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Blue Phosphorescence with High Quantum Efficiency Engaging the Trifluoromethylsulfonyl Group to Iridium Phenylpyridine Complexes

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Supporting Information

ABSTRACT: Incorporation of an electron-withdrawing -SO₂CF₃ substituent to cyclometalating C^N-phenylpyridine (ppy) ligand resulted in an expected blue-shifted phosphorescence in the corresponding homoleptic $Ir(ppySCF_3)_3$ complex, showing the emission of $\lambda_{em} = 464$ nm at 300 K. One of its heteroleptic derivatives, modified by a pyrazolyl borate LX ligand, Ir(ppySCF₃)₂(bor), exhibited further blueshifted phosphorescence of λ_{em} = 460 nm at 300 K. Cyclic voltammograms (CVs) and density-functional theory (DFT) calculations supported the efficacy of the electron-withdrawing capability of the SO₂CF₃ substituent lowering HOMO energy and obtained widened bandgaps and resumed blue emissions for all of the iridium complexes studied. The



homoleptic complexes of both substituents, $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$, reached the higher quantum yields (Φ_{PL}) of (0.89) and 0.72), respectively. Similarly, emission quantum yields (Φ_{PL}) of the heteroleptic derivatives were reported to be (0.75, 0.83, and 0.87) for Ir(ppySCF₃)₂(acac), Ir(ppySCF₃)₂(bor), and Ir(ppySCF₃)₂(pic), respectively. Emission kinetics support the enhanced quantum efficiency when k_r and k_{nr} values are compared between Ir(ppySCF₃)₃ and Ir(ppySF)₃, and both values favorably contribute to attaining a higher quantum efficiency for Ir(ppySCF₃)₃. Among solution-processed multilayered devices having an ITO/PEDOT:PSS/TCTA:Ir dopant (10:1, w/w)/TmPyPB/Liq/Al structure, a heteroleptic dopant, Ir- $(ppySCF_3)_2(bor)$, exhibited better device performance, reporting an external quantum efficiency (EQE) of 1.14%, current efficiency (CE) of 2.31 cd A⁻¹, and power efficiency (PE) of 1.21 lm W⁻¹, together with blue chromaticity of CIE_{xy} = (0.16, 0.32).

INTRODUCTION

Among the remaining tasks in OLED material development, securing a highly efficient blue phosphorescent dopant has been one of the major challenges. $^{1-\tilde{1}5}$ The choice of phosphorescent transition metal and engaging it through bidentate ligands with conjugated σ -donor and π -acceptor functionalities were a common synthetic strategy.^{1,4,9,16-19} However, even before attempting exotic ligand design, a well-known bandgap adjustment from phenylpyridine (ppy) ligand has not yet been fully addressed in terms of ligand derivatization and its correlation to the photophysical property of the resulting iridium dopant. For example, the most popular strategy to obtain blue-emitting phosphorescent Ir complex has been set up by incorporating an electron-withdrawing group (EWG) at the phenyl moiety of ppy ligand, as shown in Scheme 1. The EWG can stabilize the highest occupied molecular orbital (HOMO), resulting in an increased bandgap of Ir complexes.^{4,9,19} Several EWGs, such as fluorine (-F),^{20–27} trifluoromethyl $(-CF_3)$,^{4,20,25–32} nitro $(-NO_2)$,^{33–35} cyano (-CN),^{36–39} and sulfonyl $(-SO_2R)^{40-48}$ have been used to induce such blue emissions from Ir(III) complexes.

Scheme 1. Blue Emission Tuning via the Incorporation of Electron-Withdrawing Groups on the C^N-Phenyl Pyridine (ppy) Ligand and Variation of the Ancillary Group (L^X)



Recently, it has been realized that the fluoro sulfonyl $(-SO_2F)$ group is stronger than any other of the EWGs mentioned above, and the utility of this functional ligand thus produced the corresponding Ir complexes exhibiting blue-shifted phosphor-

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Scheme 2. Molecular Structures of Sulfonyl Group-Substituted Iridium(III) Complexes



Ir(ppySCF₃)₃

EXPERIMENTAL SECTION

escence. Additionally, a higher phosphorescence quantum efficiency of those iridium complexes was reported, and its origin was proven to be the stronger σ -bond at C_{Ph}-Ir, and hence destabilizing the ³MC state originating from the corresponding σ^* -orbital of C_{Ph}-Ir.⁴⁸ To further support this argument that the stronger the electron-withdrawing power it has, the more stabilized HOMO that is attributed to it, and yet the more destabilized ³MC state it bears, the Hammett value (σ_n) of $-SO_2CF_3$ is 0.96, and larger than that of $-SO_2F_1$ 0.91. Our motivation of introducing the most EWD group, $-SO_2CF_3$, lies in confirmation of the substituent effect, which not only portrays the known structure and property relationship but also realizes how much deeper blue color coordinate and/or emission quantum efficiency we can achieve from the substitution.

Since our earlier work dealt only with a series of the heteroleptic iridium dopants from the -SO₂F substitution, $Ir(ppySF)_2(LX)$,⁴⁸ this work is rather comprehensive and includes the remaining homoleptic complex, Ir(ppySF)₃, as well. Scheme 2 shows that a complete set comprising both $-SO_2F$ and $-SO_2CF_3$ groups is in the list. The synthesis of all the SO₂F derivatives is nontrivial, and most of the products were fully characterized, including the X-ray structures of all of the heteroleptic complexes. Within the scope of the elucidation of wide bandgap and emission enhancement, the following experimental protocols have been established in this work. First, HOMO energy control by either $-SO_2F$ or $-SO_2CF_3$ has been measured by CV and confirmed from the serial DFT calculations. Second, steady-state photochemistry and photodynamic studies estimated the efficacy of the dopants produced by the $-SO_2CF_3$ substitution. From those approaches, the blue phosphorescence origin from the -SO₂CF₃ substitution and their excited state properties have been unveiled. Also, albeit the most efficient device had not been manufactured due to the unsublimable nature of the blue dopants produced, the choice from the heteroleptic complex, $Ir(ppySCF_3)_2(bor)$, proves to be a better option for the electroluminescence device fabricated.

The general information for the Experimental Section, details for the instrumentation, DFT and TD-DFT calculation, X-ray crystallography, the device fabrication, and the synthesis of ppySF are provided in the Supporting Information.

Synthesis of 3-Bromophenyl Trifluoromethyl Sulfide (L1). Under an N₂ atmosphere, 3-bromobenzenethiol (2.00 g, 10.58 mmol) is dropwise added to a DMF solvent (5 mL) containing NaH (0.25 g, 10.57 mol) and stirred at 20 °C for 15 min. The reaction mixture is further exposed to CF₃I gas, until its color becomes yellow. The yellow crude product is extracted with CH2Cl2 and dried over anhydrous MgSO₄. After solvent evaporation under reduced pressure, the remaining residue is purified by silica gel chromatography using CH₂Cl₂/n-hexane as eluent, to give L1. Yield 20% (0.54 g). ¹H NMR $(300.1 \text{ MHz}, \text{CDCl}_3): \delta 7.82 \text{ (s, 1H)}, (7.64-7.58) \text{ (m, 2H)}, 7.31 \text{ (t, J =}$ 7.2 Hz, 1H). ESI-MS (*m*/*z*): calcd. for C₇H₄BrF₃S: 255.9169, found [M + H]+: 256.9876.

Synthesis of 1-Bromo-3-(trifluoromethylsulfonyl)benzene (L2). Under an N_2 atmosphere, the mixture of acetic acid (36 mL), L1 (0.1 g, 0.39 mmol), and hydrogen peroxide (12 mL) is heated at 120 °C for 3 h. After cooling to RT, the crude product is extracted with CH₂Cl₂ and dried over anhydrous Na₂SO₄. After solvent evaporation under reduced pressure, the remaining residue is purified by silica gel chromatography using CH₂Cl₂/n-hexane as eluent, to give L2. Yield 98% (0.11 g). ¹H NMR (300.1 MHz, CDCl₃): δ 8.17 (s, 1H), (8.00-7.95) (m, 2H), 7.56 (t, J = 8.1 Hz, 1H). ESI-MS (m/z): calcd. for $C_7H_4BrF_3O_2S$: 287.9067, found $[M + H]^+$: 288.9124.

Synthesis of 2-(3-(Trifluoromethylsulfonyl)phenyl)pyridine (**ppySCF**₃). Under an N₂ atmosphere, $Pd(PPh_3)_4$ (0.48 g, 5 mol %) is added to a dried, degassed toluene (40 mL) containing L2 (2.42 g, 8.37 mmol) and 2-(tributylstannyl)pyridine (3.08 g, 8.37 mmol). The reaction mixture is refluxed at 110 °C for 16 h. After cooling to RT, the solvent is removed under reduced pressure. The dark residue is purified by silica gel chromatography using ethyl acetate/n-hexane as eluent, to give ppySCF₃. Yield 63% (1.51 g). ¹H NMR (300.1 MHz, CDCl₃): δ 8.76 (d, J = 4.8 Hz, 1H), 8.75 (s, 1H), 8.54 (d, J = 7.8 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), (7.87–7.77) (m, 3H), 7.37 (t, J = 5.7 Hz, 1H). ESI-MS (m/z): calcd. for C₁₂H₈F₃NO₂S: 287.0228, found $[M + H]^+$: 288.0124. Synthesis of Ir(ppySCF₃)₃. A glycerol solvent (5 mL) containing

ppySCF₃ (0.95 g, 3.3 mmol) and Ir(acac)₃ (0.49 g, 1.0 mmol) is

Scheme 3. Synthetic Route to the Cyclometalating Ligands (ppySF and ppySCF₃)^a



^{*a*}Conditions: (*i*) Pd(PPh₃)₄, toluene, 110 °C, 16 h (72% yield); (*ii*) CF₃I, NaH, DMF, 20 °C, 15 min (20% yield); (*iii*) acetic acid, H₂O₂, 120 °C, 3 h (98% yield); (*iv*) Pd(PPh₃)₄, toluene, N₂, reflux, 16 h (63% yield).

Scheme 4. Synthetic Routes to the Ir(III) Complexes (Ir(ppySF)₃, Ir(ppySCF₃)₂, Ir(ppySCF₃)₂(acac), Ir(ppySCF₃)₂(pic), and Ir(ppySCF₃)₂(bor))^{*a*}



"Conditions: (i) $Ir(acac)_3$, glycerol, N₂, reflux, 24 h (39% yield); (ii) $IrCl_3 \cdot xH_2O$, 2-ethoxyethanol/water (3:1, v/v), 100 °C, 8 h; (iii) $Ir(acac)_3$, glycerol, N₂, reflux, 24 h (42% yield); (iv) acetylacetone, Na₂CO₃, 2-ethoxyethanol, 100 °C, 8 h (65% yield); (v) picolinic acid, Na₂CO₃, 2-ethoxyethanol, 100 °C, 8 h (52% yield); (vi) AgOTF, CH₂Cl₂/CH₃OH, room temperature, 2 h; (vii) potassium tetrakis(1-pyrazolyl)borate, CH₃CN, 100 °C, 12 h (24% yield).



Figure 1. Crystal structures of $Ir(ppySCF_3)_2(acac)$, $Ir(ppySCF_3)_2(pic)$, and $Ir(ppySCF_3)_2(bor)$. H atoms have been omitted for clarity. ORTEP drawings are provided in Figures S14–S16 of the SI.⁴⁹

refluxed under a N₂ atmosphere for 24 h. After cooling to RT, the reaction mixture is poured into H₂O. The resulting precipitate is collected by filtration and washed with H₂O and *n*-hexane. The crude yellow powder is purified by silica gel chromatography using ethyl acetate/*n*-hexane as eluent, to give **Ir(ppySCF**₃)₃. Yield 42% (0.44 g). ¹H NMR (300.1 MHz, CDCl₃): δ 8.19 (s, 3H), 8.12 (d, *J* = 8.4 Hz, 3H), 7.88 (t, *J* = 7.6 Hz, 3H), 7.51 (d, *J* = 4.8 Hz, 3H), 7.37 (d, *J* = 8.1 Hz, 3H), 7.17 (t, *J* = 6.2 Hz, 3H), 6.98 (d, *J* = 8.1 Hz, 3H). ESI-MS (*m*/*z*): calcd. for C₃₆H₂₁F₃IrN₃O₆S₃: 1051.0078, found [M]⁺: 1051.2353.

Synthesis of Ir(ppySF)₃. A procedure analogous to the preparation of **Ir**(**ppySCF**₃)₃ was used starting from **ppySF** (0.36 g, 1.52 mmol) and Ir(acac)₃ (0.25 g, 0.51 mmol). The product **Ir**(**ppySF**)₃ was obtained as a yellow powder. Yield 39% (0.18 g). ¹H NMR (300.1 MHz, DMSO- d_6): δ 8.60 (d, J = 8.1 Hz, 3H), 8.49 (s, 3H), 8.01 (t, J = 7.2 Hz, 3H), 7.55 (d, J = 5.4 Hz, 3H), 7.46 (d, J = 7.2 Hz, 3H), 7.38 (t, J = 6.3 Hz, 3H), 6.91 (d, J = 8.1 Hz, 3H). ESI-MS (m/z): calcd. for C₃₃H₂₁F₃IrN₃O₆S₃: 901.0174, found [M]⁺: 901.0791.

Synthesis of [(ppySCF₃)₂lrCl]₂. IrCl₃·xH₂O (0.5 g, 1.42 mmol) is added to the 8 mL of 2-ethoxyethanol/water mixture solvent (3:1, ν/ν) containing ppySCF₃ (1.02 g, 3.55 mmol) and refluxed at 100 °C under N₂ atmosphere for 8 h. After cooling to RT, the addition of H₂O (50 mL) gives a light-yellow precipitate. The yellow solids precipitated are filtered out and washed with cold *n*-hexane. The crude product was used for the next reaction, without further purification.

Synthesis of Ir(ppySCF₃)₂(acac). Under a N₂ atmosphere, [(**ppySCF**₃)₂**IrCl**]₂ (0.57 g, 0.36 mmol), acetylacetone (0.072 mL, 0.72 mmol), and Na₂CO₃ (0.13 g, 1.23 mmol) are added to the 2-ethoxyethanol solvent (10 mL) and heated at 100 °C for 8 h. After cooling to RT, the reaction mixture is poured into H₂O. The resulting precipitate is collected by filtration and washed with H₂O and *n*-hexane. The crude yellow powder is purified by silica gel chromatography using ethyl acetate/*n*-hexane as eluent, to give **Ir**(**ppySCF**₃)₂(**acac**). Yield 65% (0.20 g). ¹H NMR (300.1 MHz, CDCl₃): δ 8.48 (d, *J* = 6 Hz, 2H), 8.07 (d, *J* = 9.3 Hz, 4H), 7.95 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 6.6 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.52 (d, *J* = 8.4 Hz, 2H), 5.29 (s, 1H), 1.82 (s, 6H). ESI-MS (*m*/*z*): calcd. for C₂₉H₂₁F₆IrN₂O₆S₂: 864.0374, found [M]⁺: 864.0515.

Synthesis of Ir(ppySCF₃)₂(pic). Under a N₂ atmosphere, $[(ppySCF_3)_2IrCl]_2$ (0.57 g, 0.36 mmol), picolinic acid (0.09 g, 0.72 mmol), and Na₂CO₃ (0.13 g, 1.26 mmol) are added to the 2-ethoxyethanol solvent (10 mL) and heated at 100 °C for 8 h. After cooling to RT, the reaction mixture is poured into H₂O. The resulting precipitates are filtered out and washed with H₂O and *n*-hexane. The crude yellow powder is purified by silica gel chromatography using ethyl acetate/*n*-hexane as eluent, to give $Ir(ppySCF_3)_2(pic)$. Yield 52% (0.16 g). ¹H NMR (300.1 MHz, CDCl₃): δ 8.83 (d, *J* = 5.1 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), (8.18–7.91) (m, 6H), 7.62 (d, *J* = 4.2 Hz, 1H), (7.50–7.45) (m, 2H), (7.41–7.29) (m, 4H), 7.20 (t, *J* = 6.9 Hz, 1H), 6.72 (d, 7.8 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H). ESI-MS (*m*/*z*): calcd. for C₃₀H₁₈F₆IrN₃O₆S₂: 887.0170, found $[M + H]^+$: 888.0231.

Synthesis of lr(ppySCF₃)₂(bor). Under a N₂ atmosphere, the mixture of $[(ppySCF_3)_2IrCI]_2$ (0.57 g, 0.36 mmol) and silver trifluoromethanesulfonate (AgOTF, 0.19 g, 0.72 mmol) is added to the 30 mL of CH₂Cl₂/CH₃OH mixture solvent (3:1, ν/ν) and stirred at RT for 2 h. After the salts precipitated are filtered out, the filtrate was concentrated under reduced pressure. A CH₃CN solution (10 mL)

containing the crude brown residue and potassium tetrakis(1pyrazolyl)borate (0.34 g, 1.08 mmol) was refluxed at 100 °C for 12 h under N₂ atmosphere. After cooling to RT, the crude product is extracted with CH₂Cl₂ and dried over anhydrous MgSO₄. After evaporation under reduced pressure, the remaining residue is purified by silica gel chromatography using ethyl acetate/*n*-hexane as eluent, to give **Ir(ppySCF₃)₂(bor)** as a light yellow solid. Yield 24% (0.09 g). ¹H NMR (300.1 MHz, CDCl₃): δ 8.13 (s, 2H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.72 (s, 2H), (7.38–7.31) (m, 4H), 7.18 (d, *J* = 2.1 Hz, 2H), 6.94 (t, *J* = 6.6 Hz, 2H), 6.74 (s, 2H), 6.46 (d, *J* = 7.8 Hz, 2H), 6.26 (s, 2H), 6.17 (s, 2H), 6.05 (s, 2H). ESI-MS (*m*/*z*): calcd. for C₃₆H₂₆BF₆IrN₁₀O₄S₂: 1,044.1206, found [M]⁺: 1,044.7211.

RESULTS AND DISCUSSION

Synthesis and Characterization. The trifluoromethylsulfonyl-substituted cyclometalating C^N ligand (**ppySCF**₃) was prepared in three steps in an analogous manner to the synthesis of 2-(3-fluorosulfonylphenyl)pyridine (**ppySF**) (Scheme 3).⁴⁸ The trifluoromethylsulfonyl group ($-SO_2CF_3$) in the bromophenyl moiety was introduced by treatment of 3-bromobenzenethiol and CF₃I gas in DMF followed by oxidation of sulfur with H₂O₂ and acetic acid. The **ppySCF**₃ ligand was obtained using the Stille-type cross-coupling reaction of 1-bromo-3-((trifluoromethyl)sulfonyl)benzene and 2-(tributylstannyl)pyridine in a yield of 63% (Scheme 3).

With the cyclometalating ligands in hand, the final homoleptic $Ir(ppySF)_3$ and $Ir(ppySCF_3)_3$ were synthesized from treating $Ir(acac)_3$ with ligands (ppySF and ppySCF₃) (3.3 equiv) in moderate yields of 39 and 42%, respectively (Scheme 4).¹⁹ For the preparation of the heteroleptic Ir(III) complexes, the dichloro-bridged iridium dimer, $[(ppySCF_3)_2IrCI]_2$, was synthesized by reaction of $IrCl_3 \cdot xH_2O$ and the cyclometalating ppySCF₃ ligand. Subsequently, the cleavage of dichloro-bridged iridium dimer with the corresponding ancillary ligands (acac, pic, and bor) produced the desired heteroleptic $Ir(ppySCF_3)_2(LX)$ dopants (LX = acac, pic, and bor) in moderate yields of (24–65)% (Scheme 4). All compounds were fully characterized by ¹H NMR spectroscopy and ESI-mass spectrometry (see the Experimental Section and Figures S1–S13 of the Supporting Information).

X-ray Crystallographic Analysis. Figure 1 shows molecular structures of $Ir(ppySCF_3)_2(acac)$, $Ir(ppySCF_3)_2(pic)$, and $Ir(ppySCF_3)_2(bor)$ analyzed via X-ray crystallography of single crystals grown in CH₂Cl₂ solution. Crystal symmetries were determined as follows: an *orthorhombic* space group *Pccn* for $Ir(ppySCF_3)_2(acac)$, a *trigonal* space group *P*₃ for $Ir(ppySCF_3)_2(pic)$, and a *triclinic* space group *P*₁ for $Ir(ppySCF_3)_2(bor)$. Their molecular structures contained *trans*-N,N of pyridine moieties and *cis*-C,C geometry of phenyl moieties in the cyclometalated ligand. The lateral angle for *trans* N–Ir–N was 176.4(3)° for $Ir(ppySCF_3)_2(acac)$, 175.5(5)° for

 $Ir(ppySCF_3)_2(pic)$, and $172.0(2)^\circ$ for $Ir(ppySCF_3)_2(bor)$. Lateral *trans* N–Ir–N bonds were bent from linear structures. In particular, $Ir(ppySCF_3)_2(bor)$ was largely distorted, due to the bulky bor ancillary ligand.

Bond lengths between iridium and donor atoms of ancillary ligands were longer than those of the main ligand, as listed in Table 1. This means that the ancillary ligand was less tightly

Table 1. Bond Distances (Å) between Ir and Donor Atoms of Ligands in Heteroleptic Ir Complexes

Ir(ppySCl	$F_3)_2(acac)$	Ir(ppySC	$(F_3)_2(pic)$	Ir(ppySCF ₃) ₂ (bor)			
$Ir-C_{ph}$	1.991(7)	$Ir-C_{ph}$	1.966(2)	Ir-C _{ph}	1.993(6)		
			1.935(2)		2.009(5)		
Ir-N _{py}	2.047(7)	Ir-N _{py}	2.043(1)	Ir-N _{py}	2.045(4)		
			2.046(1)		2.049(4)		
$Ir-O_{acac}$	2.140(5)	$Ir-N_{pic}$	2.144(1)	$Ir-N_{bor}$	2.140(5)		
		$Ir-O_{pic}$	2.144(1)		2.158(5)		

bound to the Ir center, compared to the main ligand. Indeed, bond lengths of Ir–O and Ir–N of the ancillary ligand were in the ranges (2.140(5)-2.144(1)) and (2.140(5)-2.158(5)) Å, respectively. Ir–N_{py} bond lengths of the main ligand were in the range (2.043(1)-2.049(4)) Å, which were less deviated by the ancillary ligand. This may be attributed to the axial formation of *trans* N_{py}–Ir–N_{py} bonds. However, Ir–C_{ph} bond lengths varied in the range (1.935(2)-2.009(5)) Å, indicating that the ancillary ligands and their donor atoms resulted in different electronic and steric environments.^{31,48} Ir(ppySCF₃)₂(bor) had the longest Ir–C_{ph} bond length, probably due to the distorted structure caused by the bulky ancillary ligand.

Steady-State Absorption Properties. Relating to previous examples of the heteroleptic iridium complexes of the type $Ir(ppySF)_2(LX)$ with a $-SO_2F$ group at ppy ligand, ⁴⁸ Figure 2a



Figure 2. UV-vis absorption spectra of (a, upper) heteroleptic Ir(III) complexes $(Ir(ppySCF_3)_2(acac), Ir(ppySCF_3)_2(pic), and Ir(ppySCF_3)_2(bor))$ and (b, lower) homoleptic Ir(III) complexes $(Ir(ppySCF_3)_3 \text{ and } Ir(ppySF)_3)$.

shows absorption spectra of their analogues of Ir-(ppySCF₃)₂(acac), Ir(ppySCF₃)₂(pic), and Ir-(ppySCF₃)₂(bor) in CH₂Cl₂ at 300 K. These absorption spectra showed strong bands at <320 nm that could be attributed to the ${}^{1}\pi{-}\pi{}^{*}$ transition of ppy ligands [ligand centered (${}^{1}LC$) transition]. The broad absorption band at (320-420) nm could be assigned to the spin-allowed metal-toligand charge transfer (¹MLCT) transition in the singlet state. A spin-forbidden triplet MLCT (³MLCT) band was observed at wavelengths (420–483) nm with very weak absorbance. Although heteroleptic Ir complexes contained two identical cyclometalated ligands as the chromophore, their absorption spectra were strongly affected by the ancillary ligand. Their onset positions in the absorption spectra varied substantially, as shown in the enlarged spectra of Figure 2a. The onset of Ir-(ppySCF₃)₂(acac) was observed at longer wavelength than in other complexes. The onset of Ir(ppySCF₃)₂(bor) was observed at the shortest wavelength. Such an ancillary ligand effect resembles those found in the $-SO_2F$ congeners.⁴⁸

For homoleptic complexes, the absorption spectrum of $Ir(ppySCF_3)_3$ was observed at shorter wavelength compared to that of $Ir(ppySF)_3$, indicating that a strong EWG might have increased the bandgap. ¹LC bands of $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$ were observed at around 275 nm. They were more intense than those of heteroleptic complexes as shown in Figure 2b, probably due to one more ppy ligands in the homoleptic complex. The onset wavelengths of ³MLCT absorption for $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$ were (471 and 473) nm, respectively.

Steady-State Phosphorescence Properties. Figure 3 shows the steady-state photoluminescence (PL) spectra measured at (300 and 77) K. The strong blue emission originated from triplet excited states with both the π - π * and MLCT characteristics. The photophysical properties of heteroleptic complexes were significantly affected by variation in ancillary ligands. Emission maxima of heteroleptic Ir-(ppySCF₃)₂(acac), Ir(ppySCF₃)₂(pic), and Ir-(ppySCF₃)₂(bor) were observed at (485, 469, and 460) nm, respectively. Such blue-shifts induced by changes in ancillary groups from -acac to -bor could be explained as degrees of stabilization of the Ir metal center. The electron-withdrawing ability of the ancillary ligand is increased in the order of acac < pic < bor. These trends are in line with those reported for other heteroleptic Ir complexes.^{31,48}

At 300 K, the emission maximum of $Ir(ppySCF_3)_3$ was 464 nm, which was blue-shifted by 6 nm compared to that of $Ir(ppySF)_3$ (470 nm). Such a hypsochromic shift might be due to a slightly increased electron-withdrawing ability of the $-SO_2CF_3$ substituent, compared with that of the $-SO_2F$ substituent in the phenyl moiety. Consequently, a substituent change from $-SO_2F$ to $-SO_2CF_3$ resulted in a larger bandgap of the series of heteroleptic Ir complexes (see Table 2).

At 77 K, Ir complexes showed a well-developed vibronic structure in emission spectra with a rigidochromic shift to shorter wavelengths of about (5-10) nm, compared with those at 300 K, as shown in Figure 3b. Usually, solvent reorganization is significantly impeded in a rigid matrix. Thus, the emission is observed at higher energy regions at 77 K.⁵⁰ The 0–0 emission bands of heteroleptic complexes (Ir(ppySCF₃)₂(acac), Ir-(ppySCF₃)₂(pic), and Ir(ppySCF₃)₂(bor)) were (475, 463, and 455) nm, respectively. The 0-1 emission bands were observed at longer wavelengths, as listed in Table 2. The spacing (Δv_{00-01}) between 0–0 and 0–1 vibronic bands was in the range (1,410-1,530) cm⁻¹, which might correspond to C-C stretching modes between phenyl and pyridyl rings or to the stretching of aromatic rings.^{51,52} In the heteroleptic complexes, the $\Delta \nu_{00-01}$ value was 1,411 cm⁻¹ for Ir(ppySCF₃)₂(acac), $1,474 \text{ cm}^{-1}$ for $Ir(ppySCF_3)_2(pic)$, and $1,528 \text{ cm}^{-1}$ for Ir(ppySCF₃)₂(bor) with increasing order of acac < pic < bor ancillary ligands.



Figure 3. Emission spectra of Ir complexes (a) in anaerobic CH₂Cl₂ (at 300 K, $\lambda_{ex} = 355$ nm) and (b) in a glassy 2-methyltetrahydrofuran matrix (at 77 K, $\lambda_{ex} = 355$ nm).

Table 2.	Photop	hysical	and	Electrocl	hemical	Paramete	rs of	ÍIr	Compl	lexes
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	Em. at 300 K			Em. at 77 K								
Complexes	λ_p [nm]	$[\mu s]^{ au_{ m p}}$	$\phi_{ ext{PL}}$	$[10^5 s^{-1}]$	${k_{\rm nr} \over [10^5 { m s}^{-1}]}$	$\lambda_{\rm p} [{\rm nm}]$	$[\mu s]^{ au_{ m p}}$	$\begin{bmatrix} E_{\text{ox}} \\ eV \end{bmatrix}$	$E_{\rm LUMO}/E_{\rm HOMO}$ [eV] ^a	$\begin{bmatrix} E_g^{\text{opt}} \\ [eV]^{b} \end{bmatrix}$	$E_{ m LUMO}/E_{ m HOMO}$ [eV] (theo) ^c	$E_{g}(\text{theo})$ [eV] ^c
Ir(ppySCF ₃) ₂ (acac)	485	1.40	0.75	5.36	1.79	475, 509	3.47	0.86	-3.05/-5.66	2.61	-2.09/-5.90	3.81
Ir(ppySCF ₃) ₂ (pic)	469	1.98	0.87	4.39	0.66	463, 497	3.01	1.04	-3.16/-5.84	2.68	-2.27/-6.05	3.78
Ir(ppySCF ₃) ₂ (bor)	460	3.58	0.83	2.32	0.48	455, 489	4.07	1.17	-3.24/-5.97	2.73	-2.26/-6.28	4.02
Ir(ppySCF ₃) ₃	464	1.41	0.89	6.31	0.78	457, 491	2.26	0.90	-2.99/-5.70	2.71	-2.25/-6.18	3.93
Ir(ppySF) ₃	470	1.53	0.72	4.71	1.83	461, 495	2.44	0.87	-2.98/-5.67	2.69	-2.30/-6.23	3.93

^{*a*}The HOMO level was determined using the following equation: E_{HOMO} (eV) = $-e(E_{\text{ox}} + 4.8)$. The LUMO level was determined using the following equation: E_{LUMO} (eV) = $e(E_{\text{HOMO}} + E_{g}^{\text{opt}})$. ^{*b*}The E_{g}^{opt} values were calculated using the maximum wavelength of the 0–0 emission band measured at 77 K. ^{*c*}The values were obtained from the DFT calculation results.

At 77 K, the 0–0 emission band of $Ir(ppySCF_3)_3$ was observed at 457 nm, which was blue-shifted compared to that of $Ir(ppySF)_3$ at 461 nm. The $\Delta \nu_{00-01}$ values of homoleptic $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$ were (1,518 and 1,500) cm⁻¹, respectively. The change in $\Delta \nu_{00-01}$ value implies that the C–C bond strength is affected by the electron-withdrawing ability and bulkiness of the ancillary ligand. The $\Delta \nu_{00-01}$ value correlates directly with the color purity of the emission spectra. Color purity deteriorates with increasing $\Delta \nu_{00-01}$ value.

Another important factor affecting color purity is the Huang– Rhys factor *S*, which represents the structural distortion ΔQ between excited and ground states.^{51,53,54} *S* is defined as the intensity ratio of the 0–0 and 0–1 vibrational band in I_{01}/I_{00} . At 77 K, the *S* values of $Ir(ppySCF_3)_2(acac)$, $Ir(ppySCF_3)_2(pic)$, and $Ir(ppySCF_3)_2(bor)$ were (0.41, 0.45, and 0.48), respectively. The *S* values for $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$ were (0.45 and 0.56), respectively. In terms of $\Delta \nu_{00-01}$ and *S* values, the color purity of $Ir(ppySCF_3)_2(acac)$ was superior to the others. At 300 K, S values of all Ir complexes were in the range (0.69–0.75), suggesting that structural displacement occurred easily in the excited triplet state. Moreover, at 300 K, Δv_{00-01} values were increased in the order of $Ir(ppySCF_3)_2(acac)$ (968 cm⁻¹), $Ir(ppySCF_3)_2(pic)$ (1,234 cm⁻¹), and $Ir(ppySCF_3)_2(bor)$ (1,365 cm⁻¹). On the other hand, Δv_{00-01} values were 1,269 cm⁻¹ for $Ir(ppySCF_3)_3$ and 1,169 cm⁻¹ for $Ir(ppySF)_3$. The Δv_{00-01} values at 300 K were smaller than those at 77 K. This means that structural displacement and the main deactivation process can occur through lower energy vibrations at 300 K. Phosphorescence quantum yields (Φ_{PL}) were determined in the range (0.72–0.89) at 300 K, as listed in Table 2.

Photodynamic Properties. Figure 3 shows the emission decay profiles measured in anaerobic CH_2Cl_2 at (300 and 77) K. Table 2 shows that the phosphorescence emission lifetimes (τ_p)

were in the range $(1.40-1.98) \ \mu$ s, except for Ir-(ppySCF₃)₂(bor) of 3.58 μ s, which was remarkably longer than other complexes. The τ_p (4.07 μ s) of Ir(ppySCF₃)₂(bor) in the 2-methyl tetrahydrofuran (MTHF) matrix at 77 K was also longer than those of other complexes of (2.26-3.47) μ s (Table 2).

Radiative (k_r) and nonradiative (k_{nr}) rate constants were calculated using the following equation: $k_r = \Phi_{PL}/\tau_p$ and $k_{nr} =$ $(1/\tau_p) - k_r$. The k_r values for Ir complexes were at least 2.5-fold greater than the k_{nr} values. This result indicates that the primary deactivation process involves radiative phosphorescence, although the nonradiative pathway is non-negligible. The k_{nr} value of $Ir(ppySF)_3$ was 2-fold greater than that of $Ir-(ppySCF_3)_3$. Table 2 shows that the k_{nr} values increased in the order $Ir(ppySCF_3)_2(bor) < Ir(ppySCF_3)_2(pic) < Ir-(ppySCF_3)_2(acac)$. This trend can be interpreted based on the energy gap. The k_{nr} value is usually governed by the energy gap, as depicted in the following eq 1:⁵⁵

$$\ln(k_{\rm nr}) \propto (-\gamma/\hbar\omega_{\rm M}) \times (\Delta E) \tag{1}$$

where, γ is expressed in terms of molecular parameters, $\omega_{\rm M}$ is the maximum and dominant vibrational frequency, and $\Delta E_{\rm T-S}$ represents the energy gap between the excited triplet and ground states.

In this work, experimental energy gaps were determined from the 0–0 vibronic peaks of the corresponding phosphorescence at 300 K. Figure 4 shows that the $\ln(k_{nr})$ of the ³MLCT state



Figure 4. Relationship between $\ln(k_{nr})$ and the energy gap (ΔE_{T-S}) of homoleptic complexes (**Ir**(**ppySCF**₃)₃ and **Ir**(**ppySCF**₃)₂ (**acac**), **Ir**(**ppySCF**₃)₂(**pic**), and **Ir**(**ppySCF**₃)₂(**bor**)).

increased linearly for the ΔE_{T-S} values of both homoleptic and heteroleptic complexes. Despite fewer data, $\gamma/\hbar\omega_{\rm M}$ values were estimated from the slope values as follows: -27.72 eV^{-1} for homoleptic, and -12.53 eV^{-1} for heteroleptic Ir complexes, which were close to the low vibrational energy of *ca*. (290 and 644) cm⁻¹, respectively. This result indicates that the nonradiative deactivation process might have been promoted through low-frequency vibrational relaxation.

In the case of heteroleptic complexes, it is difficult to specify which vibration modes are involved in *ca.* 290 cm⁻¹, because many vibration modes are gathered in the range. However, the vibration of homoleptic complexes of ca. 644 cm⁻¹ might be specified as the asymmetric and symmetric O=S=Odeformation modes, which are usually observed in the range $(500-600) \text{ cm}^{-1.56}$ While $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$ retain a similar ligand structure, the vibrational relaxation of $Ir(ppySCF_3)_3$ through O=S=O motion may be efficiently inhibited by bulky $-CF_3$, rather than -F. As a result, the k_{nr} value of $Ir(ppySCF_3)_3$ is ca. 2.35-fold smaller than that of $Ir(ppySF)_3$. The Φ_{PL} for $Ir(ppySCF_3)_3$ is slightly higher (ca. 1.24-fold) compared to that of $Ir(ppySF)_3$, as listed in Table 2. This may be due to the larger k_r value (ca. 1.34-fold) of $Ir(ppySCF_3)_3$ than that of $Ir(ppySCF_3)_3$ has no direct correlation with the increasing k_r value but helps support the enhanced Φ_{PL} efficiency of $Ir(ppySCF_3)_3$.

Electrochemical Properties. Figure 5 shows the electrochemical behaviors that were examined by cyclic voltammetry



Figure 5. Cyclic voltammograms of Ir(III) complexes (1 mM) in the oxidation sides in CH_3CN in the presence of 0.1 M TBAP; scan rate of 100 mV s⁻¹.

(CV). All iridium compounds exhibited a reversible oxidation process in CH₃CN solution. Oxidation waves may be assigned to the Ir^{III}/Ir^{IV} redox couple.⁵⁷ The onset potentials of oxidation waves were in the range (0.86-1.17) V vs Fc/Fc⁺ for the five complexes. For homoleptic complexes, the oxidation potential (0.90 V) of $Ir(ppySCF_3)_3$ was more stable than that of $Ir(ppySF)_3$ (0.87 V), indicating that the $-SO_2CF_3$ substituent stabilized the HOMO level more than the -SO₂F substituent. For heteroleptic complexes, the oxidation potentials of Ir(ppySCF₃)₂(acac), Ir(ppySCF₃)₂(pic), and Ir- $(ppySCF_3)_2(bor)$ were (0.86, 1.04, and 1.17) V vs Fc/Fc⁺, respectively. Change of the ancillary ligand resulted in different oxidation potential. Ancillary ligands can modulate the physical properties of heteroleptic complexes due to their intrinsic ligand field strength and electronic interaction with the central metal ion. Usually, a stronger field strength of ancillary ligand has a directly proportional relationship with its π -acceptor properties that strengthens the back-bonding ability, leading to a hypsochromic shift in phosphorescence emission. This ancillary effect is reported for well-known Ir complexes.⁵⁸ Indeed, the emission maxima of three known heteroleptic Ir complexes (FIr(acac), FIr(pic), and Fir6 (FIr(bor); $FIr(LX) = (C^N)_2 Ir$ -(LX) (C^N = 2-(2,4-difluorophenyl)pyridine)) were observed at (484, 472, and 458) nm, respectively (see the corresponding structures in Figure S17 of the SI).^{21,59,60} In this work, the hypsochromic shift in the phosphorescence spectra was observed in the order $Ir(ppySCF_3)_2(acac) > Ir$ -



Figure 6. Frontier molecular orbitals (HOMO and LUMO) of Ir(III) complexes in their optimized geometries in singlet state. E_g values indicate the bandgap energy between the HOMO and the LUMO.

 $(ppySCF_3)_2(pic) > Ir(ppySCF_3)_2(bor)$. Therefore, we could easily deduce that the field strength of the ancillary ligand increased in the order acac (O^O) < pic (O^N) < bor (N^N). The Ir(III) complexes containing strong ligand-field ancillary ligand showed large oxidation potential value.

Table 2 summarizes the oxidation potentials of Ir complexes. The HOMO was calculated using the following eq 2 with standard ferrocene value of -4.8 eV to vacuum level:

$$E_{\text{HOMO}} (\text{eV}) = -(E_{\text{ox}}^{\text{onset}} - E_{\text{Fc/Fc}}^{+} + 4.8) \text{ eV}$$
 (2)

Using the CV data, HOMO levels were determined to be in the range -(5.66-5.97) eV, as listed in Table 2. The LUMO level can usually be determined by using the reduction onset potential in the CV spectrum, but we could not obtain the reduction potentials of Ir complexes due to their limited CV window. However, the three complexes (Ir(ppySCF₃)₂(bor), Ir-(ppySCF₃)₃, and Ir(ppySF)₃) show a tiny irreversible peak in the reduction potentials but due to their low intensity and obscurity, it is not use for the calculation of LUMO energy level.Therefore, we determined the LUMO level using optical bandgap based on the following empirical relationship (eq 3):

$$E_{\rm LUMO} (\rm eV) = -(E_{\rm HOMO} - E_{\rm g}^{\rm opt})$$
⁽³⁾

where E_{g}^{opt} was the optical energy bandgap. In this study, we determined the E_{g}^{opt} values using the maximum wavelength of the 0–0 emission band measured at 77 K. The E_{g}^{opt} values of Ir(ppySCF₃)₂(acac), Ir(ppySCF₃)₂(pic), and Ir-(ppySCF₃)₂(bor) were (2.61, 2.68, and 2.73) eV, respectively. The E_{σ}^{opt} values of Ir(ppySCF₃)₃ and Ir(ppySF)₃ were (2.71 and 2.69) eV, respectively. The LUMO levels were in the range -(2.98-3.24) eV, as listed in Table 2. The HOMO and LUMO levels of homoleptic $Ir(ppySCF_3)_3$ were slightly more stabilized than those of $Ir(ppySF)_3$. In the case of heteroleptic complexes, both HOMO and LUMO levels shifted to lower energy in the following order: $Ir(ppySCF_3)_2(acac) > Ir(ppySCF_3)_2(pic) >$ $Ir(ppySCF_3)_2(bor)$. Since the energy shifts of the HOMO levels were larger than those of the LUMO levels, the energy gaps between HOMO and LUMO increased in the same order of $Ir(ppySCF_3)_2(acac) < Ir(ppySCF_3)_2(pic) < Ir$ $(ppySCF_3)_2(bor)$. These results indicate that the ancillary

ligand plays an important role in energy gap control. The order of HOMO and LUMO levels is denoted in the scheme of the fabricated structure of the OLED device, which will be discussed later.

Density Functional Theory (DFT) Calculations. To further improve our understanding of their structural, electronic, and photophysical properties, DFT and TD-DFT investigations were carried out in both singlet (S_0 , ground) and triplet (T_1 , excited) states. Theoretical calculations were performed using the Gaussian 09 program.⁶¹ We applied a B3LYP function with LANL2DZ basis set for Ir atom and 6-31G(d,p) basis set for other atoms. $^{62-64}$ Preferentially, we performed geometry optimization under C_1 and C_3 symmetries for heteroleptic and homoleptic complexes, respectively. Figure 6 shows the frontier molecular orbitals (FMO) and their energy levels of Ir complexes. The HOMO was localized on the iridium center and extended to the phenyl moiety of the cyclometalating ligand. The LUMO was mainly localized on the pyridine moiety of the cyclometalating ligand, with a small portion of the d orbital character of the iridium center. The HOMO was mainly localized on the ortho- and para-sites of the phenyl ring with respect to the iridium atom, while orbital nodes were at the metasites of the phenyl ring. The LUMO predominantly resided on the two meta-sites relative to the iridium center, showing nodes at the ortho- and para-sites. The HOMO was also found in the ancillary ligand. However, the LUMO had no orbital distribution in the same position. When a substituent was attached at the position having significant electron density in the MO, strong electronic interaction was possible through this particular position. However, a substituent introduced at the node position of the MO showed weak interaction with the main chromophore. Therefore, the substitution on the para-site of the phenyl-moiety of ppy ligand had more influence on the electronic structure of the HOMO, in line with the results of electrochemical characterization.

The difference in Hammett parameter was only 0.05 between $-SO_2F$ and $-SO_2CF_3$ substituents at the *para* position of the phenyl ring. However, $Ir(ppySCF_3)_3$ and $Ir(ppySF)_3$ showed significant differences in E_{ox} , emission maxima, and the calculated Δ HOMO. Meanwhile, heteroleptic Ir complexes had additional electron-withdrawing capacity of ancillary ligands



Figure 7. Optimized triplet excited state structures and the highest singly occupied molecular orbital (HSOMO) and the lowest singly occupied molecular orbital (LSOMO) of Ir(III) complexes.



Figure 8. Structures of device with energy levels of materials and chemical structures of the materials used.

(bor > pic > acac) bound to the iridium center. As a result, Ir(ppySCF₃)₂(bor) exhibited a larger HOMO energy stabilization than $Ir(ppySCF_3)_2(pic)$ or $Ir(ppySCF_3)_2(acac)$. However, LUMO energy stabilization was limited by less MO contribution of the ancillary ligand. For homoleptic complexes, the contributions of iridium to HOMOs of Ir(ppySCF₃)₃ and Ir(ppySF)₃ were about (58 and 57)%, respectively, as listed in Table S1 of the SI. On the other hand, the contribution of their ligand to LUMOs was about 98%. Therefore, the lowest energy transition from HOMO to LUMO is a characteristic MLCT transition. Iridium contributions of (49-53)% to the HOMOs of heteroleptic complexes were slightly lower than their corresponding contributions to the HOMOs of homoleptic complexes (Table S1 of the SI). The contribution of ancillary ligands was very low at (5-9)%, suggesting that the ancillary ligands had no role in MLCT transitions. On the other hand, the total contributions of iridium and ancillary ligands to LUMOs

were (6-9)%. This result indicates that the MLCT transitions involved in emissions originated from cyclometalating ligands.

Tables S2–S6 of the SI give the dominant electronic transitions and oscillator strengths as determined by TD-DFT calculation. The lowest energy transition for Ir complexes was calculated at around 450 nm with zero oscillation strength, corresponding to the transition between the HOMO and the LUMO. This is a perfect forbidden transition for the triplet manifold in the theoretical calculation. Other significantly intense bands corresponded to transitions in the singlet state. Simulated absorption bands also matched well with the experimental ones, as shown in Figure S18 of the SI. The calculated HOMO energy levels showed similar trends under the altered oxidation potentials in CV spectra, as shown in Figure 5. However, the HOMO energy level of $Ir(ppySCF_3)_3$ was calculated to be slightly higher than that of $Ir(ppySF)_3$. The LUMO energy levels were in the range -(2.09-2.30) eV, in



Figure 9. Performances of the devices bearing series of Ir(III) complexes. (a) J-V-L characteristics, (b) current efficiency (CE)-current density (*J*) curves, (c) power efficiency (PE)-current density (*J*) curves, and (d) external quantum efficiency (EQE) as a function of current density (*J*).

Table 3. Electroluminescence C	Characteristics	of OLEDs
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Dopant	$V_{\rm on}^{\ a}$ (V)	$\lambda_{\text{peak}}^{b}$ (nm)	EQE^{c} (%)	CE^d (Cd/A)	PE^{e} (lm/W)	CIE ^f
Ir(ppySCF ₃) ₂ (bor)	6.40	466, 497	1.14	2.31	1.21	(0.16, 0.32)
Ir(ppySCF ₃) ₃	10.25	470, 498	0.74	1.68	0.41	(0.24, 0.44)
Ir(ppySF) ₃	11.45	477(sh), 505	0.71	1.89	0.56	(0.26, 0.48)
<i>a</i>	h			<i>d</i>		m f_1

^{*a*}Turn-on voltage at 1 nit. ^{*b*}Peak wavelength at 1 nit. ^{*c*}Max external quantum efficiency. ^{*d*}Max current efficiency. ^{*e*}Max power efficiency. ^{*j*}The commission internationale de L'Eclairage (CIE) coordinates at 1 nit.

which the energy variation of LUMO was smaller, compared to the HOMO variation.

Structures in the triplet state were optimized using the unrestricted B3LYP (UB3LYP) method with the same basis set under triplet multiplicity. Figure 7 shows the frontier orbitals and their energy levels of optimized structures in the triplet state. The highest singly occupied molecular orbital (HSOMO) distributions in the lowest-lying triplet state were similar to the LUMO distributions in the singlet state. The triplet HSOMO existed at lower energy level than the singlet LUMO energy level. For heteroleptic Ir complexes, the HSOMO levels were stabilized in the order $Ir(ppySCF_3)_2(acac) > Ir$ - $(ppySCF_3)_2(pic) > Ir(ppySCF_3)_2(bor)$. The lowest singly occupied molecular orbital (LSOMO) distribution resembled the HOMO distribution, in which the orbital was located on the iridium ion and the phenyl moiety of the cyclometalating ligand. This means that the emission originated from the HSOMO state has the MLCT character of the triplet manifold.

Device Performance. OLED devices bearing Ir complexes were fabricated through a partial solution process. Their electroluminescent (EL) characteristics were then investigated. Bulky $-SO_2F$ and $-SO_2CF_3$ groups may suppress the selfquenching and triplet-triplet annihilation (TTA) between complexes in the OLED device.⁶⁵ Thus, we did not observe any significant concentration dependency of dopant. Figure 8 shows the structures of devices: ITO (150 nm, anode)/PEDOT:PSS (40 nm)/TCTA:Ir complexes (30 nm: 10 wt %)/TmPyPB (35

nm)/Liq (1 nm)/Al (150 nm, cathode). The poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) was used as hole injection layer (HIL). The emitting layer consisted of tris(4-carbazoyl-9-ylphenyl)amine (TCTA) as host materials, and Ir complexes were used as phosphorescent dopants. The host material TCTA has specific properties of wide bandgap (3.3 eV), high glass transition temperature (T_g) , moderate hole-transporting ability, and high triplet energy.^{66,6} The 1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB) and 8quinolinolato lithium (Liq) were used as the electron transport layer (ETL) and the electron injection layer (EIL), respectively. They were deposited by thermal evaporation onto the emitting layer under high vacuum. The triplet energies of TCTA (2.86 eV) and TmPyPB (2.8 eV) were higher than those of the triplet state of Ir complexes, which facilitated efficient energy transfer from hosts to dopants. Figure 9 depicts the current density (J)voltage-luminance (J-V-L), current efficiency-current density, power efficiency-current density, and EQE-current density of the fabricated OLED devices. Table 3 summarizes the performances of these devices. Among them, Ir- $(ppySCF_3)_2(bor)$ exhibited a turn-on voltage of 6.40 V with its device performance characterized by external quantum yield (EQE) of 1.14%, current efficiency (CE) of 2.31 cd A^{-1} , and power efficiency (PE) of 1.21 lm W^{1-} .

Figure 10 shows the EL spectra of the Ir complexes that were measured at similar wavelength to the photoluminescence (PL) spectra. However, the EL spectra were less structured compared



Figure 10. Electroluminescence spectra of devices bearing Ir(III) dopants recorded at 1 nit.

to those in the glassy matrix at 77 K, or even in solution at 300 K. In particular, the EL spectra of homoleptic Ir complexes changed drastically in the relative intensity of vibronic bands. Although the host and ETL materials were also emissive chromophores, no emission peaks were detected in the EL spectra. This result indicated that energy transfer occurred efficiently from the host to the dopant emitter in these OLED devices. The EL spectra slightly shifted to the longer wavelength (*ca*. (1–7) nm) than the photoluminescence (PL) spectra in solution (Table 3). Table 3 shows the Commission International de L'Éclairage (CIE) color coordinates of these OLED devices.

For the devices bearing homoleptic and heteroleptic Ir complex dopants, EL spectra and CIE coordinates were distinguished by both the main and ancillary ligands. Among them, the device bearing $Ir(ppySCF_3)_2(bor)$ showed bluer CIE coordinate (0.16, 0.32), and its EL spectrum displayed the shortest wavelength, compared with the others. However, its device performance was not optimized, because its device fabrication was limited, due to the unsublimable nature of Ir complexes. The poor performances of our fabricated devices when compared to the results reported in typical OLED devices based on the sublimable materials are thought to be caused by the drawbacks of the solution processed method such as the lack of optimal alignment of energy level derived from limitation of multilayer deposition, poor film morphology, and easy crystallization upon spin-coating.⁶⁸ Regarding the relatively low performance relative to the results of similar solutionprocessed OLED device, such discrepancy might be due to different manufacture conditions and process parameters because the overall performance of the OLED device is generally variable according to the device fabrication conditions including the thickness of the common layers, such as HIL (PE-DOT:PSS), host material (TCTA), and doping degree (wt %) of Ir dopant in the emitting layer. Indeed, unlike material used in a previous report, we used the blue-emitting Ir(III) dopant series and TmPyPB as dopant and ETL material instead of greenemitting **BPyPmIr** and TPBI (2,2',2"-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole)), respectively.⁶⁹ Above all, a less smooth alignment of HOMO levels between PEDOT:PSS (5.2 eV) and TCTA (5.9 eV), which weakens its hole injection ability in the device, is thought to be the biggest reason for low performance.

CONCLUSIONS

To achieve blue phosphorescence, we developed new homo-/ heteroleptic Ir complexes using a combination of cyclometalating C^N ligand bearing -SO₂F and -SO₂CF₃ substituents and ancillary ligands, such as acac, pic, and bor. As a result of fine-tuning of EWG $(-SO_2-R)$ from $-SO_2F$ to $-SO_2CF_3$, the emission maximum of homoleptic Ir(ppySCF_3)_3 having stronger EWG was blue-shifted by 6 nm compared to $Ir(ppySF)_3$. In addition, $Ir(ppySCF_3)_3$ ($\Phi_{PL}= 0.89$) showed higher quantum efficiency compared with $Ir(ppySF)_3$ (Φ_{PI} = 0.72), which had been elaborated by the larger k_r value (*ca.* 1.34fold) of Ir(ppySCF₃)₃ than that of Ir(ppySF)₃. For heteroleptic complexes, further modification with variation of ancillary ligands from acac to bor generated a hypsochromic shift in the emission spectra. Among them, $Ir(ppySCF_3)_2(bor)$ emitted largely blue-shifted phosphorescence that might be due to the synergistic effect of combining SO₂CF₃-substituted C^N cyclometalating ligand and ancillary ligand bor. These trends are consistent with increased HOMO-LUMO bandgap and discernible HOMO stabilization, which were confirmed by photophysical and electrochemical analysis and DFT calculation. All SO₂R-substituted Ir complexes exhibited high emission quantum yields of (0.72-0.89) in anaerobic CH₂Cl₂ at 300 K. Therefore, we fabricated OLED devices using these Ir complexes as dopants. Among them, the $Ir(ppySCF_3)_2(bor)$ OLED device showed potential blue phosphorescence characterized by the bluest chromaticity with $CIE_{x,y} = (0.16, 0.32)$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02672.

Experimental details; NMR spectra; ESI-mass spectra; crystallographic data, optimized geometries, and TD-DFT assignment; X-ray crystallographic data (PDF)

Accession Codes

CCDC 1919505, 1919522, and 1919544 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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