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Design and Synthesis of Blue-Emitting Cyclometalated Iridium(III) Complexes Based on Regioselective Functionalization

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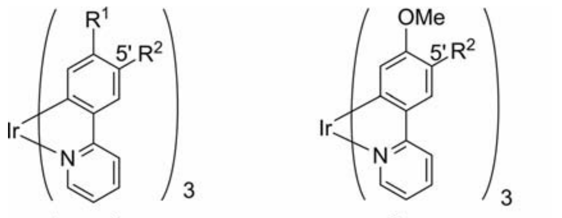
A series of tris-cyclometalated Ir^{III} complexes were prepared by regioselective substitution reactions (formylation, thiocyanation, and iodination) and subsequent conversions (cyanation, cross-coupling reaction, reduction, and oxidation) on a 2-(4′-methoxyphenyl)pyridine (mppy) ligand of *fac*-[Ir(mppy)$_3$]. The introduction of electron-withdrawing groups such as CHO, CN, and sulfonyl groups (SO$_2$Me, SO$_2$Ar) at the 5′-position of the phenyl ring of the mppy portion induces a considerable blueshift in luminescence emission (from 495 nm to approximately 465 nm) in degassed organic solvents.

Introduction

Cyclometalated iridium(III) complexes such as *fac*-[Ir(ppy)$_3$] (**1**; ppy = 2-phenylpyridine) and *fac*-[Ir(tpy)$_3$] [**2**; tpy = 2-(4′-tolylpyridine)] (Scheme 1) have received considerable attention because of their unique photophysical properties, which include high luminescent quantum yields (e.g., Φ for **1** is 0.4), short phosphorescent lifetimes (τ in about microsecond order), and emission-color tuning by appropriate control of the ligand structure.[1] The strong spin–orbital coupling of Ir^{III} metal ion in the complexes facilitates efficient intersystem crossing (ISC) from the singlet excited state to the triplet excited state, thereby resulting in strong phosphorescence at room temperature. These attractive photochemical properties make such Ir^{III} complexes important candidates for use as phosphorescent emitters in organic light-emitting diodes (OLEDs),[1,2] oxygen detection,[3] sensors for metal ions,[4] luminescent probes for biological systems,[5] photoreductants,[6] and photoredox catalysis.[7] The most extensively investigated applications are phosphorescent emitters, which exhibit red, green, and blue phosphorescence emission for highly efficient OLEDs.[1,2] To date, promising red-[2b,2d,2h] and green-[2a,2i] emitting Ir^{III} complexes for phosphorescent OLEDs have been reported, and much research has been focused on the design and synthesis of Ir^{III} complexes that emit a blue color. Since the highest occupied molecular orbital (HOMO) of Ir^{III}–ppy-based complexes (such as **1**) is located on the phenyl π and Ir d orbitals, and the lowest unoccupied molecular orbital (LUMO) is mainly on the pyridine ring, it has been proposed that the introduction of electron-withdrawing groups on the phenyl ring stabilizes the HOMO energy level, thereby resulting in an increase in the HOMO–LUMO energy gap.[1g] The modification of Ir^{III} complexes with electron-withdrawing groups such as fluoro, trifluoromethyl,[8] cyano,[9] formyl,[10] or sulfonyl groups[11] have been attempted to achieve this. Typically, fluoro-substituted ligands are most widely used in representative blue-emitting Ir^{III} complexes such as FIrpic,[2c,12g] FIrtaz,[12g] and their analogues (Scheme 2).[12] Indeed, the introduction of a fluorine atom is useful for the design and synthesis of a blue-color Ir^{III} complex. However, it is described that OLED devices based on fluorine-substituted Ir^{III} complexes such as FIrpic tend to have short device operational lifetimes, since Ir^{III} compounds may undergo a cleavage of the C–F bond on the ligand during device fabri-



1: R^1 = R^2 = H (Ir(ppy)$_3$)
Em 514 nm (in CH$_2$Cl$_2$)
2: R^1 = Me, R^2 = H (Ir(tpy)$_3$)
Em 512 nm (in CH$_2$Cl$_2$)
3: R^1 = Me, R^2 = NH$_2$ (Ir(atpy)$_3$)
Em 581 nm (in CH$_2$Cl$_2$)
4: R^1 = Me, R^2 = CHO
Em 477 nm (in CH$_2$Cl$_2$)
5: R^1 = Me, R^2 = CN
Em 478 nm (in CH$_2$Cl$_2$)

6: R^2 = H (Ir(mppy)$_3$)
7: R^2 = CHO
8: R^2 = CN
9: R^2 = SCN
10: R^2 = SO$_2$Me
11: R^2 = SO$_2$Tol
12: R^2 = SO$_2$PhCl
13: R^2 = SH
14: R^2 = SMe
15: R^2 = I

Scheme 1.

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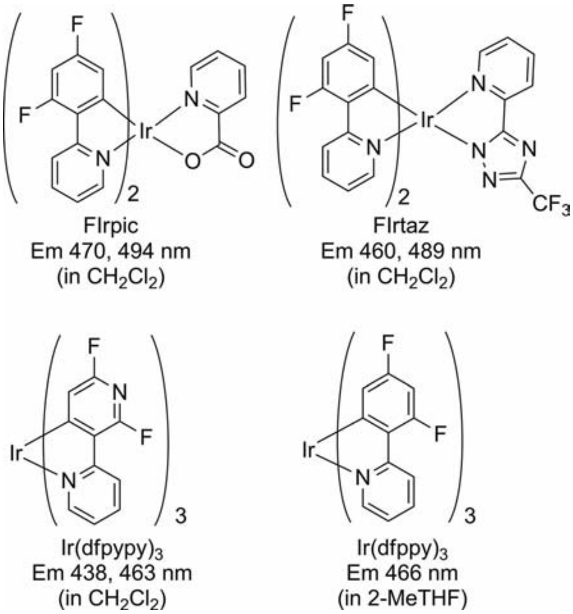
cation and operation.[13] Therefore, the development of cyclometalated Ir^{III} complexes with fewer or without the fluorine atoms on the ligand is important.[12s,12t] Examples of blue-emitting tris-cyclometalated Ir^{III} complexes[14] that exhibit a somewhat higher thermal stability and luminescent efficiency[2h,2i] are relatively limited {e.g., [Ir(dfpypy)$_3$][14d] and [Ir(dfppy)$_3$][2i,12q]}.



Scheme 2.

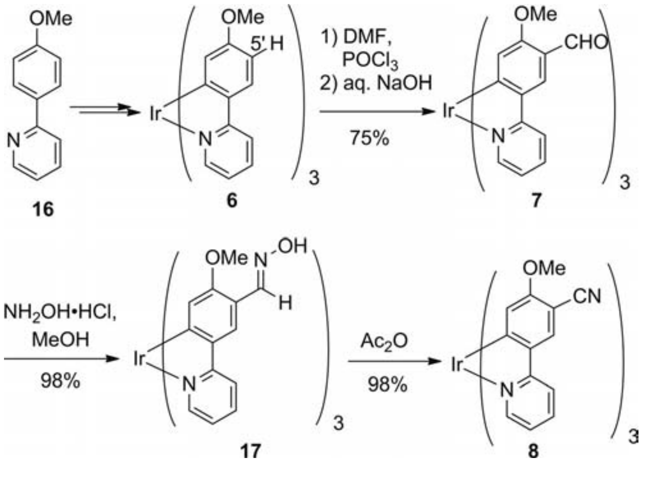
Generally, *fac*-tris-cyclometalated Ir^{III} complexes are prepared by the reaction of $IrCl_3$ or [Ir(acac)$_3$] (acac = acetylacetonate) with the corresponding ligands under high thermal conditions (170–220 °C).[2h,2i,14,15] On the other hand, regioselective substitution reactions after the preparation of cyclometalated Ir^{III} complexes would be an alternative method to prepare functionalized Ir^{III} complexes, which are otherwise difficult to prepare. However, successful attempts to functionalize ligands bound to the Ir^{III} complexes are few in number.[16]

We recently reported the regioselective halogenation, nitration, and formylation of *fac*-[Ir(ppy)$_3$] (**1**) and *fac*-[Ir(tpy)$_3$] (**2**) at the 5′-position (*para* to the C–Ir bond) of the phenyl ring, and their subsequent conversions to amino, formyl, and cyano groups (**3**, **4**, and **5** in Scheme 1).[17] As summarized in Scheme 1, *fac*-[Ir(atpy)$_3$] (**3**), which contains three amino groups at the 5′-position, exhibits a red luminescence emission in CH_2Cl_2 at 581 nm, which is a much longer wavelength than that of **2** (green emission at 512 nm). In addition, the color of the emission of **3** in aqueous solutions is dependent on the pH of the aqueous solutions. Namely, the red (around 600 nm) changes to green (at around 530 nm) when the amino groups are protonated, possibly because the electron-donating NH_2 group is switched to an electron-withdrawing $(NH_3)^+$ group. On the other hand, the introduction of electron-withdrawing groups such as CHO and CN groups at the same position (**4** and **5**), induces an approximately 30 nm blueshift in the emission wavelength (blue emission at 477 and 478 nm in CH_2Cl_2, respectively). These results suggest that modifications at the 5′-position of the tpy ligand of **2** can be effective for the color-tuning of Ir^{III} complexes.

In this manuscript, we report on the synthesis of tris-cyclometalated Ir^{III} complexes **7**–**12** (Scheme 1) by regioselective substitution reactions (formylation, thiocyanation, iodination) and subsequent conversions (cyanation, cross-coupling reaction, reduction, and oxidation) on a 2-(4′-methoxyphenyl)pyridine (mppy) ligand of *fac*-[Ir(mppy)$_3$] (**6**) shown in Scheme 1 and their photochemical properties.

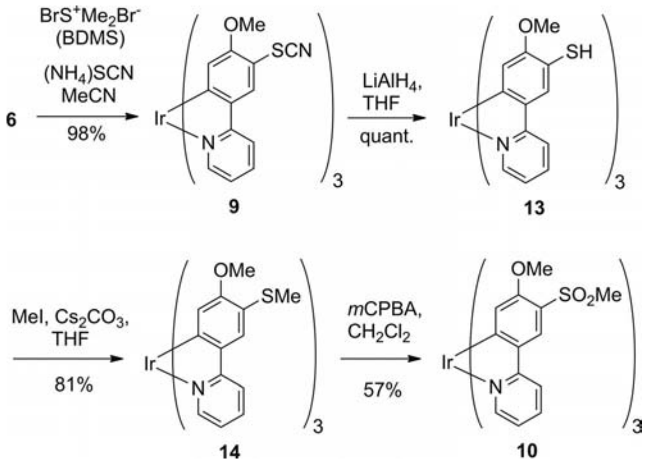
Results and Discussion

In this study, complex **6** was selected for use as a key platform for new blue-emitting Ir^{III} complexes, since its emission wavelength is observed at 481 nm in EtOH/MeOH glass at 77 K, which is 12 nm shorter than that of **2** under the same conditions, as reported by Watts and co-workers.[15] To direct the color of the emission of tris-cyclometalated Ir^{III} complexes to the blue region, a variety of electron-withdrawing groups (CN, CHO, SCN, SO_2Me, and SO_2Ar groups) were introduced at the 5′-position of **6**. The preparation **6** was carried out starting from 2-(4-methoxyphenyl)pyridine **16** through a dichloro-bridged dimer, [{(mppy)$_2$IrCl}$_2$] by using the synthetic procedure reported by Thompson and co-workers.[2i] The formylation of **6** was then carried out with DMF and $POCl_3$ (Vilsmeier reaction) to give the tris(formyl) derivative **7** in 75% yield (Scheme 3) following a previously reported method.[17] At this point, **7** was converted into the tris(hydroxyimino) derivative **17** in 98% yield by treatment with $NH_2OH\cdot HCl$, followed by reaction with Ac_2O to afford the tris(cyano) derivative **8**.[17,18]



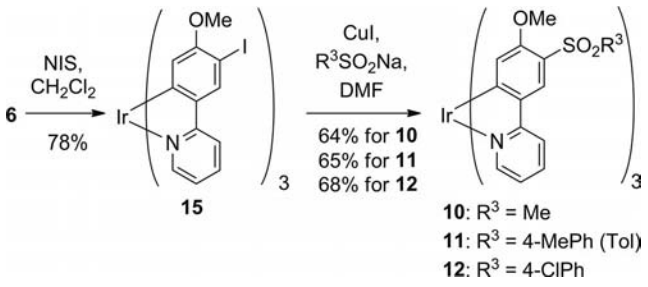
Scheme 3.

The thiocyanation of **6** was performed using bromodimethylsulfonium bromide (BDMS) and ammonium thiocyanate [$(NH_4)SCN$][19] to give **9** in 98% yield (Scheme 4). The tris(thiocyano) derivative **9** was readily reduced to the tris(thiol) derivative **13** with $LiAlH_4$ at 0 °C, which was then methylated to give the tris(methylthio) derivative **14**. The desired tris(mesyl) derivative **10** was produced in 57% yield by the oxidation of **14** with *meta*-chloroperbenzoic acid (*m*CPBA).



Scheme 4.

To introduce sulfonyl groups, we iodinated **6** by reaction with *N*-iodosuccinimide (NIS) to obtain **15** in 78% yield,[17] and cross-coupling reactions of **15** with sodium *p*-toluenesulfinate or sodium 4-chlorophenylsulfinate in the presence of CuI in DMF at 110 °C gave **11** and **12** (Scheme 5).[20] The tris(mesyl) derivative **10** was also directly obtained from **15** in 64% yield by treating it with sodium methanesulfinate.[21]



Scheme 5.

UV/Vis and Luminescence Spectra of Substituted [Ir(mppy)$_3$] Complexes

UV/Vis spectra of the Ir complexes **6**–**15** (10 μM) in CH_2Cl_2 at 298 K are shown in Figure 1 and their photochemical and electrochemical data are summarized in Table 1. The strong absorption bands in the ultraviolet region at 250–350 nm were assigned to the $^1\pi$–π^* transition of the mppy ligands. The weak shoulder bands at 350–450 nm can be assigned spin-allowed singlet-to-singlet metal-to-ligand charge transfer (^{1}MLCT) transitions, spin-forbidden singlet-to-triplet ^{3}MLCT transitions, and $^3\pi$–π^* transitions.[2i,11a,14]

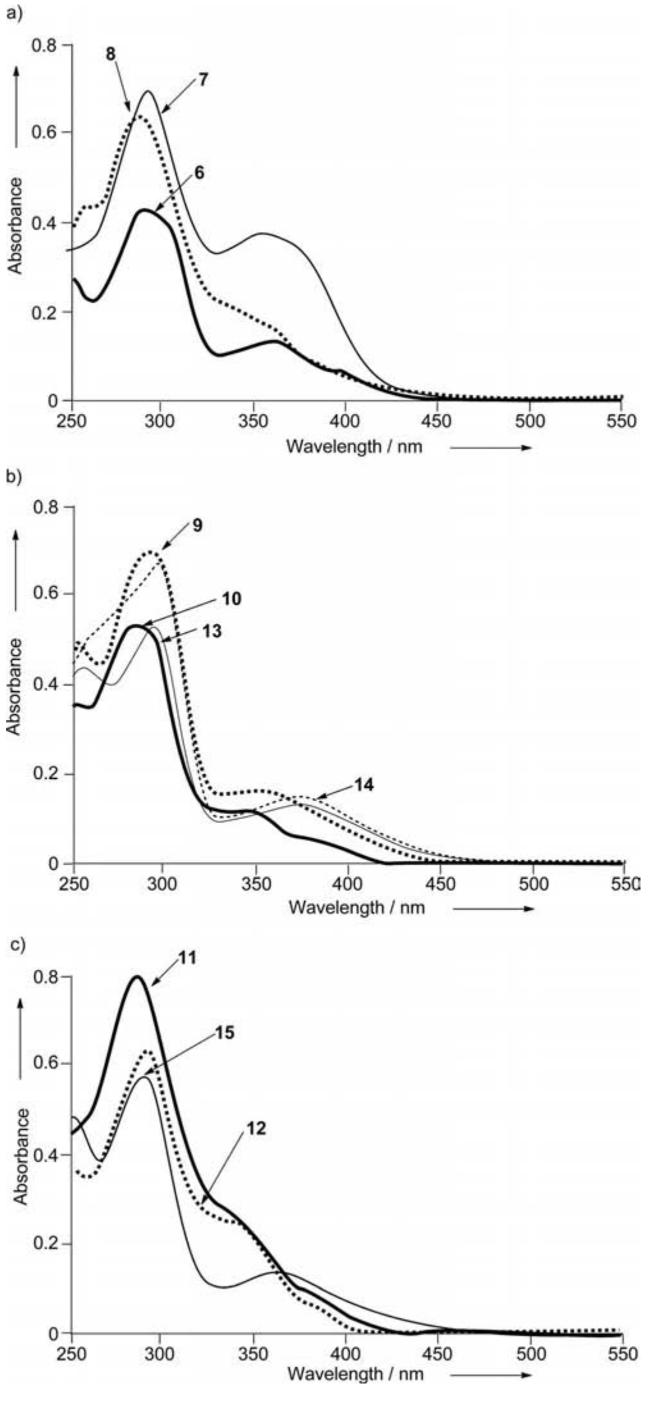


Figure 1. UV/Vis spectra of Ir^{III} complexes in CH_2Cl_2 at 298 K. (a) Compound **6** (bold curve), **7** (plain curve), and **8** (bold dashed curve). (b) Compound **9** (bold dashed curve), **10** (bold curve), **13** (plain curve), and **14** (plain dashed curve). (c) Compound **11** (bold curve), **12** (bold dashed curve), and **15** (plain curve); [Ir complex] = 10 μM.

Luminescence spectra of [Ir(mppy)$_3$] derivatives **6**–**15** (10 μM) in degassed CH_2Cl_2 were measured at 298 K as shown in Figure 2. All of the Ir^{III} complexes were excited at 366 nm. The data for the emission wavelength and luminescent quantum yields (*Φ*) are summarized in Table 1. The emission maxima of **6** (495 nm) is 17 nm shorter than that

Table 1. Photochemical and electrochemical properties of the substituted $[Ir(mppy)_3]$ at 298 K.

	λ_{max} [nm] (absorption)[a]	λ_{max} [nm] (emission)[a]	Φ	τ [µs][b]	$E^{1/2}_{ox}$ [V][c]
6	289, 360	495	0.65	1.8	0.30
7	292, 356	463, 488	0.52	2.7	0.66
8	285	464, 492	0.60	2.6	0.73
9	293, 352	486	0.29	1.1	0.61
10	283, 340	465, 492	0.39	2.6	0.69
11	287	465, 492	0.56	2.2	0.70
12	288	463, 491	0.68	2.4	0.75
13	295, 373	511	0.21	n.d.[d]	n.d.[d]
14	297, 372	520	0.31	3.0	n.d.[d]
15	292, 364	491	0.002	<0.012[e]	0.43

[a] [Ir complex] = 10 µM in CH_2Cl_2. [b] Luminescence lifetime in CH_2Cl_2. [c] DMF that contained 0.1 M nBu_4NPF_6 (V versus Fc^+/Fc). [d] Not determined. [e] Less than detection limit on our system.

of **2** (λ_{max} = 512 nm) in CH_2Cl_2, and the luminescent quantum yield of **6** (Φ = 0.65) is higher than that of **2** (Φ = 0.50).[17] Unlike the absorption spectra, the emission spectra are affected by the electron-withdrawing ability of the substituent groups. The emission maxima of **7** and **8**, which contain CHO and CN groups, have two emission maxima at around 463 nm and around 490 m. Both complexes exhibit a blue emission as shown in Figure 2 (a) and Figure 3, and the luminescence quantum yields of **7** and **8** are comparable to that of **6**. The introduction of a thiocyano group induces only a 9 nm blueshift from **6**, and the color of the emission is green at 486 nm (Figure 2, b). The emission maxima of tris(thiol) derivative **13** prepared by the reduction of **9**, and the tris(methylthio) derivative **14** are 511 and 520 nm, respectively. These results indicate that thiol and methylthio groups act as electron-donating groups to induce a redshift in the emission.

The emission maxima of the tris(mesyl) derivative **10**, prepared by the oxidation of **14**, appear at 465 and 492 nm. The luminescence quantum yields of **9**, **13**, **14**, and **10**, prepared by subsequent conversions (Scheme 4), are somewhat lower than that of **6**. The emission spectra of **11**[22] and **12** are similar to that of **10** with luminescence quantum yields (Φ) of 0.56 and 0.68, respectively (Figure 2, c). The slightly shorter emission wavelength of **12** compared to that of **11** can be attributed to the electron-withdrawing effect of the Cl substituent at the *para* position. The Φ value of the tris(iodo) derivative **15** is quite low (Φ = 0.002),[23] and the emission maxima is observed at 491 nm. Pictures of the emission color for Ir^{III} complexes **6**, **8**, **11**, and **12** are shown in Figure 3. Luminescence lifetimes of these complexes (**6**–**12** and **14**) measured in CH_2Cl_2 at 298 K are 1.1–3.0 µs, as listed in Table 1 (see also Figure S3 in the Supporting Information), thereby supporting their luminescence emission through excited triplet states.[1,24,25]

Electrochemical Properties and Theoretical Calculations of Ir Complexes

Cyclic voltammetry of complexes **6**–**12**, and **15** were measured in anhydrous DMF that contained 0.1 M Bu_4NPF_6

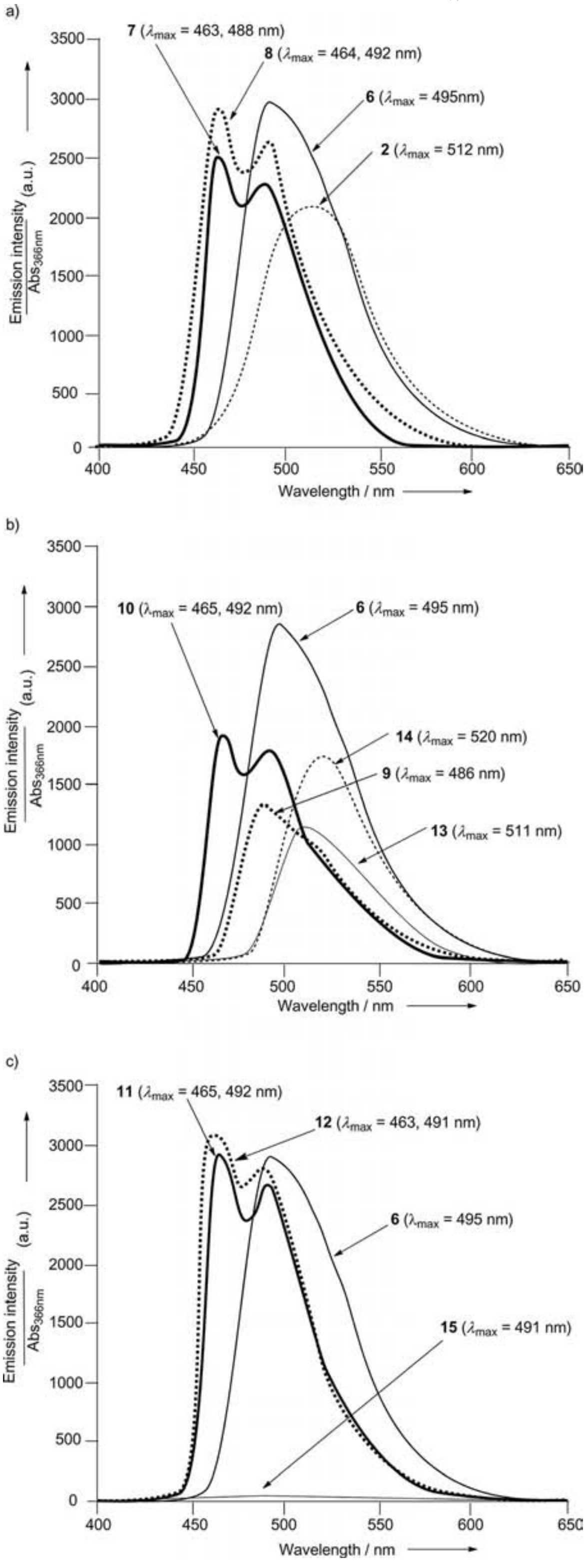


Figure 2. Emission spectra of Ir^{III} complexes in degassed CH_2Cl_2 at 298 K (excitation at 366 nm). (a) Compound **2** (plain dashed curve), **6** (plain curve), **7** (bold curve), and **8** (bold dashed curve). (b) Compound **9** (bold dashed curve), **10** (bold curve), **13** (thin curve), and **14** (plain dashed curve). (c) Compound **11** (bold curve), **12** (bold dashed curve), and **15** (thin curve). [Ir complex] = 10 µM. Units a.u. are arbitrary units, and the emission intensity was normalized with the absorbance of each compound at 366 nm, which was used for the excitation of all of the Ir complexes.

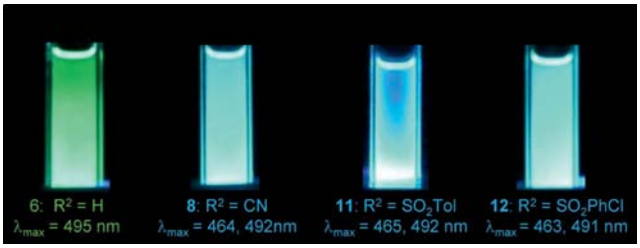


Figure 3. Photograph showing the color of the emission of Ir^{III} complex **6**, **8**, **11**, and **12** in CH_2Cl_2 ([Ir complex] = 30 μм, excitation at 365 nm).

of supporting electrolyte based on a ferrocenium/ferrocene (Fc^+/Fc) redox potential as an internal standard. The results are summarized in Table 1. These Ir^{III} complexes show quasireversible oxidation processes with a rate of 100 $m\,s^{-1}$. Whereas the half-wave oxidation potential of **6** (R^2 = H) is 0.30 V, those of **7** (R^2 = CHO), **8** (R^2 = CN), **9** (R^2 = SCN), **10** (R^2 = SO_2Me), **11** (R^2 = SO_2Tol), **12** (R^2 = SO_2PhCl), and **15** (R^2 = I) are 0.66, 0.73, 0.61, 0.69, 0.70, 0.75, 0.43 V, respectively, thereby implying that the introduction of electron-withdrawing groups causes positive shifts in the oxidation potentials (0.66–0.75 V versus Fc^+/Fc) relative to that of **6**, which suggests that these groups at the 5′-position effectively stabilize the HOMO energy levels of the $[Ir(mppy)_3]$ complex.[26] Figure 4 shows the relationship between the wavelength of emission maxima and the oxidation potentials of **6**–**12** and **15**. Although sulfonyl and cyano groups are stronger electron-withdrawing groups than a formyl group,[27] further blueshifts of **8** and **10**–**12** are not observed in compared with **7**, possibly because these groups also lower the LUMO energy level (Table S3 in the Supporting Information).

Density functional theory (DFT) calculations[28] of **6**–**15** were carried out using the Gaussian 03 program.[29] The B3LYP hybrid functional was used together with the LanL2DZ basis set for Ir and I atoms and the 6-31G basis set for H, C, N, O, S, and Cl atoms. The HOMO and LUMO energies were obtained by single-point calculation of the optimized Ir complexes. The calculated HOMO–LUMO shapes of the Ir^{III} complexes are similar, as shown in Figures S5–S10 in the Supporting Information. The HOMO orbital consists of phenyl π and Ir d orbitals, whereas the LUMO orbital is mainly localized on the pyridine ring. The HOMO and LUMO energy levels by DFT calculations (Table S3) indicate that the introduction of electron-withdrawing groups such as formyl, cyano, and sulfonyl groups stabilize the HOMO energy more than the LUMO energy, thereby resulting in a spread of the HOMO–LUMO energy gap (E_g = 3.79–3.90 eV) relative to that of **6** (E_g = 3.66 eV).[30]

Conclusion

In this manuscript, we report on the synthesis of a series of tris-cyclometalated Ir^{III} complex {*fac*-$[Ir(mppy)_3]$ (**6**)} by several regioselective substitution reactions, including formylation, thiocyanation, and iodination of the ligand. Furthermore, the chemical conversions also led to the preparation of compounds **8** and **10**–**14**. To the best of our knowledge, carbon–heteroatom bond formation such as the C–SO_2 bond by the cross-coupling reaction of the metal complexes has been not reported.[31] The introduction of electron-withdrawing groups such as CHO, CN, and sulfonyl groups (SO_2Me, SO_2Ar) at the 5′-position of **6** induces an approximately 30 nm blueshift in the luminescence emission, thereby resulting in a blue emission (463 to 465 nm) in degassed organic solvents without the fluorine substituent on the ligands.[12s,13a] The findings reported herein provide important information for the design and synthesis of new blue-emitting phosphorescent compounds. Diverse direct modifications after preparation of the parent metal complexes would provide useful methods for the molecular design and synthesis that contribute to a wide range of applications in inorganic chemistry, materials chemistry, supramolecular chemistry, photochemistry, biological chemistry, and related fields.

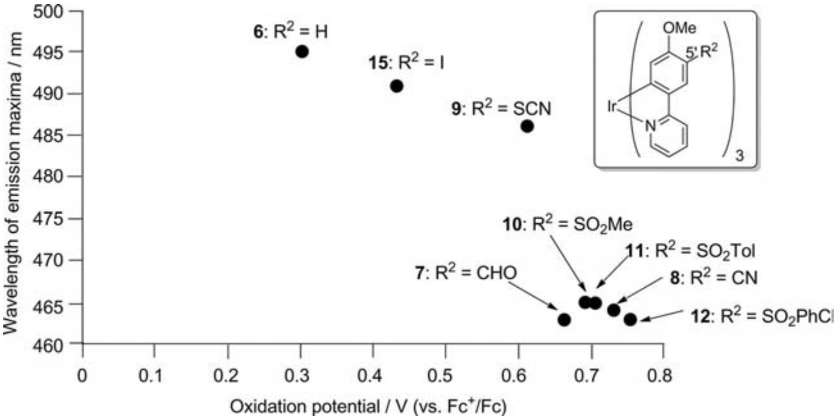


Figure 4. Plot of wavelengths of emission maxima versus the oxidation potential of **6**–**12** and **15**. For **7**, **8**, and **10**–**12**, the wavelengths at which highest emission is observed are plotted.

Experimental Section

General Information: $IrCl_3{\cdot}3H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ were purchased from KANTO CHEMICAL Co., Inc. Anhydrous CH_2Cl_2, MeCN, and DMF were obtained by distillation from CaH_2. All aqueous solutions were prepared using deionized water. Bromodimethylsulfonium bromide (BDMS)[19] and 2-(4′-methoxyphenyl)-pyridine[32] were prepared according to the reported literature procedure. Copper(I) iodide was purified according to the reported literature procedure.[33] All synthetic procedures were carried out under an atmosphere of argon. Melting points were measured with a YANACO MP33 Micro Melting Point Apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer FTIR Spectrum 100 (ATR). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a JEOL Always 300 spectrometer. Elemental analyses were performed with a Perkin–Elmer CHN 2400 analyzer. Ir^{III} complexes for elemental analyses were recrystallized from $CHCl_3$/hexane. Electrospray ionization (ESI) mass spectra were recorded with a Varian 910-MS instrument. Thin-layer (TLC) and silica gel column chromatography was performed with a Merck 5554 (silica gel) TLC plate and Fuji Silysia Chemical FL-100D, respectively.

Complex 6: A mixture of dichloro-bridged dimers, $[\{(mppy)_2\text{-}IrCl\}_2]$[34] (1.20 g, 1.01 mmol), **16** (0.561 g, 3.03 mmol), and K_2CO_3 (1.40 g, 10.1 mmol) in degassed glycerol (105 mL) was heated at 200 °C under an argon atmosphere for 24 h. After cooling the reaction mixture to room temperature, H_2O was added. The resulting precipitate was filtered off, washed with H_2O, and dried. The crude residue was purified by silica gel column chromatography ($CHCl_3$) to afford **6** as a yellow powder (0.979 g, 65% yield); m.p. > 300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3055, 2998, 2961, 2934, 2831, 1578, 1544, 1456, 1422, 1272, 1209, 1040, 840, 766, 748, 584 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.74 (d, J = 8.4 Hz, 3 H), 7.57–7.45 (m, 9 H), 6.77 (ddd, J = 1.3, 5.6, 8.1 Hz, 3 H), 6.47–6.45 (m, 3 H), 6.44 (s, 3 H), 3.55 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 54.63, 106.57, 118.03, 120.53, 120.62, 125.15, 135.70, 136.96, 146.92, 160.67, 163.90, 166.36 ppm. ESI-MS: m/z calcd. for $C_{36}H_{30}IrN_3O_3$ $[M]^+$: 743.1888; found 743.1892. $C_{36}H_{30}IrN_3O_3{\cdot}0.66CHCl_3$: calcd. C 53.42, H 3.75, N 5.10; found C 53.58, H 3.88, N 4.99.

Complex 7: Phosphorous oxychloride (1.6 mL) was added dropwise to dry DMF (4 mL), and the resulting mixture was stirred at room temperature for 1 h, after which **6** (0.300 g, 0.403 mmol) was added to obtain a yellow solution. After stirring at 80 °C for 18 h, the deep-red reaction mixture was allowed to cool at 0 °C, and 1 M NaOH (25 mL) was then added. After stirring at room temperature for 2 h, the yellow solid was isolated by filtration and washed with water to afford **7** as a yellow powder (0.250 g, 75% yield); m.p. > 300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3070, 3002, 2961, 2933, 2837, 1664, 1573, 1531, 1419, 1400, 1283, 1219, 1146, 1021, 929, 783, 745, 726, 529 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 10.31 (s, 3 H), 8.16 (s, 3 H), 7.97 (d, J = 8.0 Hz, 3 H), 7.71 (td, J = 1.5, 8.0 Hz, 3 H), 7.47 (d, J = 5.5 Hz, 3 H), 6.96 (ddd, J = 1.1, 5.5, 8.0 Hz, 3 H), 6.52 (s, 3 H), 3.54 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 55.19, 118.18, 119.03, 119.24, 122.20, 123.16, 137.19, 137.76, 146.85, 162.40, 164.70, 176.26, 189.62 ppm. ESI-MS: m/z calcd. for $C_{39}H_{31}IrN_3O_3$ $[M + H]^+$: 828.1813; found 828.1807. $C_{39}H_{30}IrN_3O_6{\cdot}0.66CHCl_3$: calcd. C 52.44, H 3.40, N 4.63; found C 52.84, H 3.53, N 4.64.

Complex 8: Hydroxylamine monohydride (91.8 mg, 1.33 mmol) was added to a solution of **7** (110 mg, 0.133 mmol) in MeOH (25 mL). The reaction mixture was stirred at room temperature for 11 h and concentrated under reduced pressure. Water was added to the resulting residue, and the pH of the solution was adjusted to pH 5–6 by the addition of 1 M NaOH. The insoluble compounds were then collected by filtration and washed with water to afford **17** as a yellow-brown powder (116 mg, 98%); m.p. > 300 °C. IR (ATR): $\tilde{\nu}$ = 3208, 3069, 2997, 2933, 2833, 1587, 1522, 1459, 1422, 1262, 1247, 1228, 1151, 1020, 932, 780, 747, 589 cm^{-1}. ^1H NMR (300 MHz, $[D_6]$acetone/TMS): δ = 9.80 (s, 3 H), 8.30 (s, 3 H), 8.11 (s, 3 H), 8.01 (d, J = 8.4 Hz, 3 H), 7.79 (br. t, J = 7.2 Hz, 3 H), 7.62 (d, J = 5.6 Hz, 3 H), 7.07 (br. t, J = 7.2 Hz, 3 H), 6.60 (s, 3 H), 3.48 (s, 9 H) ppm. ESI-MS: m/z calcd. for $C_{39}H_{33}IrN_6O_6$ $[M]^+$: 872.2062; found 872.2068.

Ac_2O (1.5 mL) was added to **17** (13.0 mg, 14.9 μmol) and the reaction mixture was stirred at 140 °C for 2 h. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography ($CHCl_3$) to afford **8** as a yellow powder (11.9 mg, 98% yield); m.p. > 300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3075, 3008, 2933, 2831, 2213, 1584, 1523, 1464, 1423, 1281, 1251, 1231, 1148, 1020, 911, 780, 745, 629 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.84 (d, J = 8.0 Hz, 3 H), 7.80 (s, 3 H), 7.74 (td, J = 8.0, 1.5 Hz, 3 H), 7.44 (d, J = 5.5 Hz, 3 H), 7.00 (ddd, J = 1.1, 5.5, 8.0 Hz, 3 H), 6.42 (s, 3 H), 3.54 (s, 9 H) ppm. ^{13}C NMR: δ = = (75 MHz, $CDCl_3$/TMS): δ = 55.53, 93.77, 117.97, 118.38, 118.96, 122.50, 128.62, 137.46, 147.00, 161.25, 163.90, 171.76 ppm. ESI-MS: m/z calcd. for $C_{39}H_{27}IrN_6O_3$ $[M]^+$: 818.1745; found 818.1741. $C_{39}H_{27}IrN_6O_3{\cdot}0.5CHCl_3$: calcd. C 53.94, H 3.15, N 9.55; found C 53.70, H 2.80, N 9.22.

Complex 9: Compound **6** (10.0 mg, 13.4 μmol) was added to a yellow suspension of bromodimethylsulfonium bromide (BDMS)[19] (13.4 mg, 60.3 μmol) and ammonium thiocyanate (12.2 mg, 161 μmol) in MeCN (3 mL), and the reaction mixture was stirred at room temp. for 1 h. The resulting reaction mixture was quenched by sat. $NaHCO_3$ (0.5 mL), and the solid residue was removed by filtration. The residue was washed with $CHCl_3$. The organic layer was separated, washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography ($CHCl_3$) to afford **9** as a yellow powder (14.3 mg, 98% yield); m.p. 298–300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3070, 3007, 2933, 2838, 2152, 1602, 1572, 1559, 1458, 1421, 1266, 1249, 1228, 1074, 1028, 881, 779, 744, 617 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.83 (d, J = 8.0 Hz, 3 H), 7.80 (s, 3 H), 7.68 (td, J = 1.5, 8.0 Hz, 3 H), 7.48 (d, J = 5.5 Hz, 3 H), 6.96 (ddd, J = 1.1, 5.5, 8.0 Hz, 3 H), 6.40 (s, 3 H), 3.55 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 55.74, 102.33, 111.61, 118.76, 122.12, 128.30, 137.02, 138.58, 147.07, 158.45, 164.37, 167.32 ppm. ESI-MS: m/z calcd. for $C_{39}H_{27}IrN_6O_3S_3$ $[M]^+$: 914.0907; found 914.0899. $C_{39}H_{27}IrN_6O_3S_3{\cdot}0.2CHCl_3$: calcd. C 50.09, H 2.92, N 8.94; found C 50.33, H 2.53, N 8.85.

Complex 13: $LiAlH_4$ (41.3 mg, 1.09 mmol) was added to a solution of **9** (80.0 mg, 0.087 mmol) in dry THF (15 mL) that had been cooled to 0 °C, and the reaction mixture was stirred 30 min at 0 °C. After unreacted $LiAlH_4$ was destroyed by slowly adding of H_2O (20 mL) and 1 M HCl (20 mL) at 0 °C, the suspension was extracted with $CHCl_3$ (40 mL twice), dried with Na_2SO_4, and concentrated under reduced pressure to afford **13** as a yellow powder (73.5 mg, quant.); m.p. > 200 °C (dec.) (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3061, 2995, 2931, 2832, 2559, 1599, 1569, 1557, 1520, 1455, 1420, 1262, 1245, 1217, 1155, 1029, 1014, 877, 853, 1029, 1014, 877, 777, 743, 617 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.72 (d, J = 8.1 Hz, 3 H), 7.60–7.54 (m, 3 H), 7.58 (s, 3 H), 7.45 (d, J

= 5.5 Hz, 3 H), 6.82 (br. t, *J* = 6.4 Hz, 3 H), 6.41 (s, 3 H), 3.52 (s, 9 H) ppm. ESI-MS: *m*/*z* calcd for $C_{36}H_{30}IrN_3O_3S_3$ [M]$^+$: 839.1055; found 839.1058. $C_{36}H_{30}IrN_3O_3S_3{\cdot}0.33CHCl_3$: calcd. C 49.54, H 3.47, N 4.77; found C 49.49, H 3.23, N 4.83.

Complex 14: MeI (0.137 g, 0.964 mmol) and Cs_2CO_3 (0.186 g, 0.570 mmol) were added to a stirred solution of **13** (0.080 g, 0.095 mmol) in dry THF (15 mL). The reaction mixture was stirred at room temperature for 17 h, after which H_2O (40 mL) was added and extracted with $CHCl_3$ (40 mL twice). The organic layers were combined, dried with Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography ($CHCl_3$) to afford **14** as a yellow powder (0.068 g, 81%); m.p. 196–198 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3066, 2915, 2833, 1599, 1570, 1558, 1516, 1455, 1421, 1260, 1243, 1215, 1154, 1081, 1032, 1015, 884, 860, 778, 744, 617 cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS): δ = 7.76 (d, *J* = 8.4 Hz, 3 H), 7.61 (s, 3 H), 7.57 (br. t, *J* = 7.3 Hz, 3 H), 7.49 (d, *J* = 5.5 Hz, 3 H), 6.83 (br. t, *J* = 5.9 Hz, 3 H), 6.40 (s, 3 H), 3.52 (s, 9 H), 2.40 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 17.11, 55.33, 115.78, 118.00, 118.21, 121.02, 126.83, 136.06, 137.43, 147.05, 159.12, 163.27, 165.66 ppm. ESI-MS: *m*/*z* calcd for $C_{39}H_{36}IrN_3O_3S_3$ [M]$^+$: 881.1519; found 881.1519. $C_{39}H_{36}IrN_3O_3S_3{\cdot}0.5CHCl_3$: calcd. C 50.32, H 3.90, N 4.46; found C 50.03, H 3.62, N 4.38.

Complex 10: *m*CPBA (40.0 mg, 232 μmol) was added to a solution of **14** (31.4 mg, 35.6 μmol) in dry CH_2Cl_2 (6 mL) cooled to 0 °C, and then stirred at 0 °C for 1 h. It was then warmed to room temperature for 5 h. *m*CPBA (20.0 mg. 116 μmol) was added again, and the mixture was stirred at room temperature for 22 h. After the treating the mixture with 0.1 M NaOH (3 mL), the organic layer was extracted with $CHCl_3$ (10 mL twice), dried with Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography ($CHCl_3$/MeOH = 300:1) to afford **10** as a yellow powder (20.0 mg, 57% yield); m.p. > 300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3070, 3006, 2934, 2839, 1578, 1459, 1422, 1295, 1137, 955, 888, 772, 742, 534, 508 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.21 (s, 3 H), 7.96 (d, *J* = 8.1 Hz, 3 H), 7.73 (br. t, *J* = 7.9 Hz, 3 H), 7.47 (d, *J* = 5.5 Hz, 3 H), 7.00 (br. t, *J* = 6.4 Hz, 3 H), 6.46 (s, 3 H), 3.58 (s, 9 H), 3.14 (s, 9 H) ppm. ESI-MS: *m*/*z* calcd. for $C_{39}H_{36}IrN_3O_9S_3$ [M]$^+$: 977.1214; found 977.1209. $C_{39}H_{36}IrN_3O_9S_3{\cdot}0.25CHCl_3$: calcd. C 46.72, H 3.62, N 4.16; found C 46.65, H 3.44, N 4.18.

Complex 15: NIS (72.4 mg, 322 μmol) was added to a solution of **6** (60.0 mg, 80.6 μmol) in dry CH_2Cl_2 (15 mL) in the dark, and the reaction mixture was stirred at room temperature for 8.5 h. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography ($CHCl_3$/hexane = 2:1 to $CHCl_3$) to afford **15** as a yellow powder (71.0 mg, 78% yield); m.p. 247–249 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3063, 2995, 2951, 2930, 2831, 1599, 1555, 1519, 1455 1418, 1262, 1245, 1225, 1154, 1064, 1026, 871, 849, 777, 738, 603 cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS): δ = 7.95 (s, 3 H), 7.74 (d, *J* = 8.1 Hz, 3 H), 7.61 (dt, *J* = 8.1, 5.5 Hz, 3 H), 7.45 (d, *J* = 5.5 Hz, 3 H), 6.86 (br. t, *J* = 6.4 Hz, 3 H), 6.36 (s, 3 H), 3.49 (s, 9 H) ppm. ESI-MS: *m*/*z* calcd. for $C_{36}H_{27}IrN_3O_3I_3$ [M]$^+$: 1120.8787; found 1120.8805. $C_{36}H_{27}I_3IrN_3O_3{\cdot}1.2CHCl_3$: calcd. C 35.30, H 2.25, N 3.32; found C 35.15, H 1.97, N 3.26.

Complex 11: CuI (102 mg, 534 μmol) was added to a solution of **15** (50.0 mg, 44.5 μmol) in dry DMF (3 mL) and stirred at room temperature for 10 min. Sodium *p*-toluenesulfinate (95.1 mg, 534 μmol) was added, and the mixture was heated at 110 °C for 44 h. The reaction mixture was allowed to cool to room temperature, and sat. $NaHCO_3$ (15 mL) was then added. The organic layer was extracted with $CHCl_3$ (15 mL twice), dried with Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography ($CHCl_3$/hexane = 2:1) to afford **11** as a yellow powder (35.1 mg, 65% yield); m.p. > 300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3070, 3007, 2933, 2838, 2152, 1602, 1572, 1559, 1458, 1421, 1266, 1 cm^{-1}. IR (ATR): $\tilde{\nu}$ = 3068, 2932, 2837, 1573, 1458, 1422, 1299, 1281, 1228, 1145, 1097, 1069, 1016, 889, 711, 674, 567, 538 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.31 (s, 3 H), 7.97 (d, *J* = 8.4 Hz, 3 H), 7.74 (d, *J* = 8.4 Hz, 6 H), 7.73–7.70 (m, 3 H), 7.49 (d, *J* = 5.5 Hz, 3 H), 7.18 (d, *J* = 8.1 Hz, 6 H), 6.99 (br. t, *J* = 6.0 Hz, 3 H), 6.10 (s, 3 H), 3.16 (s, 9 H), 2.37 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 21.53, 55.04, 118.90, 119.28, 121.38, 122.29, 124.77, 127.91, 128.85, 137.08, 137.29, 139.45, 143.04, 146.99, 157.25, 164.47, 172.96 ppm. ESI-MS: *m*/*z* calcd. for $C_{57}H_{48}IrN_3O_9S_3$ [M]$^+$: 1205.2153; found 1205.2148. $C_{57}H_{48}IrN_3O_9S_3$ (1207.42): calcd. C 56.70, H 4.01, N 3.48; found C 56.34, H 3.80, N 3.32.

Complex 12: CuI (127 mg, 668 μmol) was added to a solution of **15** (50.0 mg, 44.5 μmol) in dry DMF (3 mL) and stirred at room temperature for 10 min. Sodium *p*-chlorobenzenesulfinate (159 mg, 801 μmol) was added, and the mixture was heated at 110 °C for 20 h. The reaction mixture was allowed to cool to room temperature, and sat. $NaHCO_3$ (10 mL) was then added. The organic layer was extracted with $CHCl_3$ (30 mL four times), dried with Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography ($CHCl_3$/hexane = 2:1) to afford **12** as a yellow powder (38.5 mg, 68% yield); m.p. > 300 °C (recrystallized from $CHCl_3$/hexane). IR (ATR): $\tilde{\nu}$ = 3073, 3003, 2940, 2840, 1567, 1525, 1459 1421, 1305, 1278, 1260, 1227, 1148, 1097, 1069, 1014, 891, 744, 709, 631, 585, 563 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.30 (s, 3 H), 7.98 (d, *J* = 8.0 Hz, 3 H), 7.81 (d, *J* = 8.4 Hz, 6 H), 7.76 (br. t, *J* = 8.0 Hz, 3 H), 7.48 (d, *J* = 5.5 Hz, 3 H), 7.36 (d, *J* = 8.4 Hz, 6 H), 7.01 (ddd, *J* = 1.1, 5.5, 8.0 Hz, 3 H), 6.12 (s, 3 H), 3.19 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 55.04, 118.86, 119.35, 120.81, 122.47, 124.74, 128.53, 129.43, 137.28, 137.44, 138.89, 140.74, 146.99, 157.14, 164.24, 173.44 ppm. ESI-MS: *m*/*z* calcd. for $C_{54}H_{39}IrN_3O_9S_3Cl_3$ [M]$^+$: 1265.0515; found 1265.0512. $C_{54}H_{39}Cl_3IrN_3O_9S_3{\cdot}0.33CHCl_3$: calcd. C 49.87, H 3.03, N 3.21; found C 49.58, H 2.89, N 3.28.

Complex **10** was also obtained by a procedure analogous to that used to prepare **11**. A mixture of **15** (5.0 mg, 4.5 μmol), CuI (10 mg, 54 μmol), and sodium methanesulfinate (8.3 mg, 81 μmol) in dry DMF (0.5 mL) was heated at 110 °C for 25 h. The resulting residue was purified by silica gel column chromatography ($CHCl_3$/MeOH = 100:1) to afford **10** as a yellow powder (2.8 mg, 64% yield).

Measurements of UV/Vis Absorption and Luminescence Spectra: UV/Vis spectra were recorded with a JASCO V-550 and V-630BIO UV/Vis spectrophotometer, and emission spectra were recorded with a JASCO FP-6200 spectrofluorometer at 298 K. Sample solutions in quartz cuvettes equipped with Teflon septum screw caps were bubbled with solvent saturated argon for 10 min before the luminescence measurements. The quantum yields of luminescence (Φ) were determined by comparison with the integrated corrected emission spectrum of a quinine sulfate standard, the emission quantum yield of which in 0.1 M H_2SO_4 was assumed to be 0.55[35] (excitation at 366 nm). For the calculation of emission quantum yields, Equation (1) was used, in which Φ_s and Φ_r denote the quantum yields of the sample and reference compound, η_s and η_r are the refractive indexes of the solvents used for the measurements of the sample and reference, A_s and A_r are the absorbance of the sample and the reference, and I_s and I_r stand for the integrated areas under the emission spectra of the sample and reference, respectively (all Ir compounds for luminescence measurements were excited at 366 nm in this manuscript). For the determination of Φ_s in mixed-solvent systems, the η values of main solvents were used for the calculation.

$$\Phi_s = \Phi_r(\eta_s^2 A_r I_s)/(\eta_r^2 A_s I_r) \qquad (1)$$

The luminescence lifetimes of sample solutions in degassed CH_2Cl_2 at 298 K were measured with a TSP1000M-PL-M (Unisoku, Osaka, Japan) instrument by using THG (355 nm) of Nd:YAG laser, Minilite I-10 (Continuum, CA, USA) as excitation source. The signals were monitored with an R2949 photomultiplier. Data were analyzed by using the nonlinear least-squares procedure.

Cyclic Voltammetry (CV): Cyclic voltammetry measurements were performed with a BAS model 660A electrochemical analyzer at room temperature in distilled DMF that contained 0.1 M $n\mathrm{Bu_4NPF_6}$ as the supporting electrolyte in a standard one-component cell under an argon atmosphere equipped with a 3 mm outer diameter glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode (Ag/AgCl in MeCN that contained 0.01 M $AgNO_3$ and 0.1 M $n\mathrm{Bu_4NClO_4}$). All solutions were deoxygenated by argon bubbling for at least 10 min before the measurements.

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[21] Unfortunately, the introduction of a trifluoromethanesulfonyl group into the Ir^{III} complex by using sodium trifluoromethanesulfinate has not been successful thus far.

[22] The emission spectrum of **11** in frozen CH_2Cl_2 at 77 K exhibits a typical rigidochromic shift (see Figure S1 in the Supporting Information and ref.[11c]). The emission maxima of **11** appear at 459 nm, and additional intense peaks appear 491 nm.

[23] We assume the low emission quantum yield of tris(iodo) derivative **15** is due to thermal deactivation through a nonradiative pathway.

[24] The luminescence lifetime of **15** is <12 ns at 298 K. Some Ir complexes with very short lifetimes (τ on the order of nanoseconds) have been reported, and it has demonstrated that their emission originates from the triplet state (see ref.[12c,12u]). Emission maxima of **15** at 77 K in frozen CH_2Cl_2 (485 and 517 nm) are almost identical to that at 298 K [491 and 517 (shoulder peak) nm] (Figure S2), thereby suggesting its emission through the triplet state.

[25] Complexes **6**–**12** and **14** have similar radiative ($k_r \approx 10^5\,s^{-1}$) and nonradiative ($k_{nr} \approx 10^5\,s^{-1}$) rate constants (Table S1 in the Supporting Information), which were calculated according to the equation $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$ (E. M. Kober, J. V. Caspar, R. S. Lumpkin, T. J. Meyer, *J. Phys. Chem.* **1986**, *90*, 3722–3734).

[26] The reduction processes for the Ir complexes measured in this manuscript are irreversible (Figure S4 in the Supporting Information). Potential gaps (E_1 [V] = $E^{ox}_{1/2} - E^{red}_{p}$) between the first oxidation ($E^{ox}_{1/2}$) and reduction (E^{red}_{p}) potential are 2.97 V for **6**, 2.98 V for **15**, 3.00 V for **9**, and 3.1–3.3 V for **7**, **8**, and **10**–**12** (Table S2). It is assumed that greater potential gaps of **7**–**12** and **15** than that of **6** result in a blueshift in the emission of **15** (4 nm), **9** (9 nm), and **7**, **8**, and **10**–**12** (approximately 30 nm).

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[30] Plot of the wavelength of emission maxima and HOMO–LUMO energy gap (E_g) of **6**–**15** indicates a nearly linear relationship; see Figure S11 in the Supporting Information.

[31] There are only a few examples of cross-coupling reactions that lead to carbon–carbon bond formation (e.g., Suzuki–Miyaura cross-coupling reactions) on halogenated ligands or triflate ligands bound to Ir^{III} (see ref.[14b,16]). For examples of cross-coupling reactions with other metal complexes, see: a) S. Chodorowski-Kimmes, M. Beley, J.-P. Collins, J.-P. Sauvage, *Tetrahedron Lett.* **1996**, *37*, 2963–2966; b) M. Hissler, A. El-ghayoury, A. Harriman, R. Ziessel, *Angew. Chem.* **1998**, *110*, 1804; *Angew. Chem. Int. Ed.* **1998**, *37*, 1717–1720; c) G. R. Pabst, O. C. Pfüller, J. Sauer, *Tetrahedron* **1999**, *55*, 8045–8064; d) C. J. Aspley, A. G. Williams, *New J. Chem.* **2001**, *25*, 1136–1147; e)

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