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Article

Regioselective Aromatic Substitution Reactions of Cyclometalated Ir(III) Complexes: Synthesis and Photochemical Properties of Substituted Ir(III) Complexes That Exhibit Blue, Green, and Red Color Luminescence Emission

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In this manuscript, the regioselective halogenation, nitration, formylation, and acylation of $Ir(tpy)_3$ and $Ir(ppy)_3$ (tpy = 2-(4′-tolyl)pyridine and ppy = 2-phenylpyridine) and the subsequent conversions are described. During attempted bromination of the three methyl groups in *fac*-$Ir(tpy)_3$ using *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO), three protons at the 5′-position (*p*-position with respect to the C−Ir bond) of phenyl rings in tpy units were substituted by Br, as confirmed by ^{1}H NMR spectra, mass spectra, and X-ray crystal structure analysis. It is suggested that such substitution reactions of Ir complexes proceed via an ionic mechanism rather than a radical mechanism. UV−vis and luminescence spectra of the substituted Ir(III) complexes are reported. The introduction of electron-withdrawing groups such as CN and CHO groups at the 5′-position of tpy induces a blue shift of luminescence emission to about 480 nm, and the introduction of electron-donating groups such as an amino group results in a red shift to about 600 nm. A reversible change of emission for the 5′-amino derivative of $Ir(tpy)_3$, $Ir(atpy)_3$, between red and green occurs upon protonation and deprotonation.

Introduction

Cyclometalated complexes play central roles as triplet emitters in the production of organic light-emitting diodes (OLEDs) because of their excellent luminescence properties.[1,2] Iridium(III) complexes such as *fac*-$Ir(tpy)_3$ **1** and *fac*-$Ir(ppy)_3$ **2** (tpy = 2-(4′-tolyl)pyridine and ppy = 2-phenylpyridine) shown in Chart 1 have long-lived excited states and high luminescence quantum yields (Φ) of 0.1−0.9,[1,2] mainly because of low-lying metal to ligand charge transfer (MLCT) (e.g., Φ for **2** has been reported to be 0.4).[2f,h,k] They are in widespread use in emission materials[3] and also as components of photoreductants,[4] photosensitizers,[5] oxygen sensors,[6] and photoredox catalysts.[7] In addition, several Ir complexes that emit blue-[8] and red-color[9] luminescence have been developed by choosing cyclometalating ligands. To our knowledge, however, examples of luminescent iridium complexes that reversibly respond to the surrounding environment (e.g., pH and metal cations) are rare.[1e,10,11]

Synthesis of various cyclometalated Ir complexes is typically conducted by heating Ir(III) salts such as $IrCl_3$ with the corresponding ligands that had been prepared in advance. Alternative synthetic methods would be the direct and regioselective modification of the metalated ligands after the Ir complexes are prepared, which would afford novel

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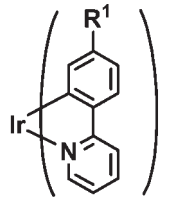
derivatives that otherwise would not be possible to obtain. For example, Stossel et al. reported in a patent[12] on the regioselective halogenation and nitration of cyclometalated Ir(III) complexes, although details of the reaction mechanisms involved in the substitutions were not reported, nor were the structures of the functionalized Ir complexes, and their photochemical properties.[13]

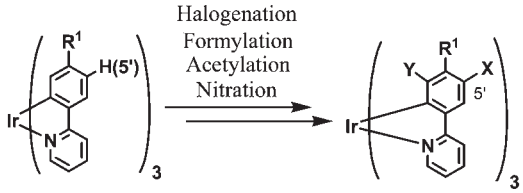
Recently, we have attempted to brominate the three methyl groups of **1** using *N*-bromosuccinimide (NBS) (3.3 equiv) and benzoyl peroxide (BPO) (0.6 equiv) in CCl_4 to obtain the Ir complex having three 2-(4′-bromomethylphenyl)pyridine units as an important intermediate for the synthesis of a new luminescent sensor for inositol 1,4,5-trisphosphate (Ins-(1,4,5)P_3).[14,15] Very interestingly, we found that the three methyl groups of *fac*-Ir(tpy)$_3$ were not brominated under these conditions and that the product was **3a**, in which three protons at the 5′-position (*p*-position with respect to the C−Ir bond) of phenyl rings in tpy units were substituted by Br (Chart 2), as described below.

Chart 1



1 : (R^1 = Me) *fac*-Ir(tpy)$_3$
2 : (R^1 = H) *fac*-Ir(ppy)$_3$

Chart 2



1 *fac*-Ir(tpy)$_3$: R^1 = Me
2 *fac*-Ir(ppy)$_3$: R^1 = H

3a : R^1 = Me, X = Br, Y = H
3b : R^1 = Me, X = I, Y = H
4a : R^1 = H, X = Br, Y = H
4b : R^1 = H, X = I, Y = H
5 : R^1 = Me, X = Y = Cl
6 : R^1 = H, X = Y = Cl
7 : R^1 = Me, X = CHO, Y = H
8 : R^1 = H, X = CHO, Y = H
9 : R^1 = H, X = $COCH_3$, Y = H
10 : R^1 = Me, X = NO_2, Y = H
11 : R^1 = H, X = NO_2, Y = H
12 : R^1 = Me, X = NH_2, Y = H

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Table 1. Results for the Halogenation of **1** and **2**

entry	Ir complex	reagent (eq.)	solvent	conditions	product	yield[a] (%)
1	**1**	NBS (3.3), BPO (0.6)	CCl_4	reflux, 1 day	**3a**	64
2	**1**	NBS (3.3)	CCl_4	reflux, 12 h	**3a**	61
3	**1**	NBS (3.3)	MeCN	r.t., 10 min	**3a**	96
4	**1**	NBS (3.3)	CH_2Cl_2	r.t., 10 min	**3a**	82
5	**1**	NBS (3.3)	Acetone	r.t., 10 min	**3a**	80
6	**1**	$(n\text{Bu})_4NBr_3$ (4.0)	MeCN	r.t., 1 h	**3a**	71
7	**1**	NIS (4.0)	MeCN	r.t.,1 day	**3b**	89
8	**1**	NIS (3.3)	CCl_4	reflux, 2 h	**3b**	60
9	**1**	$(BnMe_3)N\cdot ICl_2$ (4.0)	MeCN	r.. 16 hr	**3b**	70
10	**1**	NCS (6.9)	MeCN	r.t., 1 day	**5**	52
11	**2**	NBS (3.3), BPO (0.6)	CCl_4	reflux, 1 day	**4a**	55
12	**2**	NBS (3.3)	CCl_4	reflux, 12 h	**4a**	76
13	**2**	NBS (3.3)	MeCN	reflux, 1 h	**4a**	62
14	**2**	NIS (3.3)	MeCN	reflux, 1 day	**4b**	55
15	**2**	$(BnMe_3)N\cdot ICl_2$ (6.6)	MeCN	reflux, 1 day	**4b**	32
16	**2**	NCS (6.4)	MeCN	reflux, 1 day	**6**	61

[a] Isolated yield.

In this manuscript, the results of the regioselective halogenation (giving **3**−**6**), formylation (giving **7** and **8**), acetylation (giving **9** from **2**), and nitration (giving **10** and **11**) of **1** and **2** and their subsequent conversions are reported (Chart 2). Among the various derivatives prepared in this work, carboxy and amino derivatives represent potentially useful intermediates for introduction of various functionalities onto Ir complexes. Thus, it was expected that the well-defined C_3-symmetric structure of a cyclometalated Ir(III) complex could be a potential platform for design and synthesis of useful luminescent and photochemical tools in photochemistry, biological chemistry, analytical chemistry, medicinal chemistry, material science, and related area. In addition, the tris(5′-amino) derivative of $Ir(tpy)_3$, $Ir(atpy)_3$ **12** (atpy = 2-(5′-amino-4′-tolyl)pyridine), was prepared from **10**. The findings indicate that **12** emits a red luminescence at about 600 nm, and its emission is blue-shifted to about 500 nm upon the addition of a sufficiently strong acid to protonate the amino groups of **12**. The pH-dependent and reversible change in the emission of **12** is also reported.

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 acetonitrile (MeCN) and dimethylformamide (DMF) were obtained by distillation from CaH_2. All aqueous solutions were prepared using deionized water. Melting points were measured on a Büchi 510 Melting Point Apparatus and a YANACO MP-33 Micro Melting Point Apparatus and listed without corrections. For measurement of UV−vis and luminescence spectra in aqueous solution at given pHs, buffer solutions (CAPS, pH 10.0; CHES, pH 9.0; EPPS, pH 8.0; HEPES, pH 7.0; MES, pH 6.0; acetic acid/sodium acetate, pH 5.0, 4.0, and 3.0) were used, and the ionic strengths were appropriately adjusted with $NaNO_3$. The Good's buffer reagents (Dojindo) were obtained from commercial sources: MES (2-morpholinoethanesulfonic acid, pK_a = 4.8), HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid, pK_a = 7.5), EPPS (3-[4-(2-hydroxyethyl)-1-piperazinyl]propanesulfonic acid, pK_a = 8.0), CHES (2-(cyclohexylamino)ethanesulfonic acid, pK_a = 9.5), CAPS (3-(cyclohexylamino)propanesulfonic acid, pK_a = 10.4). IR spectra were recorded on a JASCO FTIR410 and a Perkin-Elmer FTIR-Spectrum 100 (ATR) at room temperature. ^1H NMR (300 MHz) were recorded on a JEOL Always 300 spectrometer. Elemental analyses were performed on a Perkin-Elmer CHN 2400 analyzer. Thin-layer chromatography (TLC) and silica gel column chromatographies were performed using a Merck 5554 (silica gel) TLC plate and Fuji Silysia Chemical FL-100D, respectively. Density Functional Theory (DFT) calculations were performed using Gaussian 03 at the B3LPY/LanL2DZ basis level.

Synthesis. Improved Method for the Synthesis of *fac*-Tris[2-(4′-tolyl)pyridine]iridium(III) (1)[2c,d,f−h,k,l,3,16] (Chart 1). A mixture of 2-(4′-tolyl)pyridine (7.6 g, 45.0 mmol), Na_2SO_4 (5 g, 35.2 mmol), and $IrCl_3\cdot 3H_2O$ (529 mg, 1.50 mmol) in dioxane/H_2O (1/1, 120 mL) was stirred at the reflux temperature for 1 day. After cooling to room temperature, the mixture was concentrated under reduced pressure. After adding 30 mL of water, the solution was extracted with $CHCl_3$ three times. The combined organic layer was concentrated under reduced pressure, to which Na_2SO_4 (5 g, 35.2 mmol) and dioxane/H_2O (1/1, 120 mL) were added, and the resulting mixture was stirred at the reflux temperature for 1 day. After repeating this treatment once more, the mixture was concentrated under reduced pressure. After adding 30 mL of water, the solution was extracted three times with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography ($CHCl_3$/hexane, 3:2) to afford **1** as a yellow powder (972 mg, 93% yield).

***fac*-Tris[2-(5′-bromo-4′-tolyl)pyridine]iridium(III) (3a) (Entry 1 in Table 1).** *N*-Bromosuccinimide (35 mg, 196 μmol) and benzoyl peroxide (10 mg, 41 μmol) were added to a solution of **1** (41 mg, 59 μmol) in CCl_4 (2.5 mL), and the whole was stirred at the reflux temperature for 1 day. After cooling to room temperature, the insoluble materials were removed by filtration. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/AcOEt, 1:3) to afford **3a** as a yellow powder (35 mg, 64% yield). Mp > 300 °C. IR (KBr): ν = 3026, 2917, 1601, 1560, 1468, 1421, 1354, 1256, 1157, 1065, 1034, 879, 780, 748, 605 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.80 (d, J = 7.7 Hz, 3H), 7.75 (s, 3H), 7.61 (t, J = 7.1 Hz, 3H), 7.41 (d, J = 4.4 Hz, 3H), 6.87 (t, J = 6.1 Hz, 3H), 6.65 (s, 3H), 2.18 (s, 9H). MS (m/z). Calcd for $C_{36}H_{27}Br_3IrN_3$ (M^+): 932.9364 Found: 932.9351. Anal. Calcd for $C_{36}H_{27}Br_3IrN_3$: C, 46.32; H, 2.91; N, 4.50%. Found: C, 46.45; H, 2.73; N, 4.41%.

***fac*-Tris[2-(5′-bromo-4′-tolyl)pyridine]iridium(III) (3a) (Entry 3 in Table 1).** *N*-Bromosuccinimide (17 mg, 93 μmol) was added to a solution of **1** (20 mg, 28 μmol) in MeCN (5 mL) in the dark. After stirring at room temperature for 10 min, the reaction mixture was concentrated under reduced pressure, and the resulting

(16) (a) McDonald, A. R.; Lutz, M.; von Chrzanowski, L. S.; van Klink, G. P. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **2008**, *47*, 6681–6691. (b) Stossel, P.; Fortte, R.; Parham, A.; Breuning, E.; Heil, H.; Vestweber, H. U.S. Patent US 2008/0312396 A1. An improved method for the synthesis of **1** by us is described in the Experimental Section.

residue was purified by silica gel column chromatography ($CHCl_3$) to afford **3a** as a yellow powder (25 mg, 96% yield).

***fac*-Tris[2-(5′-iodo-4′-tolyl)pyridine]iridium(III) (3b) (Entry 7 in Table 1).** *N*-Iodosuccinimide (39 mg, 172 μmol) was added to a solution of **1** (30 mg, 43 μmol) in MeCN (7.5 mL) in the dark. After stirring at the reflux temperature for 1 day, the reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/$CHCl_3$, 2:1) to afford **3b** as a yellow powder (41 mg, 89% yield). Mp > 300 °C. IR (KBr): ν = 3220, 2853, 1594, 1472, 1421, 1295, 1264, 1194, 1155, 1136, 1006, 874, 828, 783, 751, 739, 641, 583 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.99 (s, 3H), 7.79 (d, J = 8.2 Hz, 3H), 7.60 (t, J = 8.2 Hz, 3H), 7.40 (d, J = 5.5 Hz, 3H), 6.86 (t, J = 5.9 Hz, 3H), 6.68 (s, 3H), 2.21 (s, 9H). MS (m/z). Calcd for $C_{36}H_{27}I_3IrN_3$ (M^+): 1074.8945, Found: 1074.8938. Anal. Calcd for $C_{36}H_{27}I_3IrN_3$: C, 40.24; H, 2.53; N, 3.91%. Found: C, 40.61; H, 2.22; N, 4.04%.

***fac*-Tris[2-(5′-bromophenyl)pyridine]iridium(III) (4a) (Entry 12 in Table 1).** *N*-Bromosuccinimide (18 mg, 100 μmol) was added to a solution of **2** (20 mg, 31 μmol) in CCl_4 (10 mL) in the dark. The reaction mixture was stirred at the reflux temperature for 12 h and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/$CHCl_3$, 1:2) to afford **4a** as a yellow powder (21 mg, 76% yield). Mp > 300 °C. IR (KBr): ν = 3033, 3012, 2987, 2948, 2854, 2339, 1733, 1716, 1698, 1683, 1652, 1558, 1540, 1471, 1417 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.84 (d, J = 7.9 Hz, 3H), 7.73 (d, J = 1.8 Hz, 3H), 7.64 (t, J = 8.3 Hz, 3H), 7.48 (d, J = 5.5 Hz, 3H), 6.92 (t, J = 7.5 Hz, 3H), 6.91 (dd, J = 8.2, 1.8 Hz, 3H), 6.66 (dd, J = 8.1, 1.5 Hz, 3H). MS (m/z). Calcd for $C_{33}H_{21}Br_3IrN_3$ (M^+): 886.8870, Found: 886.8860. Anal. Calcd for $C_{33}H_{21}Br_3IrN_3$: C, 44.15; H, 2.39; N, 4.74%. Found: C, 44.23; H, 2.36; N, 4.68%.

***fac*-Tris[2-(5′-iodophenyl)pyridine]iridium(III) (4b) (Entry 14 in Table 1).** *N*-Iodosuccinimide (39 mg, 173 μmol) was added to a solution of **2** (34 mg, 53 μmol) in CH_2Cl_2 (13 mL) in the dark, and the reaction mixture was stirred at the reflux temperature for 1 day. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/$CHCl_3$, 1:2) to afford **4b** as a yellow powder (30 mg, 55% yield). Mp > 300 °C. IR (KBr): ν = 3038, 2244, 1600, 1557, 1467, 1414, 1306, 1251, 1133, 1059, 1024, 872, 823, 780, 750, 737, 685, 637, 568 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.90 (d, J = 1.8 Hz, 3H), 7.84 (d, J = 7.9 Hz, 3H), 7.65 (td, J = 7.1, 1.6 Hz, 3H), 7.46 (d, J = 4.4 Hz, 3H), 7.07 (dd, J = 8.1, 1.8 Hz, 3H), 6.93 (t, J = 6.1 Hz, 3H), 6.55 (d, J = 7.9 Hz, 3H). MS (m/z). Calcd for $C_{33}H_{21}I_3IrN_3$ (M^+): 1030.8476, Found: 1030.8469. Anal. Calcd for $C_{33}H_{21}I_3IrN_3$: C, 38.39; H, 2.05; N, 4.07%. Found: C, 38.54; H, 1.85; N, 4.01%.

***fac*-Tris[2-(3′,5′-dichloro-4′-tolyl)pyridine]iridium(III) (5) (Entry 10 in Table 1).** *N*-Chlorosuccinimide (30 mg, 224 μmol) was added to a solution of **1** (24 mg, 33 μmol) in MeCN (8 mL) in the dark, and the whole reaction mixture was stirred at room temperature for 1 day. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/$CHCl_3$, 1:2) to afford **5** as a yellow powder (16 mg, 52% yield). Mp. > 300 °C. IR (KBr): ν = 3648, 2946, 2921, 2852, 2337, 1733, 1716, 1698, 1683, 1652, 1558, 1540, 1506, 1455 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.84 (d, J = 8.4 Hz, 3H), 7.67 (td, J = 8.0, 1.6 Hz, 3H), 7.60 (s, 3H), 7.02 (d, J = 4.6 Hz, 3H), 6.82 (td, J = 6.6, 1.1 Hz, 3H), 2.33 (s, 9H). MS (m/z). Calcd for $C_{36}H_{24}Cl_6IrN_3$ (M^+): 898.9722, Found: 898.9702. Anal. Calcd for $C_{36}H_{24}Cl_6IrN_3$: C, 47.86; H, 2.68; N, 4.65%. Found: C, 47.66; H, 2.39; N, 4.52%.

***fac*-Tris[2-(3′,5′-dichlorophenyl)pyridine]iridium(III)·2.5CHCl$_3$ (6) (Entry 16 in Table 1).** *N*-Chlorosuccinimide (23 mg, 174 μmol) was added to a solution of **2** (18 mg, 27 μmol) in MeCN (5 mL) in the dark and the whole reaction mixture was stirred at the reflux temperature for 1 day. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/$CHCl_3$, 1:2) to afford **6** as a yellow powder (19 mg, 61% yield). Mp > 300 °C. IR (KBr): ν = 3632, 3077, 2923, 2852, 1720, 1600, 1563, 1477 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.88 (d, J = 8.2 Hz, 3H), 7.71 (td, J = 8.2, 1.6 Hz, 3H), 7.55 (d, J = 2.2 Hz, 3H), 7.07 (dd, J = 4.4 Hz, 3H), 6.82−6.92 (m, 6H). MS (m/z). Calcd for $C_{33}H_{18}Cl_6IrN_3$ (M^+): 856.9222, Found: 856.9232. Anal. Calcd for $C_{33}H_{18}Cl_6IrN_3\cdot 2.5CHCl_3$: C, 43.39; H, 2.10; N, 4.28%. Found: C, 43.06; H, 1.92; N, 4.64%.

***fac*-Tris[2-(5′-formyl-4′-tolyl)pyridine]iridium(III) (7) (Chart 4).** Phosphorus oxychloride (0.3 mL) was added dropwise to DMF (3 mL), and the resulting mixture was stirred at room temperature for 1 h, after which **1** (100 mg, 145 μmol) was added to obtain a yellow solution. After stirring at 80 °C for 16 h, the deep-red colored reaction mixture was allowed to cool at 0 °C, and 1 M NaOH (9 mL) was then added. After stirring at room temperature for 12 h, the yellow solid was isolated by filtration and washed with 10 mL of water to afford **7** as a yellow powder (109 mg, 98% yield). Mp > 300 °C. IR (KBr): ν = 3444, 2921, 2846, 2723, 1673, 1601, 1577, 1473, 1207, 1066, 929, 782, 750 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 10.19 (s, 3H), 8.09 (s, 3H), 8.03 (d, J = 8.4 Hz, 3H), 7.71 (t, J = 8.3 Hz, 3H), 7.45 (d, J = 5.3 Hz, 3H), 6.97 (t, J = 5.4 Hz, 3H), 6.70 (s, 3H), 2.44 (s, 9H). MS (m/z) Calcd for $C_{39}H_{30}IrN_3O_3$ (M^+): 779.1894, Found: 779.1891. Anal. Calcd for $C_{39}H_{30}IrN_3O_3$: C, 59.98; H, 3.87; N, 5.38%, Found: C, 59.94; H, 3.44; N, 5.48%.

***fac*-Tris{2-[(5′-hydroxymethyl)-4′-tolyl]pyridine}iridium(III)·2.5H$_2$O (15) (Chart 4).** $NaBH_4$ (51 mg, 1.4 mmol) was added to a solution of **7** (53 mg, 68 μmol) in EtOH (7 mL). The reaction mixture was stirred at room temperature for 12 h. The insoluble compounds were isolated by filtration and washed with water to afford **15** as a yellow powder (53 mg, 94% yield). Mp > 300 °C. IR (KBr): ν = 3421, 1596, 1472, 1426, 1261, 1160, 1068, 993, 923, 877, 785, 750, 633 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6/TMS): δ = 8.01 (d, J = 8.4 Hz, 3H), 7.74 (t, J = 9.0 Hz, 3H), 7.64 (s, 3H), 7.33 (d, J = 4.8 Hz, 3H), 7.02 (t, J = 7.0 Hz, 3H), 6.50 (s, 3H), 4.36 (s, 6H), 1.97 (s, 9H). MS (m/z). Calcd for $C_{39}H_{36}IrN_3O_3$ (M^+): 785.2362, Found: 785.2366. Anal. Calcd for $C_{39}H_{36}IrN_3O_3\cdot 2.5H_2O$: C, 56.30; H, 4.97; N, 5.05%, Found: C, 56.13; H, 4.46; N, 4.98%.

***fac*-Tris{2-[(5′-hydroxymethyl)phenyl]pyridine}iridium(III)·0.5H$_2$O (16) (Chart 4).** Phosphorus oxychloride (0.3 mL) was added to DMF (1.5 mL), and the resulting mixture was stirred at room temperature for 1 h, to which **2** (50 mg, 76 μmol) was added. After stirring at 80 °C for 16 h, the deep-red colored reaction mixture was allowed to cool at 0 °C, and 1 M NaOH (4.5 mL) was then added. After stirring at room temperature for 12 h, the yellow solid was isolated by filtration and washed with 10 mL of water to afford **8** as a yellow powder (50 mg, 88% yield). Mp > 300 °C. IR (KBr): ν = 2954, 2921, 2850, 1720, 1666, 1579, 1475, 1411, 1355, 1245, 1027, 784, 752, 485, 410 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 9.88 (s, 3H), 8.19 (d, J = 1.5 Hz, 3H), 8.10 (d, J = 8.4 Hz, 3H), 7.76 (td, J = 7.3, 1.5 Hz, 3H), 7.52 (d, J = 4.8 Hz, 3H), 7.26 (dd, J = 7.7, 1.6 Hz, 3H), 7.04 (t, J = 6.1 Hz, 3H), 6.98 (d, J = 7.7 Hz, 3H). MS (m/z). Calcd for $C_{36}H_{24}IrN_3O_6$ (M^+): 739.1447, Found: 739.1459.

$NaBH_4$ (16 mg, 423 μmol) was added to a solution of **8** (15 mg, 20 μmol) in EtOH (1.5 mL). The reaction mixture was stirred at room temperature for 7 h. The insoluble compounds were filtered off and washed with water to afford **16** as a yellow powder (13 mg, 86% yield from **8**). Mp > 300 °C. IR (KBr): ν = 3221, 2854, 1595, 1541, 1473, 1454, 1422, 1296, 1265, 1195, 1007, 829, 740, 642 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6/TMS): δ = 8.08 (d, J = 8.1 Hz, 3H), 7.76 (t, J = 6.9 Hz, 3H), 7.67 (s, 3H), 7.44 (d, J = 5.1 Hz, 3H), 7.09 (t, J = 6.6 Hz, 3H), 6.60−6.67 (m, 6H), 4.33 (s, 6H). MS (m/z). Calcd for $C_{36}H_{30}IrN_3O_3$ (M^+): 743.1893, Found: 743.1902. Anal. Calcd for $C_{36}H_{30}IrN_3O_3\cdot 0.5H_2O$: C, 57.36; H, 4.14; N, 5.57%, Found: C, 57.09; H, 4.27; N, 5.78%.

***fac*-Tris[2-(5′-carboxyl-4′-tolyl)pyridine]iridium(III)·3H$_2$O (17) (Chart 4).** A mixture of $NaClO_2$ (320 mg, 3.6 mmol) and $NaH_2PO_4 \cdot 2H_2O$ (1.11 g, 7.1 mmol) in water (4 mL) was added dropwise to a solution of **7** (309 mg, 0.40 mmol) and 2-methyl-2-butene (830 mg, 12 mmol) in DMSO (16 mL) at room temperature. After stirring at room temperature for 12 h, the mixture was concentrated under reduced pressure, to which 1 M aq. HCl was added. The resulting solid was filtered off and washed with water and MeOH to afford **17** as a yellow powder (260 mg, 74% yield). Mp > 300 °C. IR (KBr): ν = 3415, 2965, 1683, 1583, 1473, 1238, 1054, 1031, 781 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.23 (s, 3H), 8.16 (d, J = 8.2 Hz, 3H), 7.84 (t, J = 7.9 Hz, 3H), 7.42 (d, J = 5.9 Hz, 3H), 7.17 (t, J = 7.1 Hz, 3H), 6.57 (s, 3H), 2.24 (s, 9H). MS (m/z). Calcd for $C_{39}H_{30}IrN_3O_6$ (M^+): 827.1742, Found: 827.1735. Anal. Calcd for $C_{39}H_{30}IrN_3O_6 \cdot 3H_2O$: C, 53.05; H, 4.11; N, 4.76%, Found: C, 52.75; H, 3.78; N, 4.51%.

***fac*-Tris[2-(5′-carboxylphenyl)pyridine]iridium(III)·3H$_2$O (18) (Chart 4).** A mixture of $NaClO_2$ (220 mg, 2.3 mmol) and $NaH_2PO_4 \cdot 2H_2O$ (0.76 g, 4.9 mmol) in water (3 mL) was added dropwise to a solution of **8** (15 mg, 20 μmol) and 2-methyl-2-butene (570 mg, 8.2 mmol) in MeCN (1 mL) at 70 °C. After stirring for 12 h, the mixture was cooled to room temperature and concentrated under reduced pressure. The resulting solid was washed with water and MeOH to afford **18** as a yellow powder (10 mg, 59% yield). Mp > 300 °C. IR (KBr): ν = 3064, 3046, 1716, 1698, 1683, 1671, 1652, 1635, 1587 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.35 (s, 3H), 8.16 (d, J = 8.2 Hz, 3H), 7.83 (t, J = 7.0 Hz, 3H), 7.66 (d, J = 5.3 Hz, 3H), 7.30 (d, J = 7.9 Hz, 3H), 7.07 (t, J = 6.4 Hz, 3H), 6.85 (d, J = 7.9 Hz, 3H). MS (m/z). Calcd for $C_{36}H_{24}IrN_3O_6$ (M^+): 785.1272, Found: 785.1268. Anal. Calcd for $C_{36}H_{24}IrN_3O_6 \cdot 3H_2O$: C, 51.42; H, 3.84; N, 5.00%, Found: C, 51.20; H, 3.43; N, 4.95%.

Compound 19·MeOH (Chart 4). *N*,*N*-Diisopropylethylamine, (*i*Pr)$_2$NEt, (56 mg, 433 μmol) and PyBOP (226 mg, 434 μmol) were added to a solution of **17** (90 mg, 107 μmol) and *N*-*tert*-butyloxycarbonyl-1,2-ethylenediamine[17] (69 mg, 431 μmol) in DMF (15 mL). The reaction mixture was stirred at room temperature for 10 h. The reaction mixture was concentrated under reduced pressure, and the resulting residue was extracted three times with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography ($CHCl_3$/MeOH, 10:1) to afford **19** (87 mg, 64% yield) as a yellow powder. Mp > 300 °C. IR (KBr): ν = 2934, 1631, 1586, 1530, 1474, 1424, 1366, 1248, 1164, 1072, 998, 912, 778, 752, 672 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.87 (d, J = 8.2 Hz, 3H), 7.76 (s, 3H), 7.55 (t, J = 7.5 Hz, 3H), 7.36 (d, J = 5.0 Hz, 3H), 6.83 (t, J = 6.2 Hz, 3H), 6.69 (s, 3H), 6.43 (brs, 3H), 5.11 (brs, 3H), 3.47−3.54 (m, 6H), 3.30−3.40 (m, 6H), 2.24 (s, 9H), 1.39 (s, 27H). MS (m/z). Calcd for $C_{60}H_{72}IrN_9O_9$ (M^+): 1256.5177 Found: 1256.5155. Anal. Calcd for $C_{60}H_{72}IrN_9O_9 \cdot MeOH$: C, 56.90; H, 5.95; N, 9.79%. Found: C, 56.53; H, 5.82; N, 9.42%.

***fac*-Tris[2-(5′-hydroxyimino-4′-tolyl)pyridine]iridium(III)·2.5H$_2$O (21) (Chart 5).** Hydroxylamine monohydride (31 mg, 445 μmol) was added to a solution of **7** (39 mg, 49 μmol) in MeOH (8 mL). The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure, and the resulting residue was washed with water to afford **21** as a yellow powder (41 mg, 96% yield). Mp > 300 °C. IR (KBr): ν = 2982, 2214, 1662, 1583, 1521, 1473, 1424, 1383, 1263, 1242, 1221, 1158, 1068, 936, 889, 827, 782, 749, 673 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6/TMS): δ = 9.88 (s, 3H), 8.25 (s, 3H), 8.07 (d, J = 8.2 Hz, 3H), 8.00 (s, 3H), 7.78 (t, J = 7.5 Hz, 3H), 7.60 (d, J = 5.1 Hz, 3H), 7.06 (t, J = 5.9 Hz, 3H), 6.75 (s, 3H), 2.15 (s, 9H). MS (m/z). Calcd for $C_{39}H_{33}IrN_6O_3$ (M^+): 823.2141, Found: 823.2150. Anal. Calcd for $C_{39}H_{33}IrN_6O_3 \cdot 2.5H_2O$: C, 53.78; H, 4.40; N, 9.65%, Found: C, 54.11; H, 4.39; N, 9.38%.

***fac*-Tris[2-(5′-cyano-4′-tolyl)pyridine]iridium(III)·H$_2$O (22) (Chart 5).** Ac_2O (2 mL) was added to **21** (22 mg, 25 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 washed with water to afford **22** as a yellow powder (20 mg, quant.). Mp > 300 °C. IR (KBr): ν = 2921, 2212, 1759, 1585, 1473, 1424, 1382, 1315, 1270, 1240, 1215, 1158, 1065, 1021, 914, 888, 783, 666, 640 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.88 (d, J = 8.4 Hz, 3H), 7.82 (s, 3H), 7.72 (t, J = 7.2 Hz, 3H), 7.42 (d, J = 4.8 Hz, 3H), 7.00 (t, J = 6.0 Hz, 3H), 6.66 (s, 3H), 2.31 (s, 9H). MS (m/z). Calcd for $C_{39}H_{27}IrN_6$ (M^+): 770.1903, Found: 770.1904. Anal. Calcd for $C_{39}H_{27}IrN_6 \cdot H_2O$: C, 59.37; H, 3.70; N, 10.65%, Found: C, 59.04; H, 3.96; N, 10.61%.

***fac*-Tris[2-(5′-aminomethyl-4′-tolyl)pyridine]iridium(III)·3H$_2$O (20) (Chart 5).** $BH_3 \cdot THF$ (2 mL, 1.08 M) was added to a solution of **22** (48 mg, 62 μmol) in THF (1 mL). After stirring at room temperature for 1 day, 1 M aq. HCl (1 mL) was added to the reaction mixture, followed by addition of 1 M aq. NaOH (3 mL). The solution was extracted with $CHCl_3$, and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford **20** as a yellow powder (22 mg, 42% yield). Mp > 300 °C. IR (KBr): ν = 3365, 2925, 1662, 1585, 1561, 1472, 1425, 1385, 1263, 1242, 1208, 1158, 1068, 1021, 931, 885, 750, 701 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.70 (d, J = 7.7 Hz, 3H), 7.48 (t, J = 7.5 Hz, 3H), 7.43 (d, J = 4.0 Hz, 3H), 7.06 (s, 3H), 6.74 (t, J = 6.0 Hz, 3H), 6.55 (s, 3H), 3.65 (s, 6H), 2.00 (s, 9H). MS (m/z). Calcd for $C_{39}H_{39}IrN_6$ (M^+): 782.2842, Found: 782.2842. Anal. Calcd for $C_{39}H_{39}IrN_6 \cdot 3H_2O$: C, 55.90; H, 5.41; N, 10.03%, Found: C, 55.54; H, 4.97; N, 9.66%.

***fac*-Tris[2-(5′-acetylphenyl)pyridine]iridium(III)·4H$_2$O (9) (Chart 6).** Acetyl chloride (5 μL, 70 μmol) and $AlCl_3$ (10 mg, 74 μmol) were added to a solution of **2** (9 mg, 14 μmol) in 1,2-dichloroethane (4 mL). The reaction mixture was stirred at 0 °C for 10 min. The insoluble compounds were collected by filtration and washed with water to afford **9** as a yellow powder (8 mg, 67%). Mp > 300 °C. IR (KBr): ν = 3461, 3044, 1664, 1578, 1528, 1476, 1411, 1354, 1300, 1245, 1159, 1061, 1027, 962, 827, 784, 751, 714, 670 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.32 (d, J = 1.8 Hz, 3H), 8.09 (d, J = 8.2 Hz, 3H), 7.72 (td, J = 7.5, 1.5 Hz, 3H), 7.51 (d, J = 4.8 Hz, 3H), 7.37 (dd, J = 8.1, 1.8 Hz, 3H), 7.00 (t, J = 6.6 Hz, 3H), 6.84 (d, J = 7.9 Hz, 3H), 2.51 (s, 9H). MS (m/z). Calcd for $C_{39}H_{30}IrN_3O_3$ (M^+): 781.1911, Found: 781.1901. Anal. Calcd for $C_{39}H_{30}IrN_3O_3 \cdot 4H_2O$: C, 54.92; H, 4.49; N, 4.92%, Found: C, 54.47; H, 4.03; N, 4.90%.

***fac*-Tris[2-(5′-nitro-4′-tolyl)pyridine]iridium(III)·CH$_2$Cl$_2$ (10)[12] (Chart 7).** $Cu(NO_3)_2 \cdot 3H_2O$ (25 mg, 103 μmol) was added to a solution of **1** (48 mg, 69 μmol) in Ac_2O (2 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 1 day. After 5 mL of water was added, the solution was extracted three times with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (CH_2Cl_2) to afford **10** as an orange powder (56 mg, 89% yield). Mp > 300 °C. IR (KBr): ν = 2803, 1591, 1563, 1547, 1489, 1422, 1364, 1283, 1199, 1161, 1069, 1023, 918, 822, 786, 759, 719, 699, 637 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.44 (s, 3H), 8.04 (d, J = 8.2 Hz, 3H), 7.79 (t, J = 7.7 Hz, 3H), 7.45 (d, J = 5.0 Hz, 3H), 7.05 (t, J = 6.8 Hz, 3H), 6.71 (s, 3H), 2.44 (s, 9H). MS (m/z). Calcd for $C_{36}H_{27}IrN_6O_6$ (M^+): 832.1629. Found: 832.1616. Anal. Calcd for $C_{36}H_{27}IrN_6O_6 \cdot CH_2Cl_2$: C, 48.47; H, 3.19; N, 9.17%. Found: C, 48.38; H, 2.89; N, 8.96%.

***fac*-Tris[2-(5′-nitrophenyl)pyridine]iridium(III) (11)[12] (Chart 7).** $Cu(NO_3)_2 \cdot 3H_2O$ (22 mg, 92 μmol) was added to a solution of **2**

(17) Demonchauxi, P.; Ganellinl, C. R.; Dunn, P. M.; Haylett, D. G.; Jenkinson, D. H. *Eur. J. Med. Chem.* **1991**, *26*, 915–920.

(40 mg, 61 μmol) in Ac_2O (2 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 day. After adding water (5 mL), the solution was extracted three times with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (CH_2Cl_2) to afford **11** as an orange powder (50 mg, quant.). Mp > 300 °C. IR (KBr): ν = 2923, 2854, 1563, 1492, 1322, 1106, 1047, 1027, 881, 786, 754 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.54 (d, J = 2.4 Hz, 3H), 8.12 (d, J = 7.9 Hz, 3H), 7.84 (t, J = 7.7 Hz, 3H), 7.67 (dd, J = 8.4, 2.0 Hz, 3H), 7.51 (d, J = 5.5 Hz, 3H), 7.12 (t, J = 5.7 Hz, 3H), 6.90 (d, J = 8.2 Hz, 3H). MS (m/z). Calcd for $C_{33}H_{21}IrN_6O_6$ (M^+): 790.1177, Found: 790.1146. Anal. Calcd for $C_{33}H_{21}IrN_6O_6$: C, 50.19; H, 2.68; N, 10.64%, Found: C, 49.84; H, 2.61; N, 10.37%.

***fac*-Tris[2-(5′-amino-4′-tolyl)pyridine]iridium(III)·2H_2O (12) (Chart 7).** A mixture of **10** (60 mg, 72 μmol) and $SnCl_2 \cdot 2H_2O$ (244 mg, 1.1 mmol) in EtOH (10 mL) was stirred at 50 °C. After 5 min, $NaBH_4$ (82 mg, 2.16 mmol) was added. After stirring the solution was stirred at reflux temperature for 30 min and at room temperature for 30 min, a solution of $(Boc)_2O$ (157 mg, 720 μmol) was added, and the whole mixture was stirred at reflux temperature for 3 h. After cooling to room temperature, the insoluble materials were filtered off. After 5 mL of water was added to the filtrate, the solution was three times extracted with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography ($CHCl_3$) to afford **24** (67 mg, 89% yield from **10**) as a yellow powder. Mp > 300 °C. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 8.08 (s, 3H), 7.84 (d, J = 7.8 Hz, 3H), 7.48 (t, J = 7.2 Hz, 3H), 7.40 (d, J = 5.1 Hz, 3H), 6.75 (t, J = 6.3 Hz, 3H), 6.61 (s, 3H), 6.11 (s, 3H), 2.02 (s, 9H), 1.51 (s, 27H). MS (m/z). Calcd for $C_{51}H_{57}IrN_6O_6$(M^+): 1040.3938 Found: 1040.3940.

A mixture of TMSCl (31 mg, 285 μmol) and NaI (43 mg, 285 μmol) in MeCN (5 mL) was stirred at room temperature for 15 min, to which **24** (50 mg, 48 μmol) was added. After the whole was stirred at room temperature for 10 min, the insoluble compounds were filtered off and washed with $CHCl_3$ and hexane to afford green compounds, which were purified by ionic exchange column chromatography (IRA-400 (OH^- form)) to give **12** as a red powder (34 mg, 81% from **24**). Mp > 300 °C. IR (KBr): ν = 3319, 1596, 1542, 1468, 1427, 1393, 1294, 1264, 1181, 1061, 781, 747 cm^{-1}. ^1H NMR (300 MHz, DMSO- d_6/TMS): δ = 7.76 (d, J = 7.8 Hz, 3H), 7.67 (t, J = 7.2 Hz, 3H), 7.31 (d, J = 4.8 Hz, 3H), 7.03 (s, 3H), 6.95 (t, J = 6.0 Hz, 3H), 6.33 (s, 3H), 4.09 (br, 6H), 1.81 (s, 9H). MS (m/z). Calcd for $C_{36}H_{33}IrN_6$ (M^+): 740.2365, Found: 740.2367. Anal. Calcd for $C_{36}H_{33}IrN_6 \cdot 2H_2O$: C, 55.58; H, 4.79; N, 10.80%, Found: C, 55.61; H, 4.86; N, 11.11%.

Crystallographic Study of 3a and 3b. Fine crystals were obtained from slow evaporation of **3a** ($C_{36}H_{27}Br_3IrN_3 \cdot CHCl_3$) and **3b** ($C_{33}H_{21}Br_3IrN_3$) in $CHCl_3$. All measurements were made on a Rigaku RAXIS-RAPID imaging plate area detector with graphite monochromated Mo−Kα radiation at 120.1 K for **3a** and 100.1 K for **3b**. The structures were solved by direct methods[18] and refined by full-matrix least-squares techniques. All calculations were performed using the CrystalStructure (Version 3.8, Rigaku & RAC (2007)) except for refinements, which were performed with SHELXL-97.[19]

Crystal Data for 3a. $C_{36}H_{27}Br_3IrN_3 \cdot 1.18(CHCl_3)$, M_r = 1074.43, a yellow crystal, crystal size 0.17 × 0.12 × 0.07 mm, Cubic, space group $P2_13$ (#198), a = 22.5283(4) Å, V = 11433.7(4) $Å^3$, Z = 12, D_{calc} = 1.872 g/cm^3, 7069 measured reflections, 6945 reflections with I > 2σ(I), $2\theta_{max}$ = 50.96°, $R1$ (w$R2$) = 0.035 (0.0949), GOF = 1.054, Flack parameter = 0.03(1). CCDC 770685 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 3b. $C_{36}H_{27}I_3IrN_3 \cdot 1.67(CHCl_3)$, M_r = 1273.57, a yellow crystal, crystal size 0.12 × 0.10 × 0.08 mm, Cubic, space group $P2_13$ (#198), a = 22.9303(4) Å, V = 12056.6(4) $Å^3$, Z = 12, D_{calc} = 2.105 g/cm^3, 7347 measured reflections, 7133 reflections with $I > 2\sigma(I)$, $2\theta_{max}$ = 50.6°, $R1$ (w$R2$) = 0.040 (0.1085), GOF = 1.051, Flack parameter = 0.016(8). CCDC 770686 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurements of UV−vis Absorption and Luminescence Spectra. Steady-state UV/vis absorption were recorded on a JASCO V-550 and V-630BIO UV−vis spectrophotometer and luminescence excitation and emission spectra were recorded on a JASCO FP-6500 and FP-6200 spectrofluorometer, respectively, at 25.0 ± 0.1 °C. Solution samples were degassed for 10 min before UV−vis and luminescence measurements. The quantum yields of luminescence (Φ) were determined by comparison with the integrated corrected emission spectrum of a quinine sulfate standard, whose emission quantum yield in 0.1 M H_2SO_4 was assumed to be 0.55 (excitation at 366 nm). For the calculation of emission quantum yields, the following equation was used, in which Φ_s and Φ_r depict 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 calculation.

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

Cyclic Voltammetry (CV). Cyclic voltammetry measurements were performed with a BAS model 660A electrochemical analyzer at room temperature in DMF containing 0.1 M $nBu_4N(PF_6)$ as the supporting electrolyte in a standard one-component cell under an argon atmosphere equipped with 3-mm outer diameter glassy carbon working electrode, and a platinum wire counter electrode, and the Ag/AgCl referenced electrode (Ag/AgCl in MeCN containing 0.01 M $AgNO_3$ and 0.1 M $nBu_4N(ClO_4)$). All solutions were deoxygenated by argon bubbling for at least 10 min, immediately before measurements.

Results and Discussion

Halogenation of 1 (Ir(tpy)$_3$) and 2 (Ir(ppy)$_3$). After refluxing a mixture of **1** with NBS and BPO in CCl_4 for 1 day, a single product was obtained. Its ^1H NMR ($CDCl_3$/TMS, 300 MHz) spectra (Figure S1 in the Supporting Information) indicated that the methyl groups of **1** were not brominated (Chart 2) because three methyl groups were still detected and a singlet signal, corresponding to the 5′-proton (H(5′)) on the phenyl ring of the tpy unit, had disappeared, in comparison with data for the starting material **1** (for the assignment, see Chart 2). The mass spectrum of the product gave a fragment at m/z = 933, which corresponds to the tribrominated derivative of **1** (Figure S1c in the Supporting Information),

(18) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381–388.

(19) Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

suggesting that the product is **3a**, in which the protons at the 5′-positions of the phenyl rings in the three tpy units had been substituted with Br.

The halogenation of **1** ($Ir(tpy)_3$) and **2** ($Ir(ppy)_3$) was examined under several different reaction conditions, and the results are summarized in Table 1. As stated above, the bromination of **1** and **2** with NBS in the presence of a catalytic amount of BPO in CCl_4 (under reflux temperature for 1 day) gave the corresponding tribrominated compounds, **3a** and **4a**, respectively, in moderate chemical yields (entries 1 and 11 in Table 1).

When the bromination was conducted with only NBS (3.3 equiv) in CCl_4, **3a** and **4a** were produced in moderate yields (entries 2 and 12). Interestingly, when **1** and **2** were brominated with NBS in more polar solvents such as MeCN, CH_2Cl_2, or acetone (entries 3−5 and 13), the reaction was much faster than those in CCl_4. In addition, the treatment of **1** with tetrabutylammonium tribromide ($(n\text{Bu})_4NBr_3$) in MeCN also gave **3a** (entry 6). These results suggest that this bromination likely proceeds via an ionic mechanism rather than a radical mechanism, as described below.

In the case of the iodination of **1** and **2** (to give **3b** and **4b**), similar results were obtained, as shown in Table 1 (entries 7−9 and 14−15). Treatment of **1** and **2** with NCS (3.3 equiv) in MeCN gave the several products. To investigate this aspect in detail, we treated **1** and **2** with 6 equiv of NCS and obtained 3′,5′-hexachloro complexes **5** and **6** in moderate yields, as shown in Table 1 (entries 10 and 16). We assume that, because Cl atoms have smaller diameters than Br or I, this allowed the second aromatic substitution at the 3′-position. On the other hand, the fluorination of **1** and **2** with 1-fluoro-2,6-dichloropyridinium tetrafluoroborate or *N*-fluoro-*N*′- (chloromethyl)-triethylenediamine bis(tetrafluoroborate) afforded a complex mixture of products.

Crystal Structures of Tribrominated and Triiodinated $Ir(tpy)_3$, 3a and 3b. The structure of **3a** was confirmed by an X-ray crystal structure analysis, as shown in Figure 1, which shows that the 5′-position of the three phenyl groups are all substituted with Br. The averaged N(tpy)−Ir and C(tpy)−Ir bond distances are 2.13 Å and 2.02 Å, which are almost identical to the reported values for **1**, **2**, and related Ir complexes.[2d,g,h,k,l,9b] The averaged C−Br bond distance was 1.91 Å.

The crystal structure of **3b** is displayed in Figure S2 in the Supporting Information, which shows that the 5′-positions of the three phenyl groups were all substituted with I. The averaged N(tpy)−Ir (2.14 Å) and C(tpy)−Ir (2.01 Å) bond distances are almost identical to those of the aforementioned **3a** (Figure 1), and the averaged I−C bond length was 2.11 Å, which is slightly longer than that of the Br−C bond in **3a**. Representative parameters for the crystal structure analysis of **3a** and **3b** are listed in Table 2.

Proposed Mechanism for the Selective Substitution Reactions of 1 and 2. As listed in Table 1, halogenation at the 5′-position of tpy and ppy ligands in **1** and **2** proceeds in the absence of radical initiators such as BPO, suggesting an ionic mechanism rather than a radical mechanism. Indeed, the reaction of 2-(4′-tolyl)pyridine (tpy) **13** with NBS and BPO in CCl_4 resulted in the bromination of the methyl group to afford **14** (Chart 3) possibly via a radical

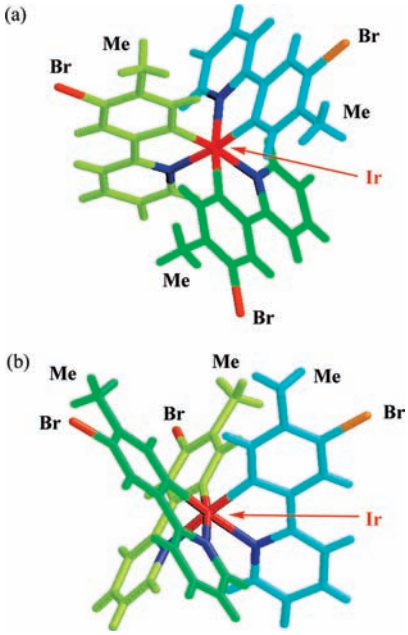
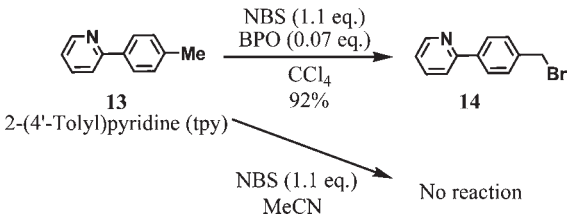


Figure 1. Top view (a) and side view (b) of stick drawings of **3a** ($Ir(5'\text{-Br-tpy})_3$). The three tpy units are shown in light blue, green-yellow, and light green, Ir in red, and Br in orange.

Table 2. Representative Parameters for the Crystal Structure Analysis of **3a** and **3b**

		3a	3b
bond lengths (Å) (averaged values)	C (2′)−Ir	2.02	2.01
	N (1)−Ir	2.13	2.14
	C (5′)−Br(or I)	1.91	2.11
dihedral angles (deg) (averaged values)	C−Ir−C	85.9	85.4
	C−Ir−N	95.8	94.3
	N−Ir−N	95.4	94.9

Chart 3

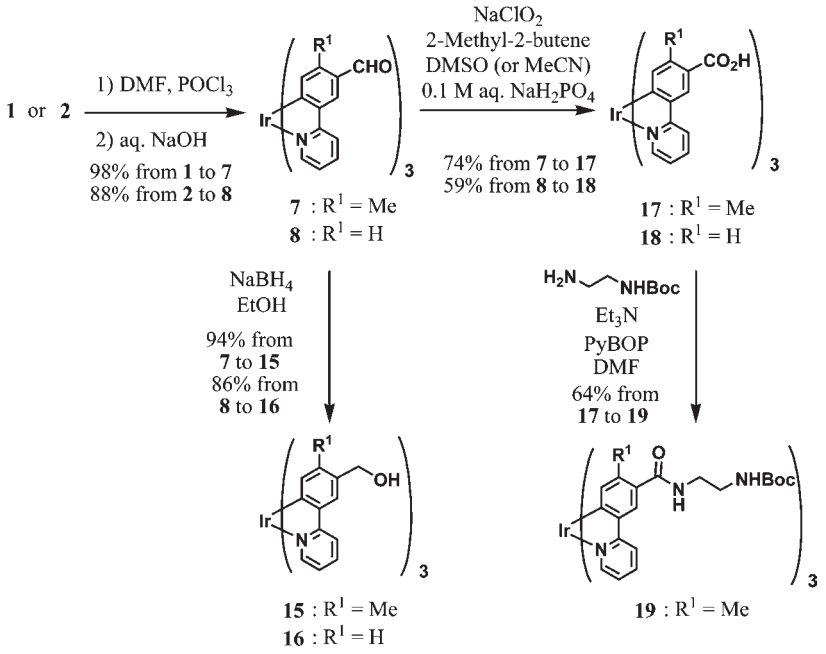


mechanism. Moreover, treatment of **13** with NBS alone resulted in a negligible reaction, providing support for the conclusion that the major mechanism involved in the 5′-halogenation of Ir complexes (e,g., **1** → **3a** in Chart 2) is somewhat different from that of the radical-mediated halogenation of **13** (→**14**) in Chart 3.

Aromatic substitution reactions of activated benzenes were previously reported by Carreno and Ruano et al.[20] For example, the reaction of electron-rich benzene derivatives such as 3-isopropyl-1,2,4-trimethoxybenzene and 1,2,4-trimethoxybenzene with NBS or NIS in CCl_4 or MeCN gives the corresponding halogenated products as major products, respectively. It is very likely that the

(20) (a) Carreno, M. C.; Ruano, J. L. G.; Sanz, G.; Toledo, M. A.; Urbano, A. *J. Org. Chem.* **1995**, *60*, 5328–5331. (b) Carreno, M. C.; Ruano, J. L. G.; Sanz, G.; Toledo, M. A.; Urbano, A. *Tetrahedron Lett.* **1996**, *37*, 4081–4084.

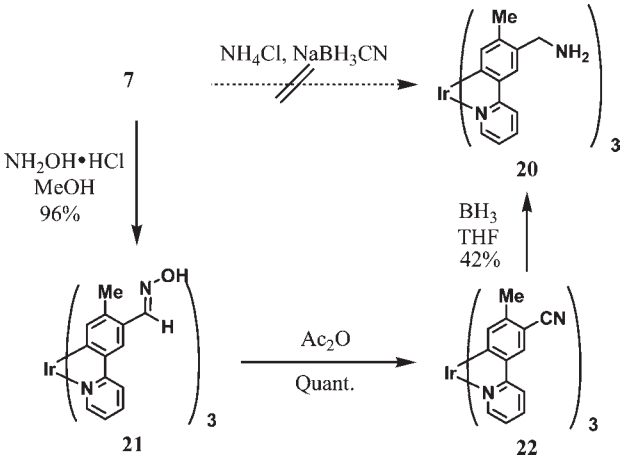
Chart 4



methoxy groups of these substrates serve as electron-donating groups to activate the benzene rings of these substrates. Considering the above facts, we assume that C−Ir bonds in **1** ($Ir(ppy)_3$) and **2** ($Ir(tpy)_3$) exhibit electron-donating effect and activate the phenyl rings of the metalated ligands to facilitate electrophilic substitution reactions at the *p*-position (5′-position) with respect to the C−Ir bonds.[21−23]

Formylation and Acetylation of Ir Complexes. Formylations of **1** and **2** were carried out with DMF and $POCl_3$ (Vilsmeier reaction) to yield tris(formyl) derivatives **7** and **8** in good yields (Chart 4). The reduction of **7** and **8** with $NaBH_4$ gave the corresponding alcohols **15** and **16**. A Pinnick oxidation ($NaClO_4$, 2-methyl-2-butene, in MeCN/0.1 M aq. NaH_2PO_4) of **7** and **8** afforded the corresponding carboxylic acids **17** and **18**, respectively. The condensation of **17** with (mono-Boc)ethylenediamine[17] in the presence of Et_3N and PyBOP (benzotriazol-1-yloxytripyrrolidinophosphonium hexafluorophosphate) in DMF yielded **19**, which could be an important intermediate to synthesize C_3-symmetric bioactive molecules.

Chart 5



These successful conversions of **7** and **8** prompted us to attempt to introduce various other functionalities onto the Ir complexes. Although we attempted the reductive amination of **7** with NH_4Cl and $NaBH_3CN$ to obtain the tris(aminomethyl) compound **20** (Chart 5), this reaction failed to proceed. Alternatively, **7** was converted to the tris(hydroxyimino) derivative **21** by treatment with $NH_2OH \cdot HCl$, followed by the reaction with Ac_2O to afford the tris(cyano) derivative **22**. Reduction of the CN groups of **22** with $BH_3 \cdot THF$ gave **20** in moderate yield (reduction of **22** to **20** with $NaBH_4 + TiCl_4$ or $LiAlH_4$ was not successful).

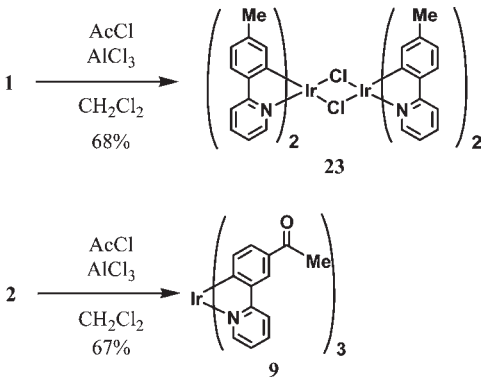
We also carried out the acetylation of **1** and **2** with AcCl and $AlCl_3$ in CH_2Cl_2 (Chart 6). The triacetylated compound **9** was obtained from **2**, while the product from **1** was tetrakis[2-(4′-tolylpyridine)(μ-dichloro)]diiridium

(21) The HOMO energy level and electron orbital density of **2** were calculated by using density functional theory (DFT) calculation (B3LYP/LanL2DZ) (ref 22). Supporting Information, Figure S3 displays that the phenyl group of the ppy unit has larger HOMO orbitals than those of the pyridine ring and that the 3′- and 5′-position of the ppy units have large HOMO orbitals, which may allow substitution reactions at those positions.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(23) In our preliminary experiments, it was suggested that halogenations (e.g.; NBS, MeCN at 70 °C) of $Ir(tpy)_2(bpy)$ (bpy = 2,2′-bipyridyl) also proceed as **1** and **2** do. Details will be reported elsewhere.

Chart 6



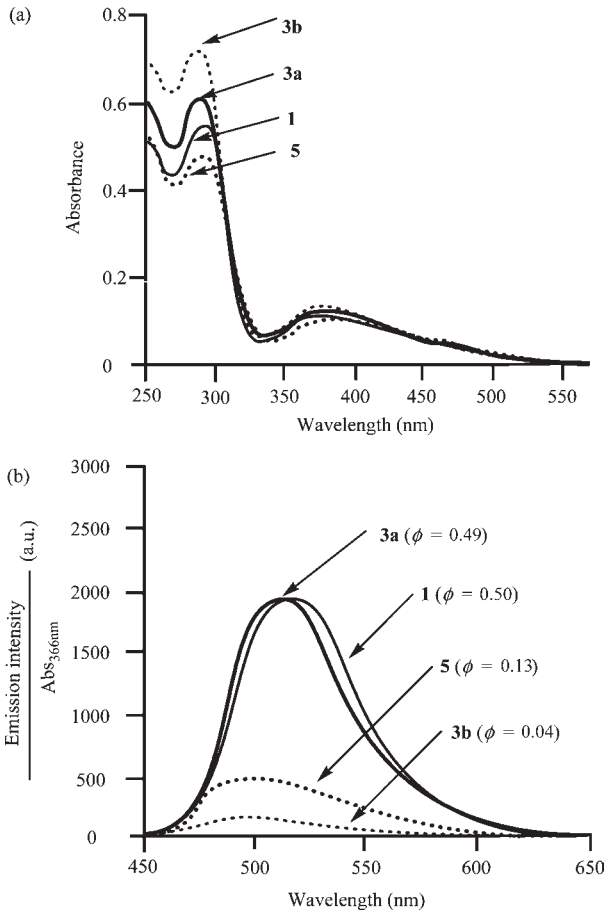


Figure 2. (a) UV−vis spectra of **1** (plain curve), **3a** (bold curve), **3b** (dashed curve), and **5** (bold dashed curve) in degassed CH_2Cl_2 at 25 °C. [Ir complex] = 10 μM. (b) Emission spectra of **1** (plain curve), **3a** (bold curve), **3b** (dashed curve), and **5** (bold dashed curve) in degassed CH_2Cl_2 at 25 °C (excitation at 366 nm). [Ir complex] = 10 μM. A.u. is arbitrary units and emission intensity was normalized with the absorbance of each compound at 366 nm, which was used for excitation of all Ir complexes.

complex **23**,[2a,k,p,9f] as confirmed by ^{1}H NMR spectra, although the mechanism for this reaction is not clear at present.

UV−vis and Luminescence Spectra of Substituted Ir Complexes. UV−vis and luminescence spectra of substituted Ir complexes, **1**, **3a**, **3b**, **5**, **7**, **10**, **19**, and **22**, were obtained, and the results are shown in Figures 2 and 3. The UV−vis spectra of **3a**, **3b**, and **5** were nearly identical to a spectrum of **1** (Figure 2a). Small shoulders at around

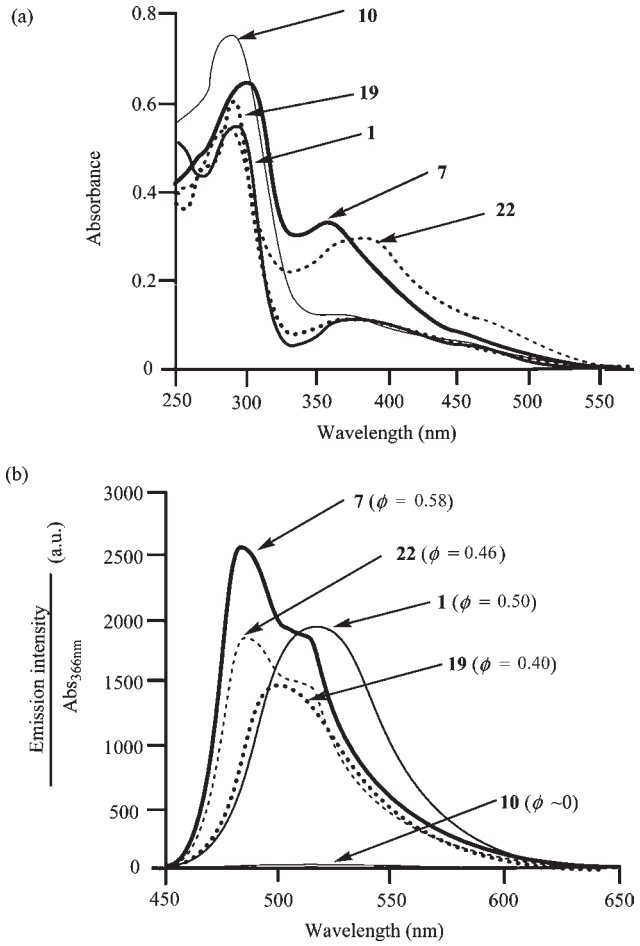


Figure 3. (a) UV−vis spectra of **1** (plain curve), **7** (bold curve), **10** (thin curve), **19** (bold dashed curve), and **22** (dashed curve) in degassed CH_2Cl_2 at 25 °C. (b) Emission spectra of **1** (plain curve), **7** (bold curve), **10** (thin curve), **19** (bold dashed curve), and **22** (dashed curve) in degassed CH_2Cl_2 at 25 °C (excitation at 366 nm). [Ir complex] = 10 μM. A.u. is arbitrary units and emission intensity was normalized with the absorbance of each compound at 366 nm, which was used for excitation of all Ir complexes.

460 nm can be assigned to metal-to-ligand charge transfer (MLCT). Excitation spectra of these four Ir complexes are shown in Figure S4a in the Supporting Information. As shown in Figure 2b and Table 3, the luminescence quantum yields (ϕ) of **3b** and **5** were lower than that of **1**.[24]

Figure 3 shows UV−vis spectra and emission spectra for **1**, **7**, **10**, **19**, and **22** (excitation spectra are shown in Figure S4b in the Supporting Information). We conclude that the introduction of electron-withdrawing moieties such as formyl and cyano groups at 5′-position of $Ir(tpy)_3$ (e.g., **7** and **22**), is responsible for the blue shift in the emission wavelength.

The UV−vis spectra of **7** and **22** exhibited a larger absorption at wavelength >350 nm than those of **1** and **10**, as shown in Figure 3a. For comparison, we collected UV−vis spectra of benzaldehyde, anisole, and anisaldehyde. As shown in Figure S5 in the Supporting Information,

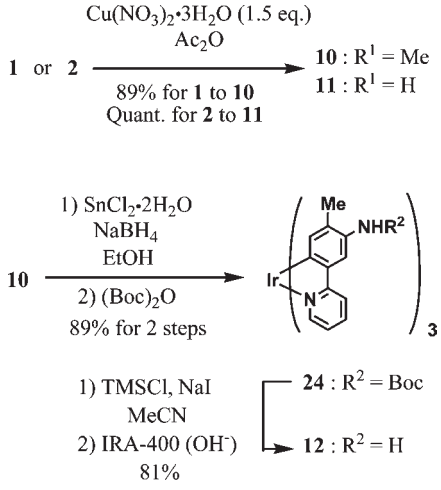
(24) It is known that the nitro group works as a strong quencher of luminescent dye (see: Munkholm, C.; Parkinson, D.-R.; Walt, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 2608–2612. Ueno, T.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2006**, *128*, 10640–10641, and references cited therein). Concerning emission spectra of hexachlorinated and triiodinated Ir complexes 3b and 5, such halogen substituents may facilitate thermal deactivation via nonradiative pathway, as suggested by the reviewer.

Table 3. Photochemical Properties of the Substituted $Ir(tpy)_3$ in CH_2Cl_2[a]

complex	λ_{max} (absorption)	λ_{max} (emission)	ϕ
1	287, 373 nm	512 nm	0.50
3a	286, 376 nm	506 nm	0.49
3b	252, 377 nm	505 nm	0.04
5	226, 366 nm	500 nm	0.13
7	289, 347 nm	477 nm	0.58
10	281, 375 nm		≈ 0
19	286, 365 nm	499 nm	0.40
22	281, 366 nm	478 nm	0.46

[a] [Ir complex] = 10 μM.

Chart 7



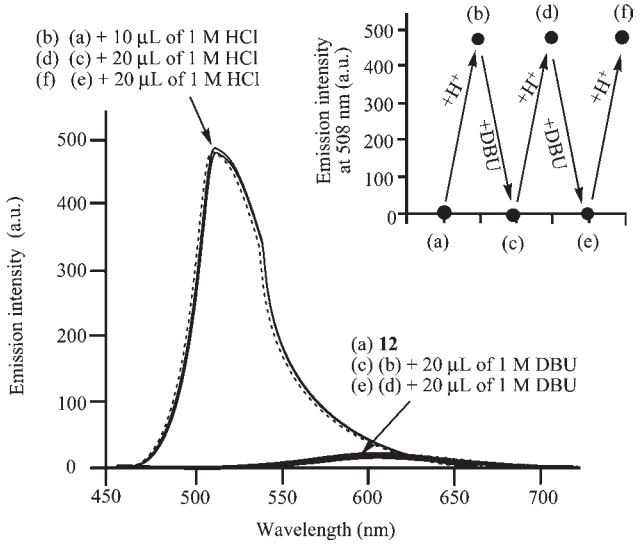


Figure 4. Change in emission spectra of **12** (10 μM) in degassed DMSO at 25 °C (excitation at 366 nm) upon the repeated addition of acid (1 M HCl in 1,4-dioxane) and base (1 M DBU in 1,4-dioxane). (a) **12** before the addition of H^+, (b) (a) + HCl, (c) (b) + DBU, (d) (c) + HCl, (e) (d) + DBU, and (f) (e) + HCl (excitation at 366 nm). A.u. is in arbitrary units. (Inset) Change in luminescence intensity at 508 nm of **12** caused by the repeated addition of HCl and DBU.

anisaldehyde exhibits a strong absorption at >250 nm, possibly because of conjugation between the electron-withdrawing formyl group and the electron-donating methoxy group. A comparison of Supporting Information, Figure S5 and Figure 3a are consistent with the electron-donating characteristics of C−Ir bonds.

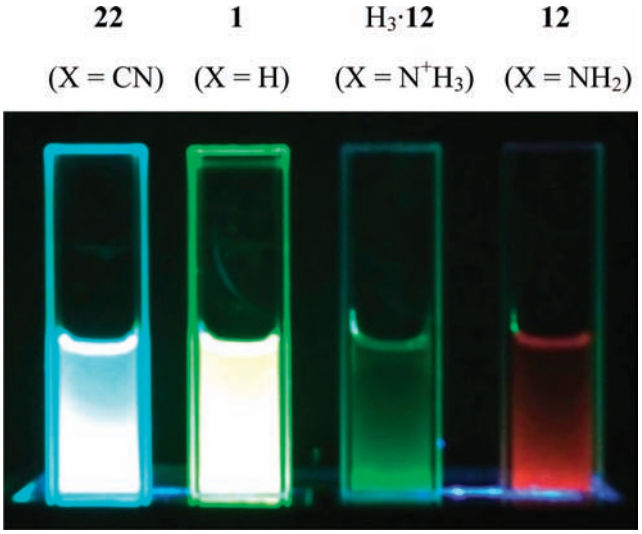


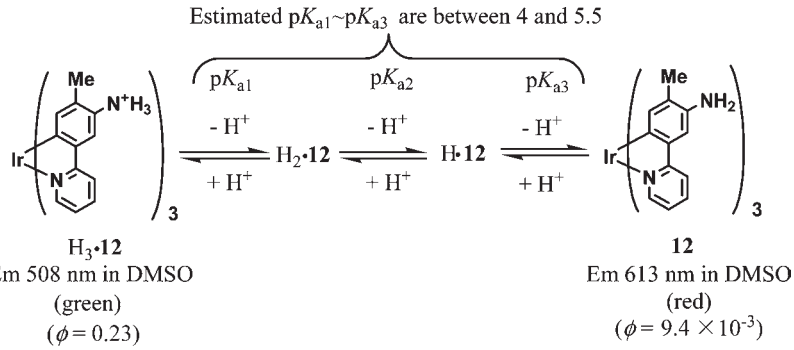
Figure 5. Photograph showing solutions of **22** (30 μM), **1** (30 μM), $H_3 \cdot$**12** (100 μM), and acid-free **12** (100 μM) in degassed DMSO/CH_2Cl_2 (1/5) at 25 °C (excitation at 365 nm).

Introduction of Amino Groups on $Ir(tpy)_3$ and Luminescence Properties Altered by the Protonation/Deprotonation of Its Amino Groups. It has been reported that the luminescence properties of Ir complexes can be altered by certain ligands and their substituent groups.[1,2,8,9] In the past decade, considerable efforts have been made to develop efficient luminescent Ir complexes that are able to emit all of the primary colors: red, green, and blue. It has been reported that the incorporation of electron-withdrawing substituents such as F and CN results in an increase in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), resulting in a blue-shift in the emission wavelength when compared to the parent complexes.[6,25] In contrast, several examples of red-color luminescent Ir complexes have also been reported.[9] It should be noted that only few examples of luminescent iridium complexes that reversibly respond to the surrounding environment have been reported.[1e,f,10]

On the basis of the aforementioned results, we assumed that electron-donating units such as an amino group may induce red-shift in the emission of Ir complexes. Therefore, we carried out the nitration (HNO_3 or $Cu(NO_3)_2 \cdot 3H_2O$ and Ac_2O) of **1** and **2** to obtain **10** and **11** according to a previously reported procedure[12] and successive reduction of the nitro groups (Chart 7). Hydrogenation of **10** with H_2 and Pd/C gave partially reduced compounds, mono- and bis(amino) complexes. The nitro groups of **10** were then reduced with $SnCl_2 \cdot 2H_2O$ and $NaBH_4$ to give **12**, which is abbreviated as $Ir(atpy)_3$ in this manuscript. Since the purification of **12** after reduction was difficult, the three amino groups of **12** were protected with Boc in situ, and **12** was isolated as 3-Boc protected derivative **24**, which was easily purified by silicagel colum chromatography. The three Boc groups of **24** were removed by treatment with TMSCl and NaI to afford the HI salt of **12**, which was purified by ionic exchange column chromatography (IRA-400, HO^- form) to give acid-free **12**.

(25) For example, Lasker et al. introduced methoxy and fluoro groups on $Ir(ppy)_3$ complex, but these complexes emit blue-color luminescence (ref 8d).

Chart 8



Interestingly, the luminescence of a solution of **12** in DMSO was found to be red, with an emission maximum at around 600 nm, as displayed in Figure 4 (bold curve a) and Figure 5 (right) ([**12**] = 100 μM, excitation at 366 or 365 nm).[26] Figure 5 shows blue colored luminescence from **22** (left), a yellow-green emission from **1** (second left), and a red emission from **12** (right). Moreover, the addition of H^+ to **12** induced a significant blue-shift (about 100 nm) in its luminescence emission, as the result of the protonation of the three amino groups (Chart 8), resulting in green emission at 508 nm, as shown in Figure 4 (plain curve b) and Figure 5 (the second from the right).[27] When a base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), was added, the red colored emission was recovered. As depicted in Figure 4 and the inset, these processes were reversible with negligible decrease in emission intensity at each step. The luminescent quantum yields (ϕ) of **12** and $H_3 \cdot$**12** in DMSO were determined to be 9.4×10^{-3} and 0.23, respectively. The lower ϕ value of acid-free **12** can be attributed to the energy gap law because of the increase in the wavelength of the emission peak.[28,29]

We carried out cyclic voltammetry (CV) measurements of **22**, **1**, and **12**,[30] from which potential gaps between the first oxidation and reduction of these Ir complexes were estimated to be 3.1 V (for **22**), 2.9 V (for **1**), and 2.6 V (for **12**), suggesting the relationship of these values with the order of their emission wavelength. CV curves of **12** and triprotonated $H_3 \cdot$**12** (prepared from **12** + 3 equiv, $HClO_4$) were undertaken to compare HOMO and LUMO levels of these two species. However, it was found that these two CV curves are almost identical (data not shown), possibly because protonation/deprotonation processes of amino groups are much faster than redox reactions on the electrode in given measurement conditions.

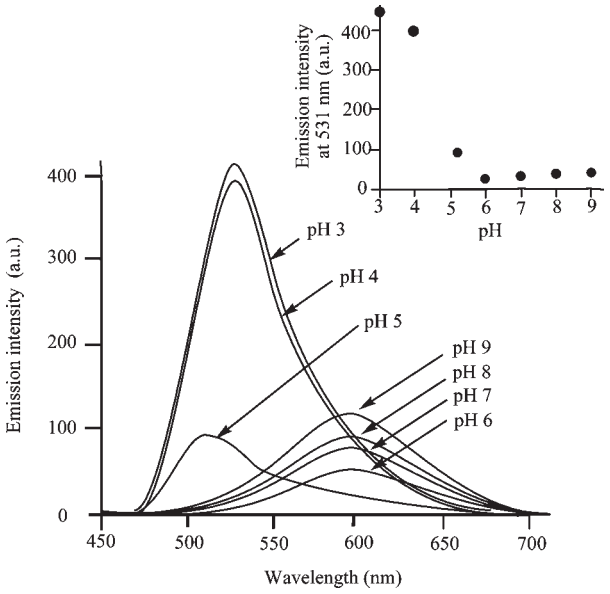


Figure 6. Change in the emission spectra of **12** (100 μM) in degassed DMSO/100 mM buffer (from pH 3 to 9) (1/6) at 25 °C. (Inset) pH-Dependent plot of emission intensity of **12** (100 μM) at 531 nm (closed circle) in degassed DMSO/100 mM buffer (1/6). Excitation at 366 nm. A. u. is in arbitrary unit.

Next, luminescence spectra of **12** in aqueous solutions at pH 3−9 were measured ([**12**] = 100 μM, exitation at 366 nm). As shown in Figure 6, a strong green emission was observed at acidic pH (531 nm at pH 3−4 and 517 nm at pH 5). In contrast, the emission shifted to about 600 nm at pH 5−6 with significant decrease in green emission at about 530 nm.[31,32] These results indicate that protonated amino groups function as electron-withdrawing groups to cause blue shift of the emission to about 500 nm. Figure 7 clearly displays that **12** responds to the pH of the aqueous solutions, changing from a yellow-green emission at an acidic pH to a red emission at neutral and basic pH.

(26) Luminescence emission spectra of **12** in organic solvents such as DMSO (and DMSO/H_2O), DMF, CH_2Cl_2, 1,4-dioxane, and THF are shown in Figure S6 in the Supporting Information. Although we could not observe apparent relationships between λ_{max} and quantum yields of its emission and the chemical properties of these solvents such as dielectric constants (ε_r) and normalized empirical parameters of solvent polarity (E_T^N), it seems that less polar solvents afford larger emission intensity.

(27) UV−vis spectral change of **12** by protonation and deprotonation are shown in Figure S7 in the Supporting Information which shows a blue shift (ca. 40 nm) of absorption upon addition of excess amount of HCl.

(28) (a) Cummings, S. D.; Eisenberg., R. *J. Am. Chem. Soc.* **1996**, *118*, 1949–1960. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193–1206.

(29) Preliminary results of DFT calculation of **12** and $H_3 \cdot$**12** suggest that the difference of the energy gaps between HOMO and LUMO between these species are very small. A detailed calculation is now underway.

(30) Typical CV curves of **1**, **22**, and **12** in DMF containing 0.1 M nBu$_4$N(PF$_6$) at 25 °C are shown in Figure S8 in the Supporting Information. A summary of potential gaps of the first oxidation and reduction of **1**, **22**, and **12** in comparison with those of benzonitrile and aniline are displayed in Figure S9 in the Supporitng Information.

(31) The pH-dependent change in UV/vis spectra of **12** (10 μM) in DMSO/100 mM buffer (pH 3−10) is shown in Figure S10 in the Supporting Information.

(32) Note that emission intensity of $H_3 \cdot$**12** and acid-free **12** in solvent systems containing water (such as DMSO/H_2O) are lower than those in other organic solvent systems (see Figure S6 in the Supporting Information), possibly because of the greater polarity of water than those of other organic solvents.

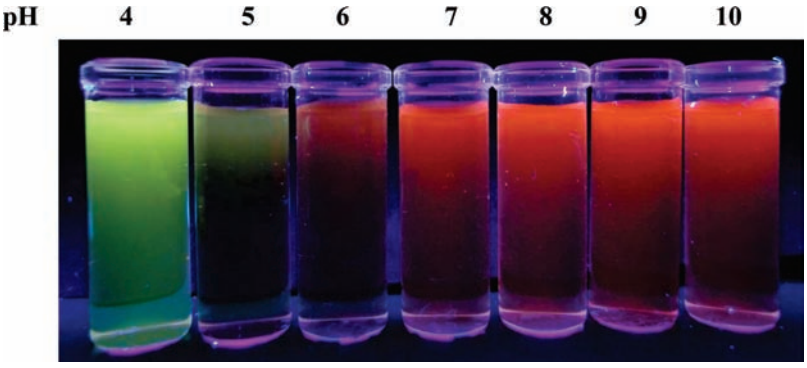


Figure 7. Photograph showing solutions of 100 μM **12** in degassed DMSO/100 mM buffer (from pH 4 to 10) (1/6) (from left to right) excited by UV light at 365 nm at 25 °C.

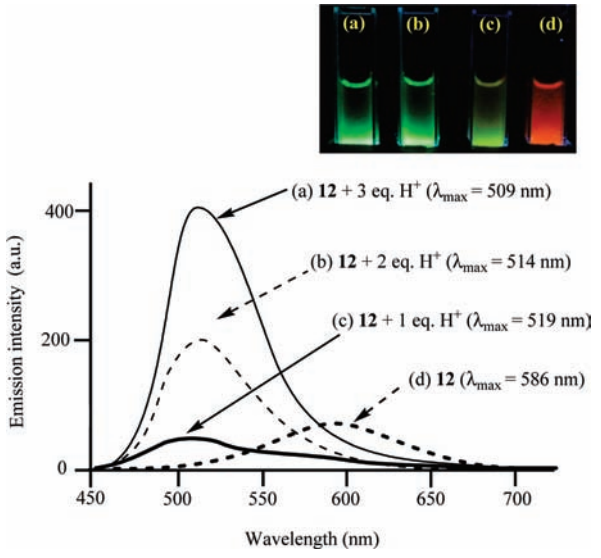


Figure 8. Emission spectra of **12** (100 μM) in degassed DMSO/H_2O (1/6) in the presence of (a) 300 μM HCl (pH ~3.9), (b) 200 μM HCl (pH ~4.6), (c) 100 μM HCl (pH ~5.3), and (d) 0 μM HCl (pH 7.3) at 25 °C. Excitation at 366 nm. A.u. is in arbitrary unit. (Inset) Photograph showing solutions of Figures 8a, 8b, 8c, and 8d (from left to right) excited by UV light at 365 nm.

Unfortunately, we could not determine the accurate pK_a values of $H_3 \cdot$ **12** because of its low solubility in water containing DMSO or MeCN at 25 °C. By potentimetric pH titration[14,15] of a suspension of **12** in DMSO/water (5/95) with I = 0.1 ($NaNO_3$) at 25 °C (data not shown), three pK_a values of $H_3 \cdot$ **12** were roughly estimated to be in the range of 4 to 5.5 (Chart 8), which are almost identical to the pK_a values of 4−5 estimated by pH-dependent luminescence spectral change shown in Figure 6 and its inset (the pK_a value of anilinium cation in water is reported to be 4.60).[33]

Emission spectra of **12** (100 μM) in the absence and the presence (1 to 3 equiv.) of HCl were undertaken in DMSO and water (1/6). As shown in Figure 8, emission of mono- ($H \cdot$ **12**), di- ($H_2 \cdot$ **12**), and triprotonated ($H_3 \cdot$ **12**) species of **12** exhibit emission maxima at about 510−520 nm (green to green-yellow emissions), and only acid-free **12** exhibits an emission maximum at about 590 nm (red emission). These results strongly suggest that protonation of three amino groups of **12** induces large blue-shift of its emission.

The results of emission titrations of **12** (100 μM) with 0.1 M aq. HCl and organic Bronsted acids such as trifluoroacetic acid (CF_3CO_2H, TFA), and methanesulfonic acid (CH_3SO_3H) in DMSO at 25 °C are shown in Figure S11 in the Supporting Information, which indicate that the first protonation at one of three amino groups of **12** induces a blue-shift of its emission from about 590 nm to about 520 nm and that the second and third protonations promote emission enhancement at about 510−520 nm. It was also found that CH_3SO_3H (pK_a = −0.6 in H_2O and pK_a = 1.6 in DMSO),[33] CF_3CO_2H (pK_a = 0.5 in H_2O[33] and pK_a = 3.45 in DMSO),[34] and HCl (pK_a = −8 in H_2O and pK_a = 1.8 in DMSO)[34] cause considerable emission enhancement of **14**.[35] On the other hand, negligible change was observed upon addition of chloroacetic acid ($ClCH_2CO_2H$, pK_a = 2.87 in H_2O at 25 °C)[33] and citric acid (pK_a = 3.13, 4,76, and 6.40 in H_2O)[33] under the same conditions and addition of $BF_3 \cdot Et_2O$ in CH_2Cl_2, which is a Lewis acid (Figure S11 in the Supporting Information), possibly because of weaker acidities than those of aforementioned acids. These functions may be applicable for use in photochemical, analytica, and biological devices.

Conclusion

In this manuscript, we report on regioselective electrophilic aromatic substitution reactions at the 5′-positions (*p*-position with respect to C−Ir bond) of phenyl rings in $Ir(tpy)_3$ and $Ir(ppy)_3$, including halogenation, formylation, acetylation, and nitration. Further chemical conversions were also carried out to afford triamine derivatives (**12**, **19**, **20**), tricarboxylic acids (**17**, **18**), and triols (**15**, **16**).

In addition, UV−vis and luminescence spectra (exitation and emission) of **1** ($Ir(tpy)_3$) and its derivatives synthesized in this work are reported. By introducing electron-withdrawing groups at the 5′-position of $Ir(tpy)_3$, the emission wavelength underwent a blue shift (**7** and **22**, see Figure 3b). On the other hand, the introduction of amino groups (electron-donating groups) at the 5′-position of $Ir(tpy)_3$ (**12**) resulted in a

(33) Speight, J. G. *Lange's Handbook of Chemistry*, 16th ed.; McGraw-Hill: New York, 2005.

(34) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

(35) As shown in Supporting Information, Figure S11, emission enhancement of **12** upon addition of aq. HCl is smaller than that upon addition of $MeSO_3H$ regardless of the stronger acidity of HCl than that of $MeSO_3H$, possibly because of the existence of water in the solvent system (see Figure S6 in the Supporting Information and ref 32 in this manuscript).

significant red shift in the luminescence emission (at ca. 590−600 nm) compared to its parent complex **1**. Moreover, it was found that the emission of **12** can be converted to a green color upon protonation of its amino groups in a reversible manner (Figure 4−8).

This information will be useful for the future design and synthesis of novel luminescence metal complexes and their applications in inorganic chemistry, material sciences, photochemistry, biological chemistry, analytical chemistry, medicinal chemistry, and related fields.

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Supporting Information Available: Figures S1−S11, and Tables and CIF files (Tables S1∼S8) for **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.