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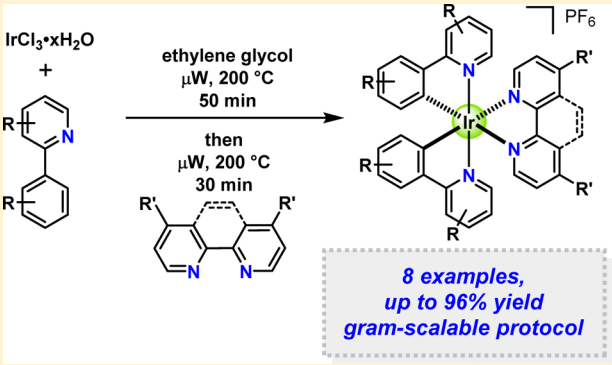
Microwave-Assisted Synthesis of Heteroleptic Ir(III)$^+$ Polypyridyl Complexes

Timothy M. Monos, Alexandra C. Sun, Rory C. McAtee, James J. Devery, III, and Corey R. J. Stephenson*

Department of Chemistry, Willard Henry Dow Laboratory, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

Supporting Information

ABSTRACT: We report a rapid, one-pot, operationally simple, and scalable preparation of valuable cationic heteroleptic iridium(III) polypyridyl photosensitizers. This method takes advantage of two consecutive microwave irradiation steps in the same reactor vial, avoiding the need for additional reaction purifications. A number of known heteroleptic iridium(III) complexes are prepared in up to 96% yield. Notably, this method is demonstrated to provide the synthetically versatile photosensitizer $[Ir(ppy)_2(dtbbpy)]PF_6$ in >1 g quantities in less than 5 h of bench time. We envision this method will help accelerate future developments in visible-light-dependent chemistry.



INTRODUCTION

The development of visible-light-mediated redox catalysis is an energy conscious response to the multifaceted challenges of chemical sustainability.[1] In this context, photoabsorbing Ru(II) and Ir(III) polyimine complexes have been widely applied in organic light-emitting diodes (OLEDs),[2] organic synthesis,[3,4] polymer synthesis,[5,6] oxygen sensors,[7] and bioanalytical devices.[8] The field of photoredox catalysis has adopted Ru(II) and Ir(III) complexes in preference to other metals[9,10] due to the fact that these complexes are bench-stable solids with highly efficient photophysical properties and tunable reactivity. Such characteristics have enabled these complexes to be used in the exploration of small-molecule synthesis,[3,4] natural product synthesis,[11−13] and multicatalytic technologies[14−17] in an effort to develop safe and sustainable synthetic methods.

Among the variety of known polypyridyl Ir(III) complexes,[18] the cationic, heteroleptic Ir(III) complexes represent a relatively new class of photosensitizers. The ligand scaffold (Figure 1A) is a combination of two cyclometalating ligands [(C^N) = arylpyridine] and one dative ligand [(N^N) = bipyridine] that gives rise to a substitutionally inert, photoexcitable species.[19] Such heteroleptic complexes were originally developed by Bernhard, Malliaras, and co-workers to improve upon Ru(II)- and neutral Ir(III)-based electroluminescent materials.[20,21] Ir(III)$^+$ chromophores exhibit superior chemical stability and higher quantum yield compared to those of the corresponding Ru(II) materials. This boost in performance has been attributed to the improved photophysical characteristics of ligand field stabilization energy and decreased nonradiative quenching tendencies.[22]

A significantly notable characteristic of the Ir(III)$^+$ heteroleptic complexes is the spatial separation of redox events that allows for individual redox tuning. Specifically, the HOMOs are understood to exist between the Ir metal center and the C^N ligand, and the LUMOs are separately located on the N^N ligand (Figure 1B). Bernhard and Malliaras experimentally demonstrated this phenomenon by comparing the redox events of various fluorinated Ir(III)$^+$ complexes. In this manner, incorporation of fluorine substituents on the C^N ligand increased the oxidation potential by 100 mV, while the reduction potential was minimally affected.[21] Additionally, this phenomenon was observed spectroscopically by King and Watts, who detected two separate metal-to-ligand charge transfer (MLCT) emission peaks from the excitation of $Ir(ppy)_2(bpy)^+$: one emission peak corresponded to the MLCT−N^N transition (major process), and the second corresponded to the MLCT−C^N transition (minor process).[23] These results support the notion that the HOMOs and LUMOs are spatially separated and that orthogonal electrochemical modulation is possible through the independent variation of the C^N and N^N ligand electronics.[24]

Despite the great utility of these compounds, synthetic methods for their production are time- and energy-intensive. These requirements can limit the screening diversity of catalysts during project development, thus minimizing the actual benefits of this design aspect. By convention, there are two methods for producing Ir(III)$^+$ polypyridyl complexes (Scheme 1). Both of these methods rely on the initial synthesis of an $[(C^N)_2Ir\text{-}\mu\text{-}Cl]_2$ dimer. From this intermediate, a dative bipyridyl ligand

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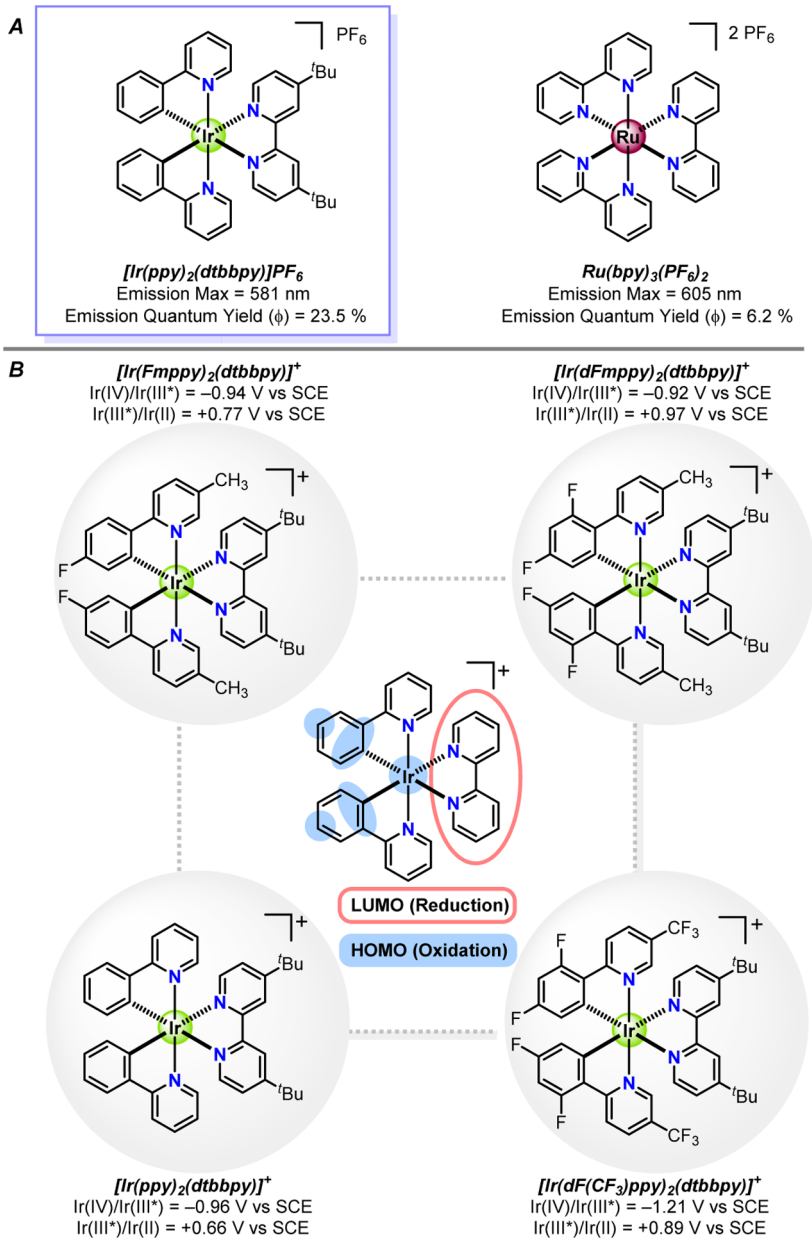

Figure 1. (A) Comparison of the archetypical Ru and Ir polyimine complexes and (B) orthogonal tuning of $Ir(III)^+$ redox behavior based on ligand choice.

can be introduced by either cracking the dimer by silver salt metathesis[25] or by an additional reflux step with the dative ligand.[26] In both cases, these multistep processes require between 12 and 24 h, totaling greater than 48 h for the synthesis of a single complex.

We have alleviated the time and energy requirements necessary for the synthesis of heteroleptic $Ir(III)^+$ complexes through microwave heating.[39] Microwave heating utilizes polar solvents for highly efficient internal temperature regulation,[27−31] allowing for rapid temperature equilibration and, in many cases, enhanced reaction kinetics.[28,32] Microwave heating has proven beneficial in a number of contexts including transition metal catalysis,[30] continuous flow processing,[33] and combinatorial chemistry.[27] These reports bolster this technique as a *bona fide* method for reliably heating, scaling, and conducting synthetic operations in a reasonable time frame.[34] In this report, we detail the application of microwave heating toward the synthesis of heteroleptic $Ir(III)^+$ complexes in a high-yielding, operationally simple protocol, which can be completed in 3 h.

We identified the benefits of microwave heating in the application of organometallic $Ir(III)^+$ complex synthesis because of the canonically chosen reaction solvent, ethylene glycol. Ethylene glycol is one of the best solvents for microwave heating, boasting a "heating" factor quotient ($\tan \delta$) of 1.350. This quotient is quantified by the ratio of the dielectric loss factor (ε''), which indicates heating efficiency, over the dielectric constant (ε'), which describes the polarization of the molecule, and indicates the possibility of microwave excitation (eq 1). For example, these values range from ethylene glycol to nonpolar solvents such as toluene (1.350 and 0.040, respectively) (Figure 2).[35]

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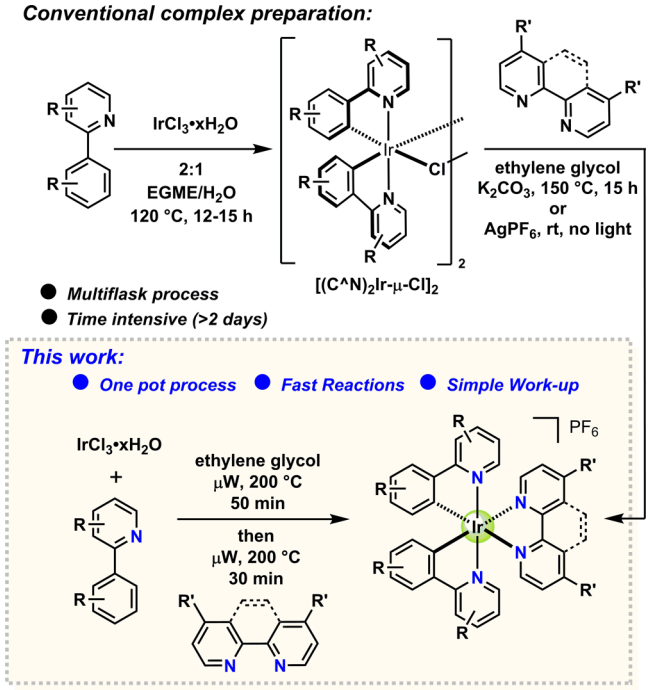
Scheme 1. Synthesis of Ir(III)$^+$ Complexes



$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \qquad (1)$$

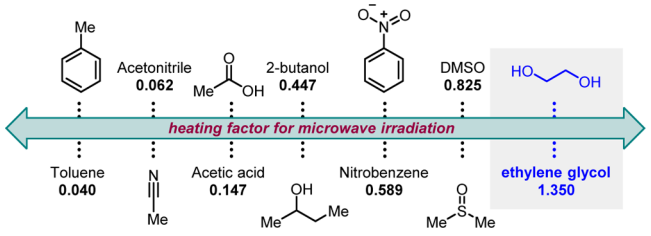


Figure 2. Values of tan δ (heating factor) for common solvents in organic synthesis.

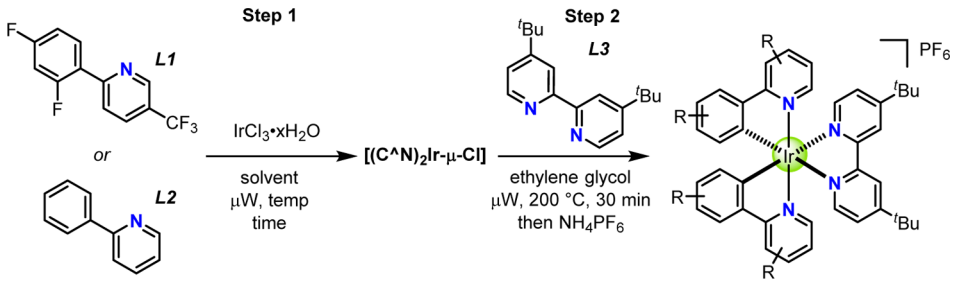
Additionally, we sought microwave heating as an optimal tool for catalyst synthesis because the reaction course from $IrCl_3 \cdot xH_2O$ to $Ir(C^N)_2(N^N)^+$ displayed diagnostic color and solubility changes (see Supporting Information for details). The organometallic Ir complexes were differentially colored and soluble in ethylene glycol, whereas the $IrCl_3 \cdot xH_2O$ was an insoluble black powder. We later followed this with a formal optimization of the two ligation processes.

RESULTS AND DISCUSSION

In our initial studies, we investigated the generation of the $[Ir(dF(CF_3)ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ dimeric species en route to $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$. We highlight the synthetic process with this C^N ligand because we sought a robust cyclometalation protocol capable of utilizing either electron-deficient or electron-rich C^N ligands, while notably the cyclometalation of electron-poor arylpyridines was expected to be more difficult. Heating a mixture of $IrCl_3 \cdot xH_2O$ and 2 equiv of 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (**L1**) in ethylene glycol with microwave irradiation provided $[(dF(CF_3)ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ in 40% yield after 1 h (Table 1, entry 1). This reaction was visibly heterogeneous, consisting of amorphous green solids which were attributed to unreacted $IrCl_3$. Increasing the equivalents of **L1** provided a slight increase in yield to 52% (entry 2). The highest yield of the $[(dF(CF_3)ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ dimer (59%) was obtained with 8 equiv of the cyclometalating **L1** ligand after 1 h of reaction time (entry 3). Extending the reaction time or changing the reaction temperature (250 °C, in triethylene glycol monoethyl ether) failed to increase dimer yield and only resulted in dimer decomposition (entries 4 and 5). Under identical reaction conditions, the $[(ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ dimer was isolated in 84% yield (entry 6). While the use of 8 equiv of **L1** or **L2** is seemingly excessive, the high ligand concentration is thought to neutralize the stoichiometric HCl generated during cyclometalation. Additionally, the mass balance of 2-phenylpyridine ligands could be recovered by an organic extraction and column purification following the reaction.

The second step of the one-pot sequence was performed by simply opening the microwave reaction vial, adding 4,4′-di-*tert*-butyl-2,2′-bipyridine (**L3**), and recapping for another irradiation cycle. Notably, this avoided the addition of silver salts[25] or

Table 1. Optimization of Reaction Conditions



entry	ligand	temperature/solvent	equiv	step 1 time (% yield)	step 2 (% yield)
1	**L1**	200 °C/ethylene glycol	2	1 h (40)	
2	**L1**	200 °C/ethylene glycol	4	1 h (52)	
3	**L1**	200 °C/ethylene glycol	8	1 h (59)	96
4	**L1**	200 °C/ethylene glycol	8	4 h (0)	
5	**L1**	250 °C/triethylene glycol monoethyl ether	8	1 h (0)	
6	**L2**	200 °C/ethylene glycol	8	1 h (84)	98

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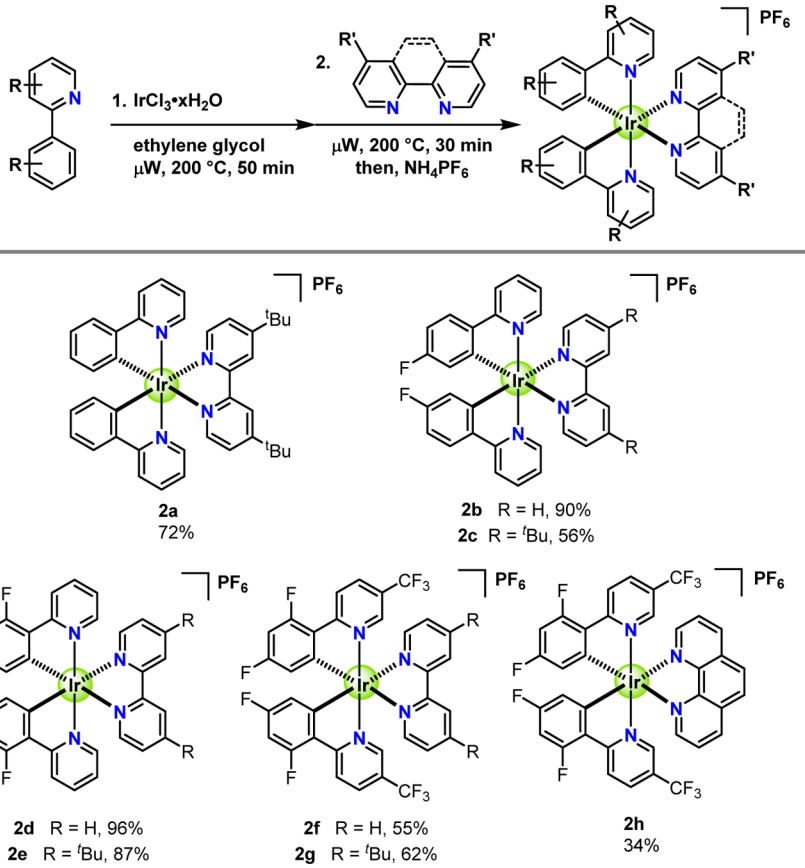
Table 2. Scope of the Ir(III)$^+$ Complexes[a]



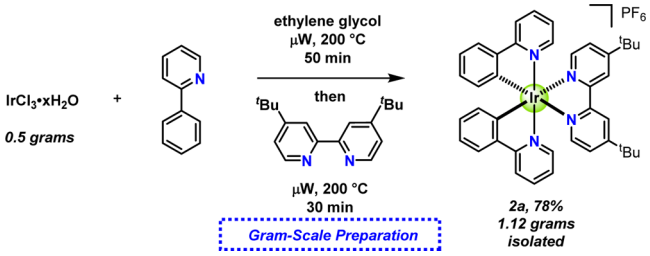
[a]Reaction conditions: (1) 1.0 equiv of $IrCl_3 \cdot xH_2O$ (50 mg or 100 mg) and 8.0 equiv of cyclometalating ligand in ethylene glycol (5 mL) and microwave irradiation (200 °C) for 50 min; (2) 1.5 equiv of dative ligand added to the reaction solution, followed by microwave irradiation (200 °C) for 30 min.

exogenous base (K_2CO_3)[26] in order to facilitate the second ligation event. Conversion of the dimeric $[(dF(CF_3)ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ complex to $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ was successfully accomplished using 1.5 equiv of the N^N ligand **L3** and microwave heating for 30 min, followed by anion metathesis with ammonia hexafluorophosphate to give a 96% isolated yield (entry 3, step 2). Conversion of the $[(ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ dimer gave the $[Ir(ppy)_2(dtbbpy)]PF_6$ complex in high yield (entry 6, step 2).

With optimized conditions in hand, we explored the scope of our method for the preparation of synthetically useful and known heteroleptic Ir(III)$^+$ complexes (Table 2).[19] The conditions proved efficient for generating the Ir(III)$^+$ complex **2a** with 2-phenylpyridine (**L2**) as the C^N ligand and 4,4′-di-*tert*-butyl-2,2′-bipyridine (**L3**) as the N^N ligand. Alternative difluoro- and monofluoro-2-phenylpyridines gave the corresponding iridium complexes in 56−96% yield when partnered with the dative 4,4′-di-*tert*-butyl-2,2′-bipyridine and 2,2′-bipyridine ligands (**2b**−**2e**). A moderate decrease in reaction yield was observed when **L1** and phenanthroline ligands were used as cyclometalating and dative ligands, respectively (**2f**−**2h**).

To demonstrate the utility of this process, a gram-scale preparation of $[Ir(ppy)_2(dtbbpy)]PF_6$ was performed (Scheme 2). Satisfyingly, a 78% (1.12 g) isolated yield of complex **2a** was obtained without derivation from the optimized conditions. Notably, this reaction could be performed start to finish in less than 5 h, demonstrating a substantial advance over currently existing methods.[25,26,36] This reaction showcases the practicality of the method toward catalyst derivatization efforts.

Scheme 2. Gram-Scale Preparation of $[Ir(ppy)_2(dtbbpy)]PF_6$



In conclusion, we have reported an operationally simple, time-efficient, and scalable microwave heating method for the preparation of heteroleptic Ir(III)$^+$ complexes, an important class of photosensitizers for organic synthesis and light-emitting materials. We envision that microwave heating can provide a direct replacement for conventional heating methods in the synthesis of metal−imine complexes. Importantly, this method is ideal for metal complex diversification, wherein uniquely functionalized complexes can be synthesized from a common $[(C^N)_2Ir\text{-}\mu\text{-}Cl]_2$ intermediate in a synthetic process that is directly streamlined and capable of completion with minimal time at the bench.

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EXPERIMENTAL SECTION

General Information. All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. $IrCl_3 \cdot xH_2O$ was purchased from Pressure Chemical. NH_4PF_6 was purchased from Oakwood Products, Inc., and all ligands were obtained from Sigma-Aldrich unless otherwise specified. Microwave-heated reactions were carried out in sealed microwave flasks (2−5 mL or 10−20 mL) and heated by a Biotage Initiator$^+$ microwave synthesizer with a Robot Eight automated sampler. The temperature was monitored by an infrared sensor on the surface exterior of the vial. The pressure was monitored by a pressure transducer situated at the top of the vial. NMR spectra were obtained on a 700 MHz NMR spectrometer and a 500 MHz NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million relative to the residual acetone (δ 2.09) solvent peak.[37] Reactions were monitored by thin layer chromatography (TLC) using glass-backed, 250 μm silica TLC plates, which were visualized with ultraviolet light.

General Procedure for C^N Ligand Synthesis. *2-(2,4-Difluorophenyl)-5-(trifluoromethyl)pyridine.*[21] To a three-necked, 100 mL round-bottom flask charged with a magnetic stir bar were added 2-chloro-5-(trifluoromethyl)pyridine (3.1 g, 17.0 mmol, 0.9 equiv), 2,4-difluorophenylboronic acid (3.0 g, 19.0 mmol, 1.0 equiv), 2 M aqueous sodium carbonate (4.03 g, 38.0 mmol, 2.0 equiv), benzene (23 mL), and toluene (17 mL). The mixture was degassed by sparging with N_2 for 15 min. Then $Pd(PPh_3)_4$ (0.505 g, 0.437 mmol) was added to the reaction mixture, and degassing was continued for another 15 min. The reaction mixture was heated to reflux for 48 h to generate a yellow solution with a yellow precipitate. The progress of the reaction was monitored by TLC (85% ethyl acetate in hexanes). Upon completion of the reaction, the mixture was cooled to room temperature and then extracted with dichloromethane (4 × 20 mL), washed with brine (3 × 20 mL), and dried over Na_2SO_4. Solvent was removed under reduced pressure to give a dark brown oil, which solidified at room temperature. The crude product was purified by flash chromatography using 100% dichloromethane to afford a yellow oil, which crystallized at room temperature. The yellow oil was further dried in vacuo to afford the pure ligand in 77% yield (3.81 g, 14.7 mmol) as white crystals. NMR chemical shifts match literature values.

2-(4-Fluorophenyl)pyridine.[36] To a three-necked, 100 mL round-bottom flask charged with a magnetic stir bar were added 2-chloropyridine (2.00 g, 17.61 mmol, 1.0 equiv), 4-fluorophenylboronic acid (2.96 g, 21.14 mmol, 1.2 equiv), triphenylphosphine (0.46 g, 1.76 mmol, 0.1 equiv), 2 M aqueous potassium carbonate (6.55 g, 47.39 mmol), and dimethoxyethane (20 mL). The mixture was degassed with N_2 for 15 min. Then 2.5 mol % of $Pd(OAc)_2$ (0.1 g, 0.441 mmol) was added to the reaction mixture, and degassing was continued for another 15 min. The reaction mixture was heated to reflux for 18 h to generate an orange solution with an orange precipitate. The progress of the reaction was monitored by TLC (10% ethyl acetate/hexanes). Upon completion of the reaction, the mixture was cooled to room temperature and then extracted with dichloromethane (4 × 20 mL), washed with brine (3 × 20 mL), and dried over Na_2SO_4. Solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (0−5% ethyl acetate in hexanes) on a 30 g silica column. The pure ligand was obtained in 55% yield (1.68 g, 9.7 mmol) as a white solid. NMR chemical shifts match literature values.

General Procedure A for the Synthesis of Heteroleptic Ir(C^N)(N^N)$_2$ Complexes (100 mg Scale). To a Chemglass microwave vial (size 2−5 mL) equipped with a magnetic stir bar were added $IrCl_3 \cdot xH_2O$ (50 or 100 mg, 1.0 equiv), cyclometalating ligand (8.0 equiv), and ethylene glycol (5 mL, 32 or 64 μM). The vial was sealed and prestirred for 1 min prior to heating under microwave irradiation (200 °C, 50 min) at atmospheric pressure. After the mixture was allowed to cool to room temperature, the dative ligand was added (1.5 equiv) and the vial was heated under microwave irradiation (200 °C, 30 min) at atmospheric pressure. After being cooled to room temperature, the reaction mixture was diluted with DI H_2O (25 mL) and extracted with hexanes (3 × 20 mL). In the case of complexes **2f**−**2h**, the aqueous layer was extracted with ethyl acetate (4 × 30 mL), and the ethyl acetate extract was collected, filtered, dried over Na_2SO_4, and concentrated in vacuo. Deionized H_2O (30 mL) was combined with the mixture to generate a yellow solution with free-flowing yellow solids, to which aqueous ammonium hexafluorophosphate (2.0 g in 20 mL of deionized H_2O) was added. For complexes **2a**−**2e**, the aqueous extract was collected and heated to 75 °C for 15 min to remove remaining organic solvent. Aqueous ammonium hexafluorophosphate (2.0 g in 20 mL of DI H_2O) was added to the mixture, and the mixture was cooled in an ice bath. The resulting precipitate was collected and washed with cold DI H_2O (10 mL) and cold diethyl ether (10 mL). Finally, the precipitate was taken up in acetone and dried in vacuo. The desired product was afforded after recrystallization with acetone and diethyl ether at low temperatures.

Procedure for the 500 mg Scale Synthesis of [Ir(ppy)$_2$(dtbbpy)]PF$_6$. General procedure A was followed, using $IrCl_3 \cdot xH_2O$ (500 mg, 1.6 mmol, 1.0 equiv), 2-phenylpyridine (1.8 μL, 12.6 mmol, 8.0 equiv), and ethylene glycol (15 mL) to obtain a bright yellow solution with yellow solids. **2a** was synthesized using 4,4′-di-*tert*-butyl-2,2′-bipyridine (636 mg, 2.36 mmol, 1.5 equiv) to afford a homogeneous orange solution. **2a** was obtained in 78% yield (1.12 g, 1.22 mmol) as a yellow solid after recrystallization with acetone and diethyl ether at low temperatures.

Procedure for the 500 mg Scale Synthesis of [Ir(dF(CF)$_3$ppy)$_2$(dtbbpy)]PF$_6$. General procedure A was followed, using $IrCl_3 \cdot xH_2O$ (500 mg, 1.6 mmol), 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (3.28 g, 12.6 mmol), and ethylene glycol (15 mL). The reaction mixture was sonicated before microwave irradiation to increase homogeneity of the solution. A bright orange solution with green amorphous solids was obtained. **2g** was synthesized using 4,4′-di-*tert*-butyl-2,2′-bipyridine (636 mg, 2.36 mmol) to afford an orange solution with green solids. The reaction mixture was diluted with DI H_2O (100 mL) and extracted with hexanes (3 × 75 mL) and ethyl acetate (4 × 75 mL). The ethyl acetate extract was collected, filtered to remove unreacted $IrCl_3$ solids, dried over Na_2SO_4, and concentrated in vacuo to afford an orange oil with yellow solids. DI H_2O (75 mL) was combined with the mixture to generate a yellow solution with free-flowing yellow solids. Aqueous ammonium hexafluorophosphate (10.0 g in 100 mL of DI H_2O) was then added to the mixture, and the whole was cooled in an ice bath. The resulting yellow precipitate was collected and washed sequentially with cold DI H_2O (4 × 25 mL) and hexanes (4 × 25 mL). Finally, the precipitate was taken up in acetone and dried in vacuo to afford a mixture of yellow solids and an orange oil. **2g** was obtained in 50% yield (883 mg, 0.79 mmol) as a light yellow solid after recrystallization with acetone and diethyl ether at low temperatures.

Characterization of Heteroleptic Ir(III)$^+$ Complexes. *[Ir(ppy)$_2$(dtbbpy)]PF$_6$ (**2a**):*[38] Yellow solid (208 mg, 72%); ^{1}H NMR (acetone-d_6, 700 MHz) δ 8.88 (s, 2H), 8.23 (d, J = 8.2 Hz, 2H), 8.03−7.92 (m, 3H), 7.88 (d, J = 7.6 Hz, 2H), 7.78 (d, J = 5.7 Hz, 2H), 7.70 (d, J = 5.7 Hz, 2H), 7.12 (t, J = 6.5 Hz, 2H), 7.02 (t, J = 7.4 Hz, 2H), 6.90 (t, J = 7.3 Hz, 2H), 6.33 (d, J = 7.5 Hz, 2H), 1.40 (s, 13H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 167.9 (s), 164.0 (s), 155.9 (s), 151.0 (s), 150.2 (s), 149.0 (s), 144.0 (s), 138.6 (s), 131.5 (s), 130.3 (s), 125.5 (s), 124.9 (s), 123.5 (s), 122.3 (s), 122.0 (s), 119.9 (s), 35.5 (s), 29.5 (s).

*[Ir(Fppy)$_2$(bpy)]PF$_6$ (**2b**):*[36] Yellow solid (119 mg, 90%); ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.91 (d, J = 8.2 Hz, 2H), 8.37 (td, J = 8.0, 1.4 Hz, 2H), 8.28 (d, J = 8.2 Hz, 2H), 8.21 (d, J = 5.3 Hz, 2H), 8.11−7.97 (m, 4H), 7.87 (d, J = 5.8 Hz, 2H), 7.81−7.73 (m, 2H), 7.22 (t, J = 6.6 Hz, 2H), 6.87 (td, J = 8.8, 2.5 Hz, 2H), 5.98 (dd, J = 9.5, 2.5 Hz, 2H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 166.5 (s), 163.68 (d, J = 253.4 Hz), 156.0 (s), 153.5 (d, J = 5.8 Hz), 150.8 (s), 149.3 (s), 140.5 (s), 139.9 (s), 139.1 (s), 128.7 (s), 127.2 (d, J = 9.3 Hz), 125.0 (s), 123.7 (s), 120.1 (s), 117.4 (d, J = 17.8 Hz), 109.6 (d, J = 22.8 Hz).

*[Ir(Fppy)$_2$(dtbbpy)]PF$_6$ (**2c**):*[36] Yellow solid (88 mg, 56%); ^{1}H NMR (acetone-d_6, 700 MHz) δ 8.94 (s, 2H), 8.28 (d, J = 8.2 Hz, 2H), 8.13−7.96 (m, 4H), 7.82 (d, J = 5.5 Hz, 2H), 7.77 (dd, J = 5.8, 1.7 Hz, 2H), 7.19 (t, J = 6.2 Hz, 2H), 6.87 (td, J = 8.8, 2.5 Hz, 2H), 5.97 (dd, J = 9.5, 2.5 Hz, 2H), 1.45 (s, 18H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 166.7 (s), 164.3(s), 163.74 (d, J = 253.4 Hz), 155.8 (s), 154.1 (d, J =

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5.6 Hz), 150.4 (s), 149.1 (s), 140.5 (s), 139.0 (s), 127.2 (d, J = 9.3 Hz), 125.7 (s), 123.6 (s), 122.2 (s), 120.1 (s), 117.3 (d, J = 17.7 Hz), 109.5 (d, J = 22.9 Hz) (s), 35.6 (s), 29.5 (s).

[Ir(dFppy)$_2$(bpy)]PF$_6$ (**2d**):[36] Yellow solid (266 mg, 96%); ^{1}H NMR (acetone-d_6, 700 MHz) δ 8.94 (s, 2H), 8.62 (d, J = 8.9 Hz, 2H), 8.41 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 5.8 Hz, 2H), 7.94−7.70 (m, 4H), 6.87 (t, J = 10.3 Hz, 2H), 5.97 (d, J = 7.9 Hz, 2H), 1.43 (s, 18H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 163.8 (d, J = 7.0 Hz), 163.6 (dd, J = 255.2, 12.3 Hz), 161.4 (dd, J = 262.2, 12.3 Hz), 155.8 (s), 154.6 (d, J = 7.1 Hz), 151.0 (s), 149.8 (s), 140.2 (s), 139.8 (s), 129.0 (s), 127.9 (s), 125.1 (s)124.2 (s), 123.63 (d, J = 21.2 Hz), 113.7 (d, J = 15.8 Hz), 98.7 (t, J = 26.4 Hz).

[Ir(dFppy)$_2$(dtbbpy)]PF$_6$ (**2e**):[36] Yellow solid (135 mg, 87%); ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.96 (s, 2H), 8.41 (d, J = 8.4 Hz, 2H), 8.09 (dd, J = 14.1, 6.8 Hz, 4H), 7.90 (d, J = 5.6 Hz, 2H), 7.77 (dd, J = 5.8, 1.7 Hz, 2H), 7.24 (t, J = 6.7 Hz, 2H), 6.86−6.70 (m, 2H), 5.80 (dd, J = 8.5, 2.2 Hz, 2H), 1.43 (s, 18H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 164.6 (s), 163.9 (d, J = 7.0 Hz), 163.6 (dd, J = 255.2, 12. Hz), 161.4 (dd, J = 260.5, 12.6 Hz), 155.7 (s), 155.2 (d, J = 5.3 Hz), 150.4 (s), 149.6 (s), 139.7 (s), 127.9 (s), 125.8 (s), 124.1 (s), 123.6 (d, J = 19.4 Hz), 122.4 (s), 113.6 (d, J = 15.2 Hz), 98.6 (t, J = 26.4 Hz), 35.6 (s), 29.5 (s).

[Ir(dF(CF)$_3$ppy)$_2$(bpy)]PF$_6$ (**2f**):[36] Yellow solid (175 mg, 55%); ^{1}H NMR (acetone-d_6, 700 MHz) δ 8.90 (d, J = 8.2 Hz, 2H), 8.62 (d, J = 8.9 Hz, 2H), 8.41 (d, J = 7.4 Hz, 4H), 8.31 (d, J = 5.3 Hz, 2H), 7.98 (s, 2H), 7.87−7.73 (m, 2H), 6.87 (t, J = 10.9 Hz, 2H), 5.97 (d, J = 8.3 Hz, 2H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 167.7 (d, J = 7.0 Hz), 164.6 (dd, J = 258.7, 12.6 Hz), 162.5 (dd, J = 260.5, 12.3 Hz), 156.0 (s), 155.2 (d, J = 7.0 Hz), 151.5 (s), 146.2 (d, J = 3.5 Hz), 140.7 (s), 137.3 (s), 129.2 (s), 126.9 (s), 125.4 (s), 125.4 (q, J = 35.2 Hz), 123.9 (d, J = 19.4 Hz), 122.1 (q, J = 273 Hz), 114.5 (d, J = 17.6 Hz), 99.4 (t, J = 28.2 Hz).

[Ir(dF(CF)$_3$ppy)$_2$(dtbbpy)]PF$_6$ (**2g**):.[21,36] Yellow solid (110 mg, 62%); ^{1}H NMR (acetone-d_6, 700 MHz) δ 8.94 (s, 2H), 8.62 (d, J = 8.9 Hz, 2H), 8.41 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 5.8 Hz, 2H), 7.94−7.70 (m, 4H), 6.87 (t, J = 10.3 Hz, 2H), 5.97 (d, J = 7.9 Hz, 2H), 1.43 (s, 18H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 167.8 (s), 165.4 (s), 164.6 (dd, J = 258.7, 14.1 Hz), 162.5 (dd, J = 262.2, 12.3 Hz), 156.0 (s), 155.8 (d, J = 7.0 Hz), 151.1 (s), 145.7 (d, J = 5.3 Hz), 137.2 (s), 126.8 (s), 126.0 (s),125.2 (q, J = 33.4 Hz), 123.9 (d, J = 21.1 Hz), 122.7 (s), 122.1 (q, J = 271.1 Hz), 114.4 (d, J = 17.6 Hz), 99.2 (t, J = 26.4 Hz), 35.7 (s), 29.5 (s).

[Ir(dF(CF)$_3$ppy)$_2$(phen)]PF$_6$ (**2h**):[36] Yellow solid (56 mg, 34%); ^{1}H NMR (acetone-d_6, 500 MHz) δ 9.02 (d, J = 8.3 Hz, 2H), 8.69 (d, J = 5.1 Hz, 2H), 8.62 (d, J = 8.6 Hz, 2H), 8.46 (s, 2H), 8.35 (d, J = 8.8 Hz, 2H), 8.16 (dd, J = 8.3, 5.1 Hz, 2H), 7.87 (s, 2H), 6.99−6.85 (m, 2H), 6.08 (dd, J = 8.4, 2.2 Hz, 2H); ^{13}C NMR (acetone-d_6, 176 MHz) δ 168.0 (d, J = 7.0 Hz), 165.3 (dd, J = 257.0, 12.3 Hz), 163.2 (dd, J = 262.2, 12.3 Hz), 155.2 (s), 152.8 (s), 147.3 (s), 147.0 (d, J = 5.3 Hz), 140.3 (s), 137.7 (s), 132.4 (s), 129.1 (s), 127.9 (s), 127.4 (s), 125.7 (q, J = 35.2 Hz), 124.2 (d, J = 21.1 Hz), 122.5 (q, J = 271.0 Hz), 115.2 (d, J = 17.6 Hz), 100.0 (t, J = 26.4 Hz).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00983.

^{1}H and ^{13}C NMR of all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: crjsteph@umich.edu.

Notes

The authors declare no competing financial interest.

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The seminal works of the Konno, Schubert, and Davies labs were inadvertently omitted and are cited as ref 39 as of August 19, 2016.

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