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Nucleophilic Substitution of Fluorine Atoms in 2, 6-Difluoro-3-(pyridin-2-yl)benzonitrile Leading to Soluble Blue-Emitting Cyclometalated Ir(III) Complexes

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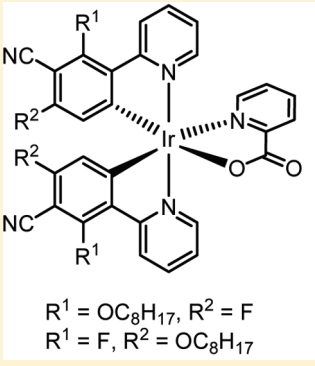
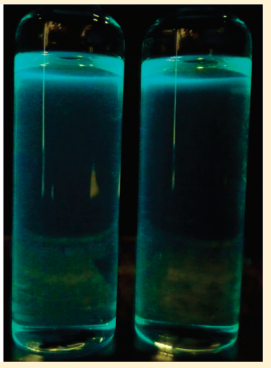
Supporting Information

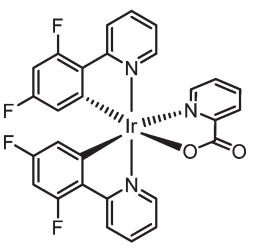
ABSTRACT: New functionalized phenylpyridine ligands and their derived heteroleptic cyclometalated Ir(III) complexes have been synthesized. The complexes possess a combination of important properties: (i) blue emission, (ii) good photoluminescence quantum yields, and (iii) good solubility in organic solvents, making them very attractive as phosphorescent dopant emitters for solution-processable light-emitting devices.



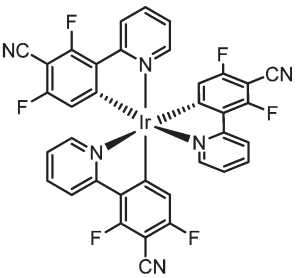


The development of blue emitters which are required for organic light-emitting diode (OLED) displays[1−4] and lighting applications[5,6] remains a significant challenge. Phosphorescent cyclometalated complexes provide improved electroluminescence efficiencies by utilizing both triplet and singlet electroexcitation pathways.[7,8] To date, at least two electron-withdrawing substituents, usually fluorine atoms, have been required on the phenyl ring of chelating phenylpyridine (ppy) ligands to decrease the HOMO energy to the extent that emission is shifted into the blue region.[9−15] One of the most widely studied complexes for blue emission is FIrpic **1**[9−11] (Chart 1). Unfortunately, FIrpic suffers two major drawbacks: (i) it has poor solubility in common organic solvents, which means that OLED devices are usually fabricated by vacuum thermal deposition, rather than by milder solution processing or ink jet printing techniques. The latter methods are preferable for low cost processing and large-area displays. (ii) Devices based on FIrpic are not long-lived. One of the degradation mechanisms is cleavage of a fluorine atom, which occurs during the harsh vacuum deposition process and possibly also during device operation.[16,17] Therefore, there is a need for analogues with (i) enhanced solubility in organic solvents to facilitate solution processing in devices and (ii) fewer fluorine atoms in the ligands, while retaining the blue emission.[18] Solution processing has the great advantage of being a room-temperature procedure for assembly of thin films, so the molecules are not subjected to the high temperatures of vacuum deposition procedures. We now report an efficient way to achieve these aims by using the new functionalized 2-phenylpyridine ligands **9a** and **9b**. The ligands are synthesized using Suzuki cross-coupling reactions; they are functionalized with long alkoxy chains to enhance solubility and they retain only one fluorine atom.

Chart 1



1 FIrpic



2 FCNIr

It has recently been reported that 2,6-difluoro-3-(pyridin-2-yl)benzonitrile **6** forms blue homoleptic phosphorescent Ir(III) complexes,[19,20] e.g. FCNIr **2**[20] (Chart 1). The electron-withdrawing cyano and fluoro substituents not only provide the large HOMO−LUMO gap required for blue emission but also make **6** reactive toward nucleophilic substitution, enabling derivatization with alkoxy chains to enhance solubility. Both of the fluorine atoms of **6** are expected to have a very similar reactivity, so the

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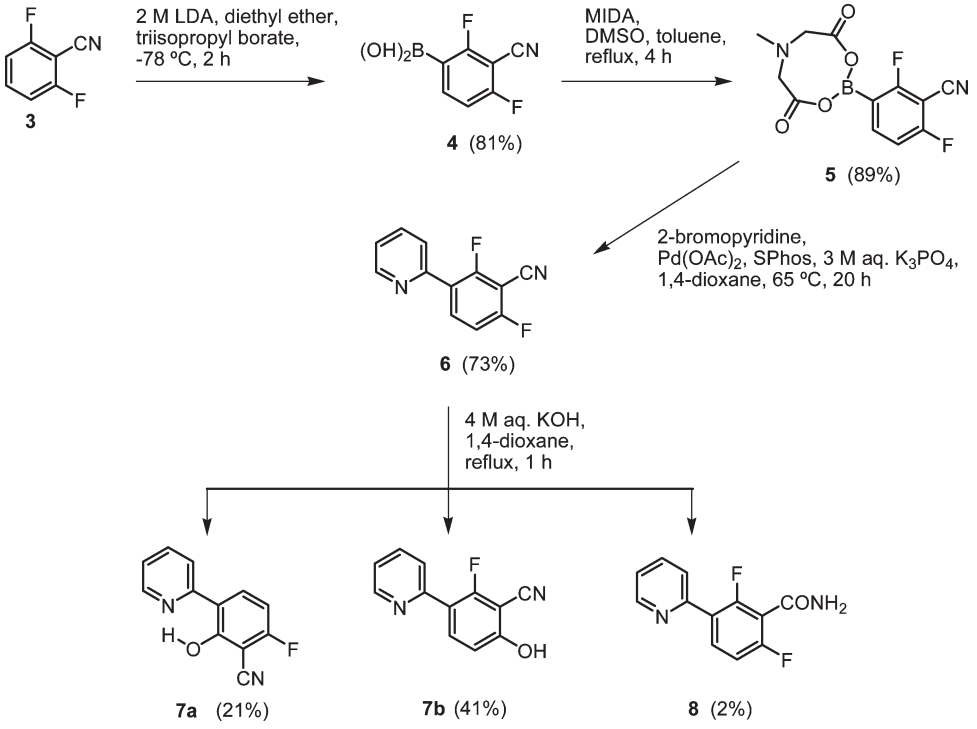
Scheme 1



success of our strategy for further functionalization lies in the ability to separate the product mixtures after replacement of a fluorine atom by a nucleophile. With this in mind, we investigated the reaction of **6** with hydroxide ions, since the resulting isomeric phenols should have significantly different properties. This is based on the possibility of intramolecular N···O−H hydrogen bonding in the phenol derivative **7a**, which is not possible in **7b**.

The synthesis and functionalization of **6** is shown in Scheme 1. Compound **3** was converted to boronic acid derivative **4** using a standard directed *ortho* metalation (D*o*M) reaction. Compound **4** was converted into the *N*-methyliminodiacetic acid (MIDA) boronate[21] derivative **5**, which was cross-coupled with 2-bromopyridine under palladium-catalyzed conditions optimized following literature protocols[21] to yield compound **6** (73% yield).[22] (The comparable reaction of **4** and 2-bromopyridine gave **6** in only 35% yield). The reaction of **6** with potassium hydroxide gave the phenol derivatives **7a** and **7b** in isolated yields of 21% and 41%, respectively. A range of conditions were explored with the best yields achieved using aqueous KOH in refluxing 1,4-dioxane, which gave synthetically viable quantities of **7a** and **7b**.[23] 2,6-Difluoro-3-(pyridin-2-yl)benzamide **8** was also isolated in very low yield. The isomers **7a** and **7b** were readily separated due to their drastically different solubility in dichloromethane; **7a** is readily soluble, whereas **7b** is insoluble, presumably due to an intramolecular N···O−H bridge in **7a**. Simple treatment of the mixture of **7a** and **7b** with dichloromethane followed by filtration allowed complete separation.

Phenol derivatives **7a** and **7b** were converted to the *n*-octyloxy derivatives **9a** and **9b**, respectively, to improve the solubility of the derived iridium complexes (Scheme 2). Subsequently, **9a** and **9b** were cyclometalated by reaction with iridium(III) chloride trihydrate in a mixture of refluxing 2-ethoxyethanol and water[24,25] to yield the intermediate dichloro-bridged species **10a**,**b**. These species were used without further purification and refluxed with picolinic acid and potassium carbonate in 1,4-dioxane to afford the desired complexes **11a** and **11b**.

To establish the versatility of the methodology, a pendant carbazole unit was attached which should increase hole transport ability[26,27] and charge recombination[28] at the emitting site. Compound **7b** was alkylated with 9-(4-bromobutyl)-9*H*-carbazole[29] to give **12** and hence **13** (Scheme 3). Complexes **11a**, **11b**, and **13** are racemic; no attempts were made to separate their Δ and Λ enantiomers.[30]

The solubilities of **11a**, **11b**, and **13** are considerably improved compared to FIrpic. Thus, 25 mg of complexes **11a** and **11b** is soluble in 1 mL of chlorobenzene, toluene, and 1,4-dioxane. Complex **13** shows good solubility in chlorobenzene and 1,4-dioxane (≥25 mg/mL) but is less soluble in toluene. The solubility of FIrpic in these solvents is ≤5 mg/mL. Solutions of **11a**, **11b**, and **13** in 1,4-dioxane (25 mg/mL) are stable to storage at 20 °C for at least 14 days: after this time, the complexes were quantitatively recovered by evaporation and their ^{1}H NMR spectra and emission spectra were unchanged.

The complexes **11a**, **11b**, and **13** show strong absorption bands in the 230−350 nm region which are assigned[9] to ligand-centered $\pi-\pi^*$ transitions and closely resemble the absorption spectra of the free ligands **9a**, **9b**, and **12** (see the Supporting Information). The complexes also show absorption bands with lower extinction in the range 350−400 nm, which are assigned to singlet and triplet metal-to-ligand charge-transfer (^{1}MCLT and ^{3}MLCT) states, following literature precedents[9] and the calculations of Hay.[31] It is not possible to distinguish the singlet and triplet absorptions, although the precedent is that the lower energy bands are predominantly triplet in character. The luminescence spectra of **11a**, **11b**, **13**, and FIrpic **1** in dichloromethane solution are shown in Figure 1, and the data are summarized in Table 1.

Efficient blue emission from iridium ppy complexes results from large HOMO−LUMO gaps. One strategy to achieve this is

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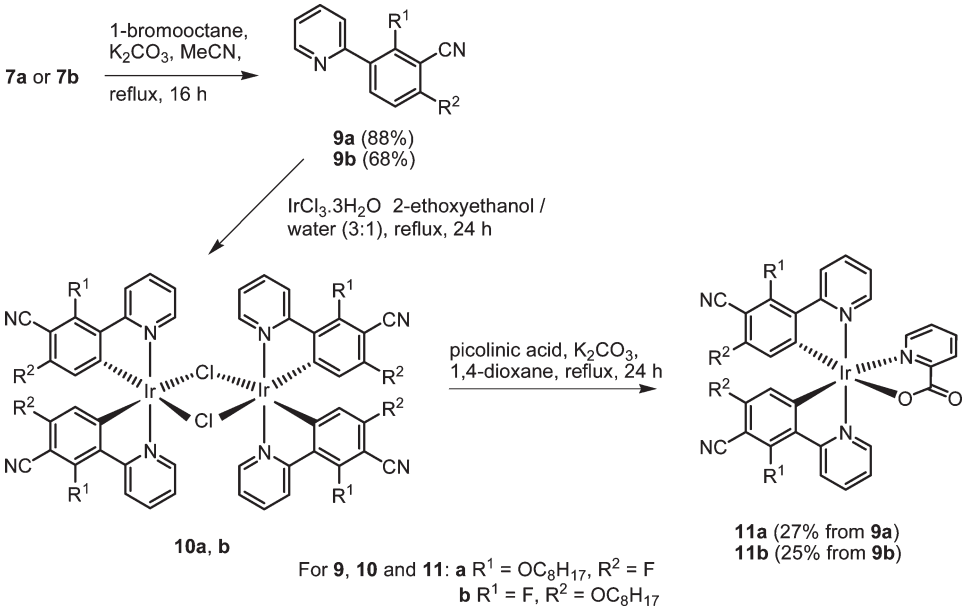
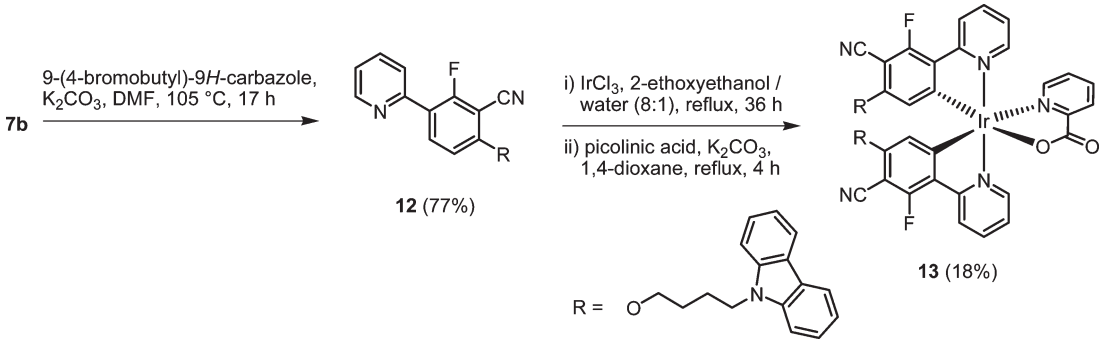
Scheme 2



Scheme 3



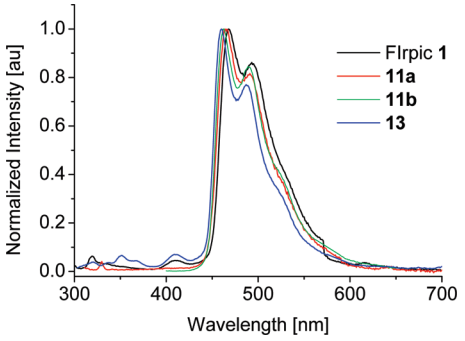


Figure 1. Emission spectra of **1**, **11a**, **11b**, and **13** in deaerated dichloromethane at 293 K.

to lower the HOMO energy by attachment of electron-withdrawing groups to the phenyl ring of the ligands.[10,11] It might be expected that the electron donating alkoxy group in complexes **11a**, **11b** and **13** would cause a bathochromic shift of the emission. However, the luminescence for **11a**, **11b**, and **13** occurs at λ_{max} values essentially the same as FIrpic **1** and is visible as bright sky-blue emission. This is because of the balance of the hypsochromic shift due to the cyano group and the bathochromic shift due to the alkoxy group resulting in similar emission wavelengths for **11a**, **11b**, **13**, and FIrpic **1**. A photograph of the solutions of **11a** and **11b** in dichloromethane excited at 365 nm is shown in the abstract. Quantum molecular calculations

Table 1. Luminescence Properties of 11a, 11b, 13, and FIrpic 1

compd	λ_{PL} (nm) CH_2Cl_2 [b]	Φ_{PL} CH_2Cl_2 [c]	lifetime τ [d] (μs)
11a	465, 487	0.30 ± 0.05	1.6
11b	464, 486	0.43 ± 0.05	1.6
13	460, 485	0.44 ± 0.05	1.8
FIrpic **1** [a]	468, 489	0.26 ± 0.05	1.9

[a] Data for FIrpic are consistent with those in ref 10. [b] Photoluminescence quantum yield, determined using an integrating sphere. [c] λ_{exc} (nm) for Φ_{PL} 315 nm for **11a**, **11b**, and **13** and 325 nm for FIrpic. PLQY data were obtained using an integrating sphere. [d] Measured in deaerated 1, 2-dichloroethane at 293 K.

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performed in the gas phase (time-dependent density functional theory: TDDFT using the B3LYP/6-31G* level) qualitatively support these observations. From these data, the HOMO−LUMO gaps of complexes **11a** (3.69 eV) and **11b** (3.72 eV) (with the structures simplified by replacing the octyl chains with methyl groups to reduce the calculation time) are located between FIrpic (3.62 eV) and the analogous complex of ligand **6** (3.79 eV). The trend in the calculated HOMO−LUMO data in line with the electron-withdrawing effect of the substituents is significant. (For further details, see the Supporting Information.) Photoluminescence quantum yields of the new complexes **11a**, **11b**, and **13** are similar to that of FIrpic **1**, measured under directly comparable conditions. Excited-state lifetimes measured in deaerated 1,2-dichloroethane at 293 K are in the microsecond regime (Table 1). Such long-lived excited states clearly suggest that the emitting state has triplet character.[9,10]

In summary, the phenylpyridine derivatives **9a**, **9b**, and **12** were synthesized and their derived heteroleptic Ir(C^N)$_2$(pic) complexes **11a**, **11b**, and **13** shown to be efficient blue emitters (Φ_{PL} 30 − 44%), whose λ_{max} and PLQY and excited state lifetime values compare favorably with FIrpic, which is the standard blue phosphor for OLEDs. Importantly, these new complexes possess significantly improved solubility in organic solvents compared to FIrpic. The good solubility and stability of the new complexes **11a**, **11b**, and **13** in solution means that their thin films for device studies can be prepared by spin-coating at room temperature in conditions which will not lead to any decomposition of the complex. This contrasts with FIrpic for which thin film formation requires vacuum deposition at high temperatures, leading to partial degradation.[16,17] Complexes **11a**, **11b**, and **13** are, therefore, very attractive as new phosphorescent blue dopants in solution-processable LEDs. The synthetic methodology should be versatile for the attachment of a range of substituents to impart additional functionality.

EXPERIMENTAL SECTION

2,4-Difluoro-3-cyanophenylboronic Acid (4). To a solution of **3** (15.0 g, 108 mmol) in diethyl ether (300 mL) at −78 °C was added a solution of lithium diisopropylamide (2 M in heptane/THF/ethylbenzene, 60 mL, 120 mmol) dropwise over a period of 40 min. The mixture was stirred at −78 °C for 1 h. Triisopropyl borate (17.2 mL, 160 mmol) was slowly added, and the reaction mixture was stirred at −78 °C for 1 h. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 1 h. Water (150 mL) was added; the mixture was stirred for 15 min. The organic layer was separated and washed with aqueous KOH (1 M, 150 mL). The aqueous solutions were combined and acidified to pH 5 with concd HCl. The product was extracted with ethyl acetate. The solvent was evaporated and the residue was dried in vacuum to yield **4** as a yellow solid (16.0 g, 81%): mp 132.5−133.5 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.13 (q, J = 14.9 Hz, 7.1 Hz, 1H), 7.65 (br s, 2H), 7.31 (t, J = 8.6 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 169.1, 166.7, 164.1, 143.7, 143.6, 143.5, 113.0, 122.8, 110.3; ^{19}F NMR (376 MHz, acetone-d_6) δ −102.55, −109.54; HRMS (ES) m/z calcd $[C_7H_4BF_2NO_2 + H]^+$ 184.0381, found 184.0380.

2,6-Difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)benzonitrile (5). A mixture of **4** (1.71 g, 9.34 mmol), methyliminodiacetic acid (MIDA) (1.51 g, 10.27 mmol), DMSO (20 mL), and toluene (40 mL) was heated under reflux with a Dean−Stark trap for 4 h. The mixture was cooled to room temperature, and water was added. The precipitate was filtered off, washed with toluene and diethyl ether and dried in vacuum to give **5** as an off-white solid (2.44 g, 89%): mp 295.5−296.6 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 8.7 Hz, 1H), 4.44 (d, J = 17.4 Hz, 2H), 4.13 (d, J = 17.3 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 141.8, 112.4, 112.3, 110.0, 62.4, 47.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ −97.70 (d, J = 7.3 Hz), −104.92 (s); HRMS (ASAP) m/z calcd $[C_{12}H_9{}^{10}BF_2N_2O_4]^+$ 294.0738, found 294.0740.

2,6-Difluoro-3-(pyridin-2-yl)benzonitrile (6). A mixture of 2-bromopyridine (1.10 g, 6.96 mmol), **5** (2.50 g, 8.5 mmol), and 1,4-dioxane (80 mL) was deoxygenated by bubbling argon for 10 min. Then 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (270 mg, 0.66 mmol), $Pd(OAc)_2$ (73 mg, 0.33 mmol), and degassed aq K_3PO_4 (3.0 M, 17 mL) were added, and the mixture was degassed for an additional 15 min. The reaction mixture was stirred under argon at 65 °C for 20 h. Toluene (40 mL) was added, and the mixture was separated. The organic layer was washed with water, dried over Na_2SO_4, and evaporated to dryness. The product was purified by column chromatography using silica gel and a mixture of petroleum ether/ethyl acetate 1:1 v/v as the eluent (R_f = 0.5) to give **6** as an off-white solid (1.10 g, 73%): mp 76−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.8, 1H), 8.35 (td, J = 6.6, 8.8, 1H), 7.82−7.79 (m, 2H), 7.35−7.32 (m, 1H), 7.20−7.16 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 161.9, 161.9, 161.8, 159.3, 150.1, 136.9, 124.3, 124.2, 123.4, 112.7, 112.6, 112.5, 112.4, 109.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −103.06 (s), −107.25 (d, J = 8.2 Hz); HRMS (ES) m/z calcd $[C_{12}H_6F_2N_2 + H]^+$ 217.0577, found 217.0576. Anal. Calcd for $C_{12}H_6F_2N_2$: C, 66.67; H, 2.80; N, 17.58. Found: C, 66.48; H, 2.60; N, 17.77.

6-Fluoro-2-hydroxy-3-(pyridin-2-yl)benzonitrile (7a), 2-Fluoro-6-hydroxy-3-(pyridin-2-yl)benzonitrile (7b), and 2,6-Difluoro-3-(pyridin-2-yl)benzamide (8). An aqueous solution of potassium hydroxide [prepared by dissolving KOH (450 mg, 8 mmol) in water (5 mL)] was added to a solution of **6** (520 mg, 2.4 mmol) in 1,4-dioxane (10 mL). The mixture was heated under reflux for 1 h and then evaporated to a volume of ca. 1 mL. Water (20 mL) was added; the mixture was gently heated with stirring to solubilize most of the residue and filtered. The solid on the filter was washed with water to give **8**. To the filtrate was then rapidly added aqueous acetic acid (2 mL of concd AcOH in 8 mL of H_2O). The precipitate was collected, washed with water, and dried under vacuum to give a mixture of **7a** and **7b**. The mixture was then heated under reflux in DCM (30 mL) for 10 min, allowed to cool to room temperature, and filtered; this operation was repeated another two times. The combined filtrates were evaporated to dryness. The residue was chromatographed on a silica gel column (eluent DCM/ethyl acetate 10:1 v/v) to give pure **7a**. The solid on the filter was dried and recrystallized from methanol to give **7b**. **7a** (110 mg, 21%): yellow solid; mp 190.5−191.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (m, 1H), 7.98 (dd, J = 9.0 Hz, J = 6.2 Hz, 1H), 7.96−7.91 (m, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.37 (ddd, J = 7.4 Hz, J = 5.1 Hz, J = 1.0 Hz, 1H), 6.72 (t, J = 8.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7 (d, J = 5.2 Hz), 164.7 (d, J = 262.3 Hz), 155.5, 145.3, 138.7, 131.3 (d, J = 11.1 Hz), 122.6, 118.9, 115.4, 111.7, 105.7 (d, J = 19.9 Hz), 92.3 (d, J = 17.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −102.46 (dd, J = 8.2 Hz, J = 6.3 Hz); UV/vis (CH_2Cl_2) λ_{max} (log ε) 232 nm (4.34), 288 (3.83), 328 (4.01); HRMS (ES) m/z calcd $[C_{20}H_7FN_2O + H]^+$ 215.0621, found 215.0616. Anal. Calcd for $C_{12}H_7FN_2O$: C, 67.29; H, 3.29; N, 13.08. Found: C, 67.40; H, 3.44; N, 13.47. **7b** (210 mg, 41%): colorless solid, mp 212.5−213.5 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.04 (br s, 1H), 8.69 (ddd, J = 4.8 Hz, J = 1.8 Hz, J = 0.9 Hz, 1H), 8.10 (t, J = 9.2 Hz, 1H), 7.90 (td, J = 7.8 Hz, J = 1.8 Hz, 1H), 7.81−7.68 (m, 1H), 7.38 (ddd, J = 7.5 Hz, J = 4.8 Hz, J = 1.0 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.3, 160.7 (d, J = 258.5 Hz), 151.0, 149.8, 137.1, 136.3 (d, J = 5.8 Hz), 123.6 (d, J = 9.1 Hz), 122.8, 117.7, 112.8, 112.3, 109.3, 89.4 (d, J = 18.6 Hz); ^{19}F NMR (470 MHz,

DMSO-d_6) δ −111.68 (dd, J = 9.5 Hz, J = 2.0 Hz); HRMS (ASAP) m/z calcd $[C_{20}H_7FN_2O + H]^+$ 215.0621, found 214.0616. Anal. Calcd for $C_{12}H_7FN_2O$: C, 67.29; H, 3.29; N, 13.08. Found: C, 67.63; H, 3.49; N, 13.37. **8** (13 mg, 2%): pale yellow solid; mp 189.5−190.5 °C; ^{1}H NMR (270 MHz, DMSO-d_6) δ 8.72 (ddd, J = 4.8 Hz, J = 1.8 Hz, J = 0.9 Hz, 1H), 8.22 (br s, 1H), 7.89−8.03 (m, 3H), 7.76 (m, 1H), 7.43 (ddd, J = 7.5 Hz, J = 4.8 Hz, J = 0.9 Hz, 1H), 6.99 (td, J = 8.7 Hz, J = 1.0 Hz 1H); ^{13}C NMR (68 MHz, DMSO-d_6) δ 162.0, 159.2 (dd, J = 250.3 Hz, J = 8.3 Hz), 158.7 (dd, J = 252.6 Hz, J = 8.7 Hz), 152.0 (d, J = 2.7 Hz), 150.5, 137.7, 132.3 (dd, J = 9.8 Hz, J = 3.9 Hz), 124.6, 124.5, 124.4 (dd, J = 12.7 Hz, J = 3.9 Hz), 123.7, 116.9 (t, J = 24.0 Hz), 112.8 (dd, J = 21.8 Hz, J = 3.6 Hz); HRMS (ES) m/z calcd $[C_{12}H_8F_2N_2O + H]^+$ 235.0683, found 235.0672.

6-Fluoro-2-(octyloxy)-3-(pyridin-2-yl)benzonitrile (9a). A mixture of **7a** (320 mg, 1.5 mmol), 1-bromooctane (288 mg, 1.5 mmol), K_2CO_3 (620 mg, 4.5 mmol), and acetonitrile (25 mL) was heated under reflux for 16 h. The mixture was filtered, and the filtrate was evaporated to dryness. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:2, v/v) as eluent to give **9a** as a pale yellow oil (430 mg, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.8 Hz, J = 0.6 Hz, 1H), 7.99 (dd, J = 8.8 Hz, J = 6.7 Hz, 1H), 7.82−7.79 (m, 1H), 7.75 (td, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.31−7.27 (m, 1H), 7.04 (dd, J = 8.7 Hz, J = 8.0 Hz, 1H), 3.89 (t, J = 6.5 Hz, 2H), 1.68−1.56 (m, 2H), 1.32−1.22 (m, 4H), 1.20 (s, 6H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (d, J = 263.1 Hz), 160.3 (d, J = 2.5 Hz), 153.4, 149.8, 137.0 (d, J = 11.03 Hz), 136.3, 130.5 (d, J = 4.2 Hz), 124.6, 122.7, 111.8, 111.4 (d, J=20.1 Hz), 97.2 (d, J = 15.3 Hz), 76.2, 31.7, 29.8, 29.1, 29.0, 25.6, 22.6, 14.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ −104.66 (t, J = 7.3 Hz); UV/vis (CH_2Cl_2) λ_{max} (log ε): 230 nm (4.13), 274 (3.81); HRMS (ES) m/z calcd $[C_{20}H_{23}FN_2O + H]^+$ 327.1873, found 327.1879. Anal. Calcd for $C_{20}H_{23}FN_2O$: C, 73.59; H, 7.10; N, 8.58. Found: C, 73.28; H, 6.90; N, 8.77.

2-Fluoro-6-(octyloxy)-3-(pyridin-2-yl)benzonitrile (9b). A mixture of **7b** (421 mg, 1.97 mmol), 1-bromooctane (330 mg, 1.71 mmol), K_2CO_3 (667 mg, 4.83 mmol), and acetonitrile (25 mL) was heated under reflux for 16 h. The mixture was filtered, and the resulting solid was washed with acetone (3 mL). Water was added to the filtrate, and the precipitate was filtered off and washed with water to give **9b** as an off-white solid (377 mg, 68%): mp 68.0−68.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 4.7 Hz, 1H), 8.24 (t, J = 9.0 Hz, 1H), 7.76 (s, 2H), 6.88 (d, J = 8.9 Hz, 1H), 4.15 (t, J = 6.5 Hz, 2H), 1.95−1.81 (m, 2H), 1.53−1.45 (m, 2H), 1.42−1.24 (m, 9H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 136.7, 136.3 (d, J = 5.7 Hz), 124.0 (d, J = 11.1 Hz), 122.6, 108.2 (d, J = 3.72 Hz), 69.9, 31.8, 29.2, 29.2, 28.8, 25.8, 22.6, 14.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −109.40 (d, J = 8.9 Hz); UV/vis (CH_2Cl_2) λ_{max} (log ε) 233 nm (4.45), 257 (4.22), 277 (4.21), 302 (3.87); HRMS (ES) m/z calcd $[C_{20}H_{23}FN_2O + H]^+$ 327.1873, found 327.1868. Anal. Calcd for $C_{20}H_{23}FN_2O$: C, 73.59; H, 7.10; N, 8.58. Found: C, 73.48; H, 6.86; N, 8.81.

Complex 11a. Compound **9a** (430 mg, 1.32 mmol) was dissolved in 2-ethoxyethanol (30 mL). $IrCl_3 \cdot 3H_2O$ (230 mg, 0.65 mmol) was dissolved in boiling water (10 mL) and added to the above solution. The mixture was heated under reflux for 24 h and then cooled to room temperature, and the yellow solid was filtered off, washed with methanol, and dried (285 mg). The intermediate **10a** was used in the next step without further purification. A mixture of **10a** (285 mg, 0.16 mmol), picolinic acid (215 mg, 1.75 mmol), and potassium carbonate (100 mg, 0.72 mmol) in 1,4-dioxane (40 mL) was heated under reflux for 24 h. The solvent was evaporated, and the product was purified by column chromatography (silica gel, eluent DCM/ethyl acetate, 1:2, v/v) to yield **11a** (180 mg, 27%): mp 107.5−108.0 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.74−8.72 (m, 2H), 8.64 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 7.7 Hz, 1H), 7.99 (td, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.84 (ddd, J = 16.1 Hz, J = 7.6 Hz, J = 1.6 Hz, 2H), 7.69 (d, J = 4.8 Hz, 1H), 7.47−7.45 (m, 1H), 7.41 (dd, J = Hz, J = 5.8 Hz, J = 1.0 Hz, 1H), 7.29−7.23 (m, 2H), 7.06−7.04 (m, 1H), 5.83 (d, J = 8.6 Hz, 1H), 5.62 (d, J = 8.6 Hz, 1H), 4.46−4.25 (m, 4H), 1.98−1.93 (m, 4H), 1.55−1.50 (m, 4H), 1.41−1.37 (m, 4H), 1.35−1.25 (m, 12H), 0.90−0.87 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 165.5, 164.5, 164.1, 162.3, 162.1, 162.0, 161.9, 161.6 (d, J = 8.5 Hz), 160.5 (d, J = 3.3 Hz), 160.4 (d, J = 3.3 Hz), 151.3, 148.5, 147.9, 138.9, 138.6 (d, J = 3.3 Hz), 133.5 (d, J = 3.3 Hz), 133.1 (d, J = 2.0 Hz), 128.7 (d, J = 19.2 Hz), 124.2, 123.7, 123.2 (d, J = 17.2 Hz), 114.4, 114.3, 114.3, 114.2, 113.4 (d, J = 3.1 Hz), 89.8 (d, J = 16.2 Hz), 88.7 (d, J = 17.2 Hz), 75.7 (d, J = 17.2 Hz), 31.7 (d, J = 4.1 Hz), 30.3, 30.2, 29.3 (d, J = 2.3 Hz), 29.2 (d, J = 2.9 Hz), 25.8 (d, J = 1.6 Hz), 22.6 (d, J = 2.6 Hz), 14.1 (d, J = 2.4 Hz); ^{19}F NMR (658 MHz, $CDCl_3$) δ −103.67 (d, J = 8.6 Hz), −104.50 (d, J = 8.6 Hz); UV/vis (CH_2Cl_2) λ_{max} (log ε) 257 nm (4.69), 287 (4.61); HRMS (ES) m/z calcd $[C_{46}H_{48}F_2{}^{191}IrN_5O_4]^+$ 963.3280, found 963.3256. Anal. Calcd for $C_{46}H_{48}F_2IrN_5O_4$: C, 57.25; H, 5.01; N, 7.26. Found: C, 57.51; H, 4.69; N, 7.44.

Complex 11b. Compound **9b** (335 mg, 1.03 mmol) was dissolved in 2-ethoxyethanol (15 mL). Water (5 mL) and $IrCl_3 \cdot 3H_2O$ (186 mg, 0.53 mmol) were added, and the mixture was heated under reflux for 24 h. Water (5 mL) was added, and the mixture was allowed to cool to room temperature. The yellow solid was filtered off, washed with methanol, and dried (347 mg). The intermediate **10b** was used in the next step without further purification A mixture of **10b** (92 mg, 0.05 mmol), picolinic acid (104 mg, 0.85 mmol), and 1,4-dioxane (30 mL) was heated under reflux for 60 h. The solvent was evaporated, and the product was purified by column chromatography (silica gel, eluent DCM/methanol, 10:1, v/v) to give **11b** (24 mg, 25%): mp 119.0−120.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, J = 5.1 Hz, 1H), 8.36 (d, J = 7.7 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.01 (td, J = 7.7 Hz, J = 1.4 Hz, 1H), 7.87−7.81 (m, 2H), 7.76 (d, J = 4.9 Hz, 1H), 7.53−7.48 (m, 1H), 7.43 (d, J = 5.1 Hz, 1H), 7.25−7.20 (m, 1H), 7.05−6.99 (m, 1H), 5.68 (s, 1H), 5.44 (s, 1H), 3.68−3.53 (m, 4H), 1.70−1.46 (m, 7H), 1.37−1.17 (m, 17H), 1.03−0.73 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 165.0 (J = 6.5 Hz), 163.7 (J = 6.5 Hz), 162.5, 161.7, 161.3, 160.7, 160.4, 151.3, 148.7, 147.9 (J = 21.8 Hz), 138.9, 138.6 (J = 8.9 Hz), 128.8 (J = 7.7 Hz), 124.9, 124.8, 123.2, 123.0, 122.5, 122.3, 122.3, 112.7, 110.8, 86.0, 85.6, 69.0, 68.8, 31.7 (J = 4.9 Hz), 29.7, 29.2 (J = 4.0 Hz), 29.1 (J = 4.0 Hz), 28.5 (J = 8.9 Hz), 25.7 (J = 8.9 Hz), 22.6, 14.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −107.99 (s), −108.44 (s); UV/vis (CH_2Cl_2) λ_{max} (log ε) 265 nm (4.79); HRMS (ES) m/z calcd $[C_{46}H_{48}F_2{}^{191}IrN_5O_4 + H]^+$ 964.3359, found 964.3339. Anal. Calcd for $C_{46}H_{48}F_2IrN_5O_4$: C, 57.25; H, 5.01; N, 7.26. Found: C, 57.56; H, 5.40; N, 6.87.

6-[4-(9*H*-Carbazol-9-yl)butoxy]-2-fluoro-3-(pyridin-2-yl)-benzonitrile (12). A mixture of **7b** (420 mg, 1.96 mmol), 9-(4-bromobutyl)-9*H*-carbazole (590 mg, 1.96 mmol) and K_2CO_3 (1.0 g, 7.25 mmol) in dry DMF (20 mL) was stirred at 105 °C for 17 h. Water (20 mL) was added, and the precipitated solid was filtered off, washed with methanol, and recrystallized from ethanol to give **12** (656 mg, 77%) as an off-white solid: mp 115.0−116.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 4.6 Hz, 1H), 8.19 (t, J = 9.0 Hz, 1H), 8.10 (d, J = 7.8 Hz, 2H), 7.79−7.74 (m, 2H), 7.52−7.41 (m, 5H), 7.30−7.20 (m, 6H), 6.72 (d, J = 9.1 Hz, 1H), 4.46 (t, J = 6.8 Hz, 2H), 4.05 (t, J = 6.1 Hz, 2H), 2.25−2.12 (m, 2H), 2.07−1.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, J = 4.23 Hz), 161.5 (d, J = 261.3 Hz), 151.1, 149.8, 140.3, 136.7, 136.3 (d, J = 5.8 Hz), 125.7, 124.0 (d, J = 9.8 Hz), 122.8, 122.7, 120.5 (d, J = 11.9 Hz), 120.4, 118.9, 111.5, 108.6, 108.1 (d, J = 3.5 Hz), 69.3, 42.6, 26.6, 25.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ −109.20 (d, J = 8.8 Hz); UV/vis (CH_2Cl_2) λ_{max} (log ε) 237 nm (4.78), 263 (4.55), 284 (4.32), 295 (4.34); HRMS (ES) m/z calcd $[C_{28}H_{22}FN_3O + H]^+$ 436.1825, found 436.1828. Anal. Calcd. for $C_{28}H_{22}FN_3O$: C, 77.22; H, 5.09; N, 9.65. Found: C, 76.88; H, 4.79; N, 9.90.

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Complex 13. A mixture of **12** (550 mg, 1.26 mmol), 2-ethoxyethanol (40 mL), $IrCl_3 \cdot 3H_2O$ (200 mg, 0.57 mmol), and water (5 mL) was heated under reflux for 36 h. The mixture was allowed to cool to room temperature, water was added, and the solid was filtered and washed with methanol to give a gray solid after drying (420 mg). This dichloro-bridged complex was used in the next step without further purification. A mixture of the complex (250 mg, 0.12 mmol), picolinic acid (85 mg, 0.69 mmol), potassium carbonate (48 mg, 0.35 mmol), and 1,4-dioxane (15 mL) was heated under reflux for 4 h. The mixture was evaporated to dryness, and the product was purified by column chromatography (silica gel, eluent DCM/ethyl acetate, 1:1, v/v) to give **13** (25 mg, 18%): mp 188.0−189.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67−8.61 (m, 1H), 8.33 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 8.6 Hz, 1H), 8.11 (t, J = 7.4 Hz, 4H), 8.07 (d, J = 8.6 Hz, 1H), 7.97 (td, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.70 (t, J = 7.9 Hz, 1H), 7.67−7.60 (m, 2H), 7.51−7.42 (m, 5H), 7.38 (t, J = 8.6 Hz, 4H), 7.29 (d, J = 5.8 Hz, 1H), 7.25−7.20 (m, 3H), 7.07−7.00 (m, 1H), 6.87−6.80 (m, 1H), 5.54 (s, 1H), 5.31 (s, 1H), 4.38−4.34 (m, 4H), 3.54−3.41 (m, 2H), 2.03−1.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 148.5, 147.9, 140.3 (d, J = 5.7 Hz), 138.7, 128.7, 125.7 (d, J = 3.5 Hz), 122.8 (d, J = 2.1 Hz), 122.4, 120.4 (d, J = 5.0 Hz), 118.9 (d, J = 8.7 Hz), 108.7 (d, J = 11.6 Hz), 68.5, 68.3, 42.5, 26.6 (d, J = 6.4 Hz), 25.8 (d, J = 4.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −107.74 (s), −108.22 (s); UV/vis (CH_2Cl_2) λ_{max} (log ε) 238 nm (5.17), 263 (5.11), 295 (5.00); HRMS (ES) m/z calcd $[C_{62}H_{46}F_2{}^{191}IrN_7O_4 + H]^+$ 1182.3258, found 1182.3259. Anal. Calcd for $C_{62}H_{46}F_2IrN_7O_4$: C, 62.93; H, 3.92; N, 8.29. Found: C, 63.35; H, 3.61; N, 8.54.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H, ^{13}C, ^{19}F NMR, mass spectra, absorption spectra, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Reference 19 reports the synthesis of compound **6** from **4** and 2-bromopyridine, but the yield is not stated and no characterization data are given for **4** or **6**. Reference 20 claims the synthesis of **6** in 88% yield from reaction of 2,6-difluoro-3-(trimethylstannyl)benzonitrile and 2-bromopyridine. However, the only characterization data reported for **6** is ^{1}H NMR data, which do not agree with our NMR data reported herein. All our characterization data are consistent with structure **6**.

(23) Alternative conditions and yields [KOH (4 M), 1,4-dioxane, reflux 1 h, or K_2CO_3 (2 M), dioxane, reflux 17 h] gave **7a** (15−18%), **7b** (15−19%), and **8** (ca. 1%). It is possible that the outcome of the reaction could be rationalized in terms of the stability of the intermediate Meisenheimer complexes (as suggested by a reviewer). However, this would need more extensive optimization, and mechanistic studies than have been performed.

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