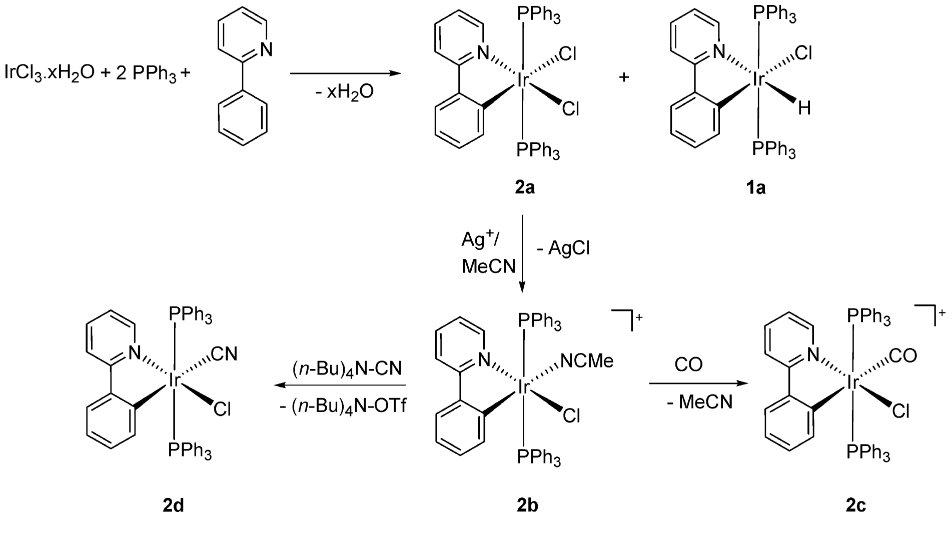
(16) Hay, P. J. *J. Phys. Chem. A* **2002**, *106*, 1634–1641.

Scheme 1. Synthesis of $[Ir(ppy)(H)(L)(PPh_3)_2]^{+,0}$ (**1a**−**d**)



Scheme 2. Synthesis of $[Ir(ppy)(Cl)(L)(PPh_3)_2]^{+,0}$ (**2a**−**d**)



such different effect has been measured between weak field ligand chlorine (**2b**−**2d**) and strong field ligand hydrogen (**1b**−**1d**) when chlorine and hydrogen are trans to the medium ligand atom nitrogen of ppy. It may now be said that blue color photoemission could be obtained by introducing a strong field ligand in the trans position to the carbon atom of the ppy ligand.

The quantum yield is known to decrease with shifting emission λ_{max} to shorter wavelength[17] and to be low for complexes having chlorine.[18] Very low Φ_{PL} are also measured in this study for complexes having two chlorine ligands. It is also noticed that **1** and **2** show lower quantum yields than the other types of complexes, $Ir(ppy)_3$[2] and $Ir(ppy)_2LL'$.[3]

Axial and Trans Ligand (PR$_3$) Effects. PPh_2Me is more basic and less bulky than is PPh_3 and makes a stronger bond with metal as seen in crystal structures of **1a**PPh_2Me (Ir−P: 2.30 Å, Figure 2) and **2b** (Ir−P: 2.39 Å, Figure 3). No significant change in photoluminescent characteristics has been observed between **1a** (emission λ_{max} at 468, 495 nm;

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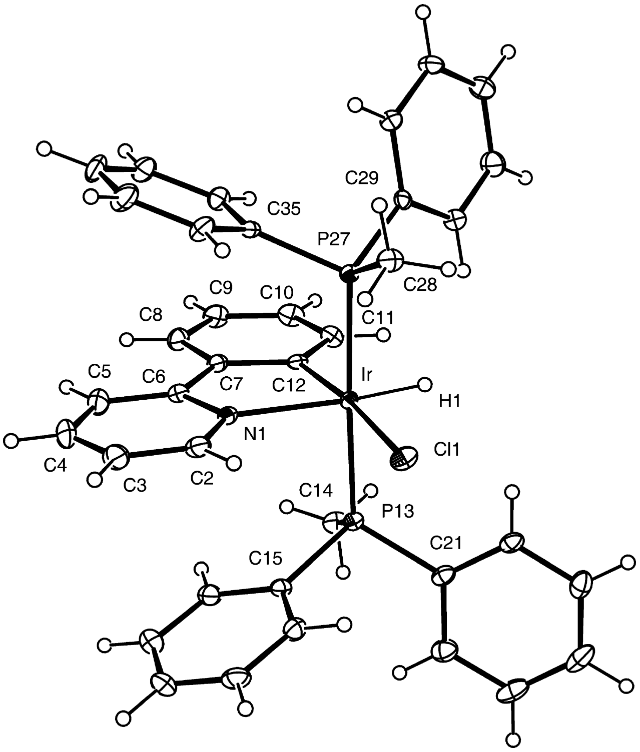

Figure 2. ORTEP of Ir(ppy)$(PPh_2Me)_2$(H)(Cl) (**1a**PPh_2Me) with 30% thermal ellipsoids probability. Bond distances (Å): Ir−N(1), 2.140(2); Ir−C(12), 2.013(3); Ir−H(1), 1.41(3); Ir−Cl(1), 2.4943(7); Ir−P(13), 2.3053(8); Ir−P(27), 2.3053(8). Bond angle (deg): N(1)−Ir−H(1), 173.8(11); C1(2)−Ir−Cl(1), 174.09 (8); P(13)−Ir−P(27), 177.31(3).

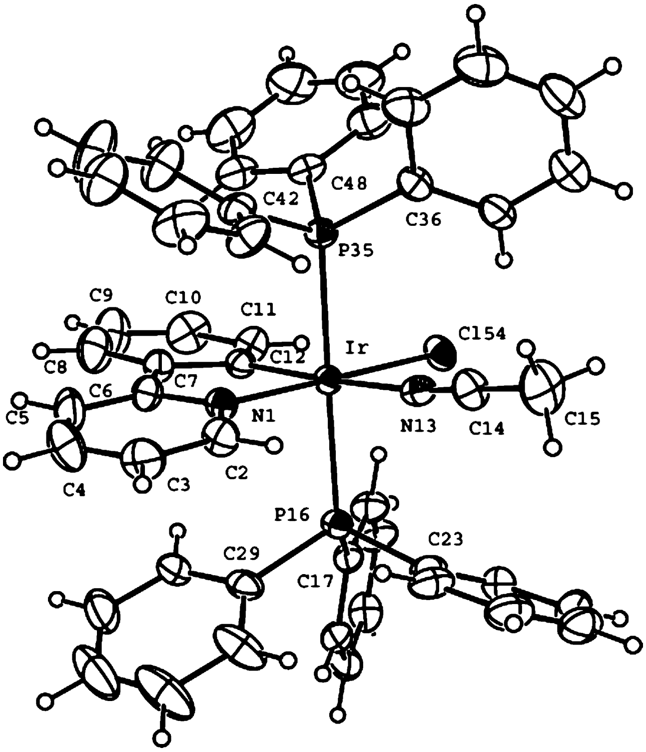

Figure 3. ORTEP of $[Ir(ppy)(PPh_3)_2(Cl)(NCMe)]^+$ (**2b**) with 30% thermal ellipsoids probability. Bond distances (Å): Ir−N(1), 2.051(6); Ir−C(12), 2.018(8); Ir−Cl(54), 2.3882(19); Ir−N(13), 2.129(7); Ir−P(16), 2.389(2); Ir−P(35), 2.391(2). Bond angle (deg): N(1)−Ir−Cl(54), 176.00(19); C(12)−Ir−N(13), 174.6(3); P(16)−Ir−P(35), 178.70(7).

$\Phi_{PL} = 0.11$) and **1a**PPh_2Me (emission λ_{max} at 467, 494 nm; $\Phi_{PL} = 0.10$) prepared by replacing the axial ligand PPh_3 of **1a** with PPh_2Me. This result may be understood by that the trans and axial ligand PR_3 is not involved in the HOMO of **1**, which is predicted by DFT calculations[19] and also by a theoretical study on $[trans\text{-}Ir(C^\wedge N)_2(PH_3)_2]^+$, showing that the axial ligand PH_3 barely affects the occupied MOs.[4b]

Table 2. Emission Spectral Data for $[Ir(ppy)(PPh_3)_2(H)(L)]^{0,+}$ (**1**) and $[Ir(ppy)(PPh^{3})_2(Cl)(L)]^{0,\ +}$ (**2**) in Degassed CH_2Cl_2 at 25 °C

compound number	L	λ_{max} (nm)	Φ_{PL}	CIE (*x*, *y*)
1a	Cl	468, 495	0.110	0.18, 0.39
1b	NCMe	456, 487	0.075	0.18, 0.32
1c	CO	452, 483	0.140	0.18, 0.30
1d	CN	457, 487	0.170	0.17, 0.27
2a	Cl	468, 494	0.008	0.18, 0.39
2b	NCMe	455, 486	0.066	0.18, 0.32
2c	CO	452, 482	0.066	0.18, 0.30
2d	CN	457, 487	0.028	0.17, 0.27

Table 3. Emission Spectral Data for $[Ir(C^\wedge N)(PPh_3)_2(H)(L)]^{0,+}$ in Degassed CH_2Cl_2 at 25 °C

compound number	*C^N*	L	λ_{max} (nm)	Φ_{PL}	CIE (*x*, *y*)
1a	ppy	Cl	468, 495	0.110	0.18, 0.39
1aF_2	F_2ppy	Cl	448, 475	0.057	0.16, 0.20
1aF_2Me	F_2Meppy	Cl	446, 473	0.053	0.16, 0.19
1b	ppy	MeCN	456, 487	0.075	0.18, 0.32
1bF_2	F_2ppy	MeCN	441, 470	0.220	0.16, 0.21
1bF_2Me	F_2Meppy	MeCN	439, 467	0.140	0.16, 0.20
1c	ppy	CO	452, 483	0.140	0.18, 0.30
1cF_2	F_2ppy	CO	441, 469	0.200	0.16, 0.20
1cF_2Me	F_2Meppy	CO	439, 465	0.170	0.16, 0.19
1d	ppy	CN	457, 487	0.170	0.17, 0.27
1dF_2	F_2ppy	CN	441, 467	0.500	0.16, 0.19
1dF_2Me	F_2Meppy	CN	439, 465	0.430	0.16, 0.18

Effects of Modification of ppy. According to DFT calculations, the HOMO is an admixture of π-orbitals of phenyl ring of ppy and d-orbitals of metal and the LUMO is primarily π-orbitals of pyridyl ring of ppy ligand. Electron withdrawing groups on the phenyl ring, therefore, would lower the HOMO energy level, whereas electron donation groups on the pyridyl ring would raise the LUMO energy level.[20]

Table 3 summarizes photoemission characteristics of **1** with modified ppy ligands. Modification of the ppy ligand seems to be an efficient method to make emission λ_{max} of **1** shifted to shorter wavelength. Well-studied ppy derivatives such as F_2ppy and F_2Meppy are good enough to make significant blue-shifts for complexes of F_2ppy and F_2Meppy to display blue color emission.

Figure 4 shows both of the two emission peaks blue shifted by modification of ppy to F_2ppy and F_2Meppy. Those two emission peaks for F_2ppy and F_2Meppy complexes in the ranges of 439−448 and 465−475 nm make their CIE coordinates to be $x = 0.16$ and $y = 0.18-0.21$, representing deep and sky blue color (Table 3 and Figure 5).

It is striking to see such large decreases in CIE coordinates especially for *y* values from 0.27−0.39 down to 0.18−0.21 by modification of ppy to F_2ppy and F_2Meppy, whereas the *x* value shows only slight decreases from 0.17−0.18 down to 0.16−0.17 for all complexes of F_2ppy and

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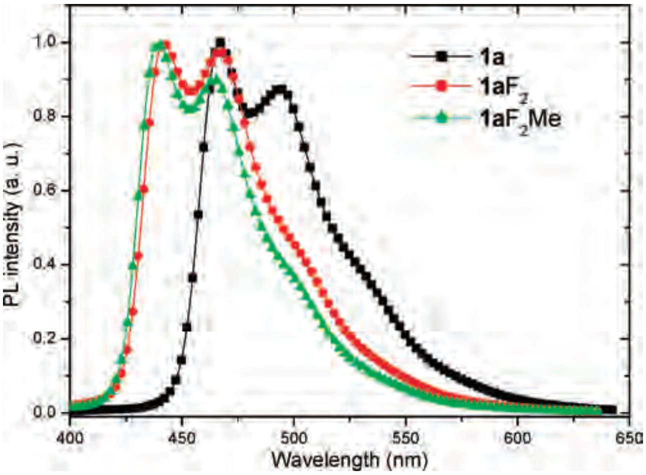
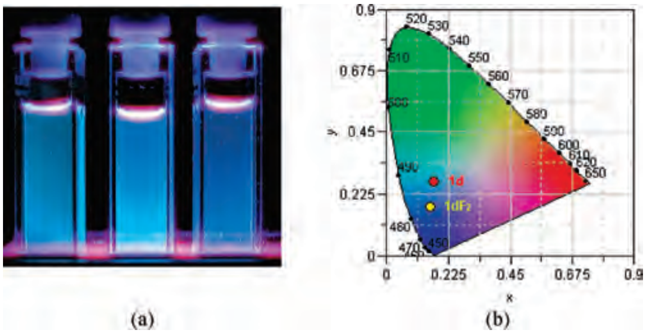


Figure 4. Normalized emission spectra of Ir(ppy)$(PPh_3)_2$(H)(Cl) (**1a**) (-■-■-), Ir(F_2ppy)$(PPh_3)_2$(H)(Cl) (**1aF**$_2$) (-●-●-), and Ir(F_2Meppy)$(PPh_3)_2$(H)(Cl) (**1aF**$_2$Me) (-▲-▲-) in degassed CH_2Cl_2 at 25 °C.



(a) (b)

Figure 5. (a) From left, photoemission cells containing Ir(ppy)$(PPh_3)_2$-(H)(CN) (**1d**), Ir(F_2ppy)$(PPh_3)_2$(H)(CN) (**1dF**$_2$), and Ir(F_2Meppy)$(PPh_3)_2$-(H)(CN) (**1dF**$_2$Me) in CH_2Cl_2. (b) CIE coordinates for **1d** and **1dF**$_2$ (**1dF**$_2$Me is not shown as it is practically the same with **1dF**$_2$).

F_2Meppy. Such low values in both x (0.16−0.17) and y (0.18−0.21) of CIE coordinates obtained in this study are, to the best our knowledge, unprecedented for Ir-ppy complexes, whereas some bis-ppy iridium and related complexes show relatively low CIE coordinates at x = 0.16−0.17 and y = 0.26−0.32.[21]

We also mention here that our preliminary experimental data (Supporting Information) obtained from the OLED device fabricated with **1aF**$_2$ show the electro emission λ_{max} at quite a short wavelength (439 nm), whereas **1aF**$_2$ emits the photo emission at 448 and 475 nm in Table 2.

Summary

Significant blue-shifts of emission λ_{max} have been obtained by replacing the weak-field ligand chlorine of Ir(ppy)$(PPh_3)_2$(H)(Cl) (where hydrogen is trans to the nitrogen of ppy) with stronger field ligands L′ to produce [Ir(ppy)$(PPh_3)_2$(H)(L′)]$^{0,+}$ (L′ = CO, CN$^-$, MeCN), which emit blue color. Blue light emission (λ_{max} = 452−457, 482−487 nm) is also obtained by replacing only one chlorine ligand that is trans to the carbon of ppy in the dichloro complex Ir(ppy)$(PPh_3)_2$$(Cl)_2$ and introducing ancillary field ligands L to produce [Ir(ppy)$(PPh_3)_2$(Cl)(L)]$^{0,+}$ (L = MeCN, CO, CN$^-$). Further blue shifts (13−22 nm) of the emission λ_{max} are measured by modification of the ppy ligand for F_2ppy and F_2Meppy complexes to display deep and sky-blue color with CIE coordinates of (x = 0.16, y = 0.18−0.21).

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Supporting Information Available: X-ray crystallographic data in CIF format and ^{1}H and ^{13}C NMR spectra and OLED studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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