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Palladium-Catalyzed C–H Bond Arylation of Cyclometalated Difluorinated 2-Arylisoquinolinyl Iridium(III) Complexes

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Abstract: The utility of C–H bond functionalization of metalated ligands for the elaboration of aryl-functionalized difluorinated-1-arylisoquinolinyl Ir(III) complexes has been explored. Bis[(3,5-difluorophenyl)isoquinolinyl](2,2,6,6-tetramethyl-3,5-heptanedionato) iridium(III) undergoes Pd-catalyzed C–H bond arylation with aryl bromides. The reaction regioselectively occurred at the C–H bond flanked by the two fluorine atoms of the difluoroaryl unit, and on both cyclometalated ligands. This post-functionalization gives a straightforward access to modified complexes in only one manipulation and allows to introduce thermally sensitive functional groups, such as trifluoromethyl, nitrile, benzoyl, or ester. The X-ray crystallography, photophysical, and electrochemical properties of the diarylated complexes were investigated. Whatever the nature of the incorporated substituted aryl groups is, all obtained complexes emit red phosphorescence (622–632 nm) with similar lifetimes (1.9–2 μs).

Since two decades, cyclometalated iridium(III) complexes have become one of the most studied class of luminescent metal complexes[1] for their potential applications ranging from photocatalysts[2] to luminescent chemosensors[3] as well as from new electroluminescent display materials to devices.[4] Much research aimed at developing novel Ir(III) phosphorescent complexes with excellent emission properties, in particular pure color and high luminescence quantum efficiency. These photophysical assets of Ir(III) complexes relies on a strategic molecular design and consequently on the convenient access to newly functionalized C^N-ligands, a crucial and determining step in the way to luminescent complexes. A plethora of examples of chemical modifications of 2-phenylpyridine (ppy) core by adding functional groups have been used as a tool to control the luminescence properties.[1,5] Moreover, the introduction of reactive functional groups on the cyclometalated ligands paves the way for bioimaging applications by tuning their photophysical properties and/or hooking up interactions with biological substrates.[6] The most widely used strategy for the preparation of *bis*-cyclometalated C^N-based Ir(III) complexes [Ir(C^N)$_2$(L^X)] (L^X is a monoanionic ligand), involves a multistep synthetic procedure, starting by the synthesis of the organic pro-ligands followed by their complexation using $IrCl_3.nH_2O$ as precursor (Figure 1, Pathway A). Although this conventional synthetic method provides the expected Ir(III) complexes in satisfactory reaction yields, the complexation steps often require drastic conditions, which are sometimes not compatible with some functionalities borne by the pro-ligands. An alternative approach to functionalize such species is to perform the C–C coupling directly on the complexes, using the so-called *"catalysis-on-the-complex"* (Figure 1, Pathway B). Besides expending the panel of functional groups that can be incorporated on the C^N-ligands, this post-functionalization strategy accelerates the synthesis of a library of novel metal complexes: *only three manipulations are required to prepare three complexes, where formerly six steps were necessary* (Figure 1 pathway A vs. B).

Following the seminal work of Williams on Suzuki cross-coupling reaction of bromo-functionalized (*bis*-terpyridyl) iridium(III) complexes (Figure 2A),[7] post modification Suzuki reactions have become a straightforward approach to tune the photophysical properties of the Ir(III) complexes.[8] A few examples of Suzuki cross-coupling reactions onto the ancillary ligand were also reported.[9]

Although Pd-catalyzed C–H bond arylation has emerged as a suitable alternative to Suzuki cross-couplings for the synthesis of poly(hetero)aryls –since no pre-functionalization is required-[10] their applications for catalytic C–H functionalization of cyclometalated ligands, has been barely explored. So far, only one procedure of *"catalysis-on-the-complex"* for C–H bond functionalization has been reported by some of us for the direct arylation of thienyl rings of tris-homoleptic *fac*-Ir(C^N-thpy)$_3$ [thpy = 2,2′-thienylpyridine], and bis-cyclometalated [Ir(C^N-thpy)$_2$(acac)] (acac = acetylacetonate) (Figure 2B).[11] The arylation took place regiospecifically at the C5–H bond position of the metalated thienyl rings, inducing a red-shifted of their emission wavelengths. In contrast, C–H bond arylation of metalated C-aryl ring in 2-arylpyridine-based Ir(III) complexes is not reported yet. This is probably due to the lower reactivity of

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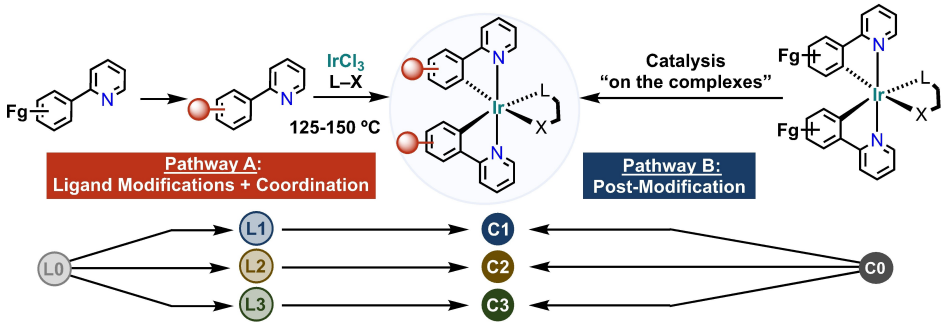

Figure 1. Different approaches to prepare functionalized Ir(III) complexes.

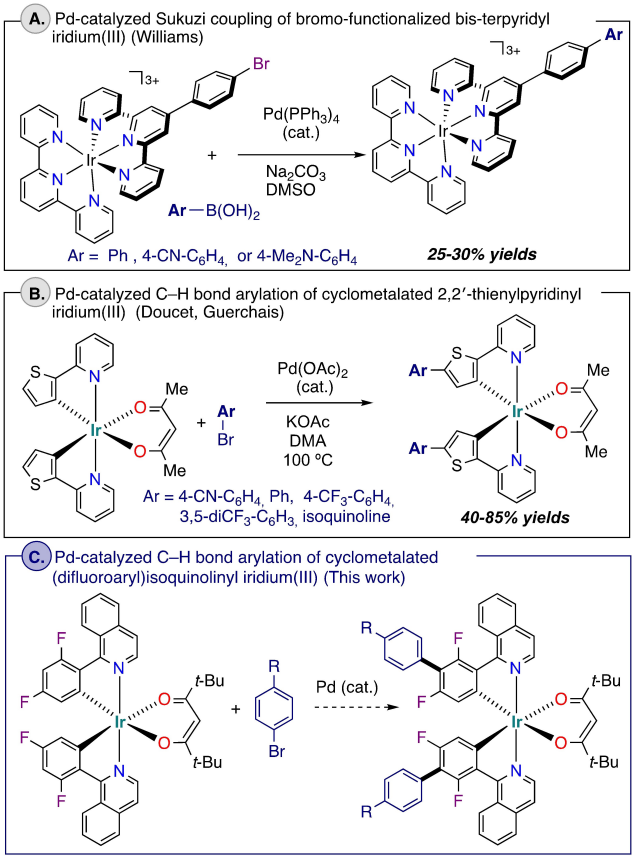

Figure 2. Pd-catalyzed arylation of cyclometalated Ir(III) complexes.

aryl C–H bond compared to heteroaryl C–H bond in Pd catalysis.[12] We have previously succeeded to perform Pd-catalyzed direct arylation of the polyfluorinated aryl unit of 2-(polyfluorophenyl)pyridine derivatives to prepare bis-cyclometalated luminescent Ir(III) complexes.[13] We showed that the incorporation of an aryl group between the two fluorine atom induces the enhancement the luminescence quantum yields of the resulting cationic Ir(III) species to near-unity. However, this synthetic approach required several manipulations to access the targeted Ir-complexes. To speed up their preparation, we decided to assess the reactivity of cyclometalated 2-arylpyridine in Pd-catalyzed C–H bond arylations (Figure 2C). Several questions remain pending about this strategy of *catalysis-on-the complex*: *i)* is the regioselectivity still driven by the F atoms or C–Ir bond will affect it? *ii)* will Ir(III) complexes be stable enough under the required catalytic reaction conditions i.e. temperature, presence of Pd catalyst, base, and additives?

Catalysis on the complex: We began our study by preparing the Ir(III) complexes **3** and **4** via reported procedures (Scheme 1).[14] Firstly, the pro-ligands 1-(2,4-difluorophenyl) isoquinoline (**1**) and 1-(3,5-difluorophenyl)isoquinoline (**2**) were obtained in 84% and 50% yields, via Suzuki coupling from the appropriate difluorinated aryl boronic acids and 2-chloroisoquinoline using 2 mol% $PdCl(C_3H_5)$(dppb) [dppb = 1,4-bis (diphenylphosphino)butane)] as catalyst in the presence of K_2CO_3 as the base in toluene-MeOH-water as a solvent mixture. Secondly, the reaction of **1** and **2** with $IrCl_3.nH_2O$ afforded the corresponding cyclometalated μ-chloro-bridged dimers, which then reacted with 2,2,6,6-tetramethylheptane-3,5-dione in the presence of a base (K_2CO_3) to produce complexes **3**[14] and **4** in 75% and 40% yield, respectively.

Having the neutral complex **3** in hands, we explored the most suitable conditions for Pd-catalyzed C–H bond arylations of the metalated difluorinated phenyl ring, namely (i) Pd-based precursors (ii) additives (ligands or bases) and (iii) solvents, using 4-bromobenzotrifluoride as the aryl source for this late-stage coupling (Table 1). The optimized conditions, namely, 4 equivalents of 4-bromobenzotrifluoride, 5 mol% $PdCl_2(CH_3CN)_2$ associated with dppb as phosphine ligand in the presence of 4 equivalents of KOPiv (KOPiv = potassium pivalate) as the base in DMA (DMA = *N*,*N*-dimethylacetamide) at 125 °C for 16 h, afforded the diarylated complex **5a** in 89% isolated yield (Table 1, entry 1). Noteworthy, a trace amount of the monoarylated complex **5b** was also detected (< 5%) by NMR spectroscopy of the crude mixture. A significant decrease in yield was observed using the stable, well-defined $PdCl(C_3H_5)$(dppb) catalyst or replacing $PdCl_2(CH_3CN)_2$ by $Pd(OAc)_2$ (Table 1, entries 2 and 3). A diphosphine ligand with a smaller bite angles, dppe (dppe = 1,2-bis(diphenylphosphino)ethane), or mono-phosphine P(2-furyl)$_3$, gave lower yields in **5a** with the additional presence of the monoarylated complex **5b** in 10–15% yield (Table 1, entries 4 and 5). When a lower amount of aryl bromide was employed, the yield of **5a** dropped without affording **5b** in a yield higher than 15% -even using only 1 equivalent of 4-

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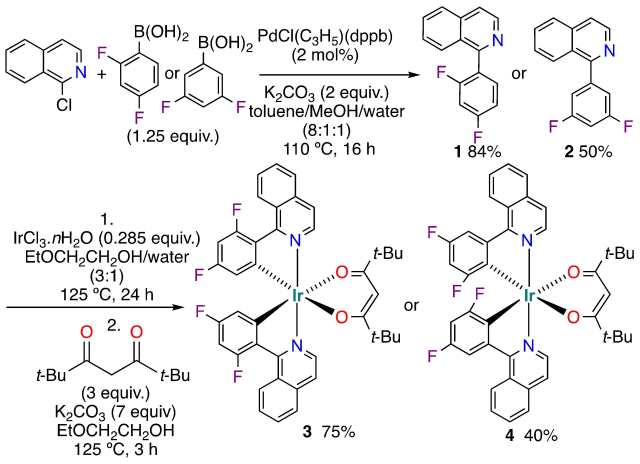
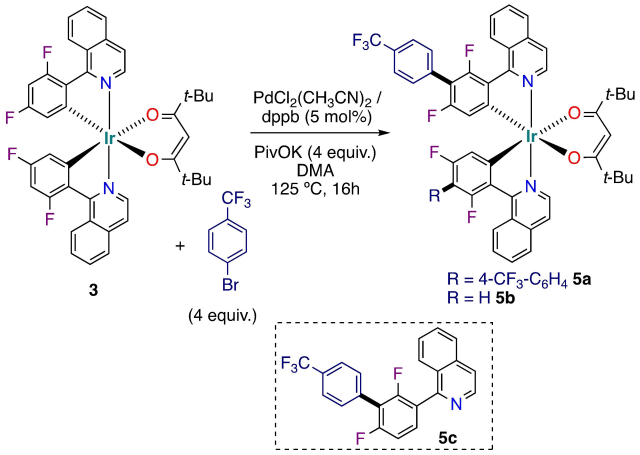


Scheme 1. Preparation of bis[2-(3,5-difluorophenyl)isoquinolinyl)](2,2,6,6-tetramethyl-3,5-heptanedionato)-Ir(III) (**3**) and bis[2-(4,6-difluorophenyl) isoquinolinyl](2,2,6,6-tetramethyl-3,5-heptanedionato)-Ir(III) (**4**).

Table 1. Control reactions of optimized conditions.



Entry	Deviation from standard conditions	Yield in **5a** [%]
1	–	89
2	$PdCl(C_3H_5)(dppb)$ as catalyst	54
3	$Pd(OAc)_2$/dppb as catalyst	62
4	dppe as ligand	28[a]
5	10 mol% tri(2-furyl)phosphine as ligand	30[a]
6	3 equiv. of ArBr	39[a]
7	1 equiv. of ArBr	24[a]
8	KOAc as base	54[a]
9	DMF as solvent	19[a]
10	NMP as solvent	28[a]
11	xylene as solvent	7[a]
12[b]	–	19[c]
13[b]	72 h	66%[c]
14[d]	–	12% (31%)[c]

[a] **5b** was also observed (< 10–15% yield). [b] reaction performed with **1** (2 equiv.) instead of **3**. [c] yield in **5c**. [d] reaction performed with **3** (1 equiv.), **1** (2 equiv.), 4-bromobenzotrifluoride (1 equiv.).

bromobenzotrifluoride, due to the formation of Ullmann-type aryl bromide homocoupling as the main side-product (Table 1, entries 6 and 7).[15] Our studies clearly show that KOPiv as base outperformed KOAc (Table 1, entry 8). Reactions carried out in other solvents than DMA such as DMF, NMP (DMF = *N*,*N*-dimethylformamide, NMP = *N*-methylpyrrolidone), or toluene gave significantly lower yields in **5a** (Table 1, entry 9–11). We also tried our optimized conditions for the C–H bond arylation of the pro-ligand **1** (Table 1, entries 12 and 13). We observed the same regioselectivity (the arylation took place at the C–H bond flanked by the two fluorine atoms while the *ortho*–*C*–H bond to the isoquinoline remains untouched). However, a longer reaction time (72 h) was required to obtain **5c** in 66% yield. We also performed a competitive reaction using 1 equivalent of 4-bromobenzotrifluoride, 1 equivalent of iridium complex **3** and 2 equivalents of proligand **1** (Table 1, entry 14). Surprisingly, the reaction was not complete and a mixture of the diarylated complex **5a** (12%) and the arylated proligand **5c** (31%) was obtained. This result suggests that the cyclometallation did not enhance the reactivity of the C–H bond but prevented the coordination of the nitrogen atom of the isoquinoline unit to Pd, which seems to deactivate the catalyst.

Kinetics studies have been performed on the reaction between complex **3** and 4-bromobenzotrifluoride (4 equivalents) in the presence of 5 mol% $PdCl_2(CH_3CN)_2$ associated with dppb using 4 equivalents of KOPiv in DMA at 125 °C (Figure 3). As expected, the reaction starts by the formation of the monoarylated complex **5b**, which is then quickly converted into the diarylated complex **5a**. The kinetic formation of **5b** shows a steady-state profile with a yield not exceeding 28%. This profile suggests that the second arylation proceed faster than the first one which might give a clue on the difficulty to obtain the mono-arylated complex **5b** in good yield.

Using these optimized reaction conditions, the direct arylation of complex **3** with 4-bromobenzonitrile, 4-bromobenzophenone, and ethyl 4-bromobenzoate was investigated in

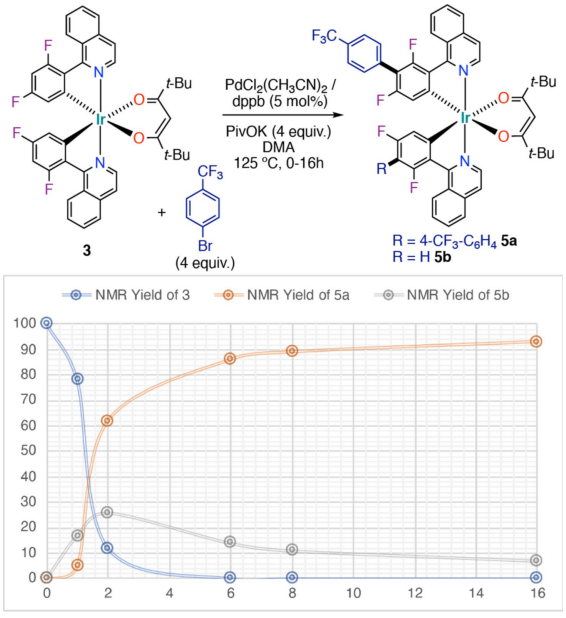


Figure 3. Kinetic profile of Pd-catalyzed C–H bond arylation of complex (**3**) with 4-bromobenzotrifluoride. ^{19}F NMR yield using fluorobenzene as internal standard.

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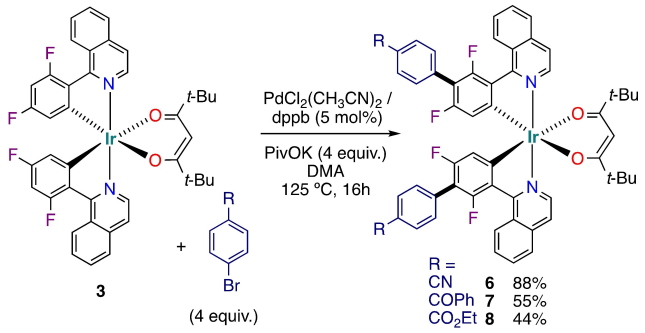
order to verify the applicability of the above method to the access to systems with sensitive functional groups (Scheme 2). In all cases, the diarylation occurred, affording the *bis*-arylated iridium complexes **6**–**8** in 88%, 55%, and 44% yield, respectively.

X-ray crystal structures: Single crystals of complexes **3**, **4**, **5a**, **7**, and **8** suitable for X-ray analysis were grown by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of the respective complexes. The X-ray crystal structures of the neutral complexes **4**, **5a**, **7**, and **8** are depicted in Figure 4. Selected bond distances and bond angles, as well as selected bite angles, are tabulated in Table S1. All neutral complexes exhibited distorted octahedral geometries, with the two C^N ligands adopting a C,C-*cis*, and *N*,*N*-*trans* configuration similar to that of the archetype complexes.[16] The Ir–C and Ir–N bond distances in all crystal structures are in the same range. The introduced aryl pendant group is not coplanar with the C^N ligand. The torsion angles between the plane of the incorporated aryl group and that of the cyclometalated phenyl ring of the two C^N ligands are 52.10(5)/43.00(6), 41.6(11)/48.1(10), and 43.4(13)/43.4(13) for **5a**, **7** and **8**, respectively. Notably, the distance between two iridium centers for adjacent complexes in the crystal packing varies slightly from 9.726 Å to 9.587 Å for the parent complexes **3** and **4**. A significant increase of Ir…Ir distance is observed of 10.088, 13.557 and 13.237 Å for the arylated complexes **5a**, **7**, and **8**, respectively. Notably, **7** exhibits the longer intermetallic distance of 13.557 Å showing the dramatic influence of the steric hindrance of the added *p*-benzophenone substituents.



Scheme 2. Post-functionalization of cyclometalated Ir(III) complex **3** via Pd-catalyzed C–H bond arylation.

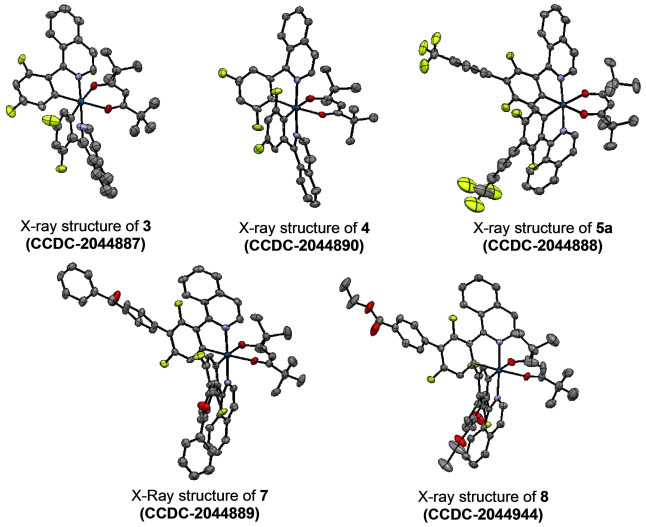


Figure 4. Solid-state structures of complexes **3**, **4**, **5a**, **7**, and **8**. hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

Electrochemical studies: Depicted in Figures S1 are cyclic voltammograms of complexes **3**–**8** recorded in deoxygenated dichloromethane with 0.1 M nBu_4NPF_6 as supporting electrolytes and with redox potentials referenced against the ferrocene/ferrocenium ($Fc^{0/+}$) oxidation couple. Complexes **3**, **4**, **5a**, **6**, and **8** show reversible oxidation waves at 0.60, 0.49, 0.63, 0.65, and 0.60 V vs. $Fc^{0/+}$, respectively, while complex **7** with a benzoyl group, exhibits a quasi-reversible oxidation wave at 0.61 V vs. $Fc^{0/+}$. These oxidation waves are negatively shifted from the Ir(III)/(IV) redox couple that is usually at around 1.0 V vs. $Fc^{0/+}$,[13b] and hence could be tentatively assigned to be the oxidation of the difluorinated 2-arylisoquinoline ligand. The oxidation couple of **3** (0.60 V) is positively shifted from that of **4** (0.49 V), which is in line with our previous report on the phenylpyridyl Ir(III) analogues[13b] and signifies the importance of the positions of the fluorine atoms, i.e. their electronic effects on the cyclometalated ligands for Ir(III) complexes. Evidently, the substituents conferred by the Pd(II)-catalyzed C–H bond arylation of the cyclometalated difluorinated 2-arylisoquinoline ligands only slightly shift the oxidation couples of **5a** and **6**–**8** for 0–0.05 V from the unsubstituted complex **3**. Among the complexes under study, **4** and **7** show identifiable but irreversible reduction wave at around 2.0 V vs. $Fc^{0/+}$, and hence the HOMO-LUMO gaps could be estimated to be around 2.6 eV, which is slightly smaller than that (2.7–2.8 eV) for the phenylpyridyl Ir(III) analogues.[13b]

Electronic absorption and emission properties: The photophysical parameters of complexes **3**–**8** are listed in Table 2, and the UV-vis absorption and emission spectra recorded in deoxygenated CH_2Cl_2 solutions are depicted in Figure 5. The salient features of the electronic absorption spectrum of these complexes are comparable to those recorded for the typical cyclometalated Ir(III) complexes.[1,2] The intense absorption bands in the 230–350 nm range could be attributed to the π-π* intraligand (IL) transitions of the difluorinated 2-arylisoquinoline ligands. The relatively weaker absorption bands in 400–500 nm

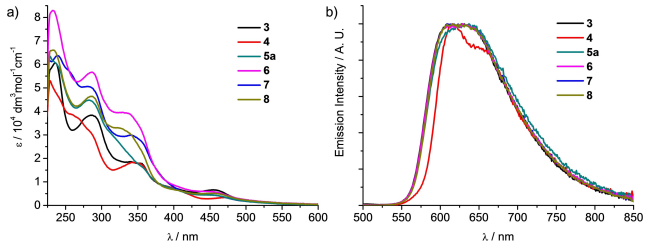


Figure 5. (a) Absorption and (b) normalized emission spectra of complexes **3**–**8** in deoxygenated CH_2Cl_2 (λ_{ex} = 365 nm, concentration ~1×10^{-5} M) at 298 K.

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Table 2. Photophysical data of complexes **3**–**8**.

Complex	Absorption[a] λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1})	Emission Medium	T [K]	λ_{max} [nm]	τ_{em} [μs]	Φ_{em}[d] [%]
3	236 (6.06), 287 (3.84), 341 (1.86), 455 (0.66)	CH_2Cl_2[b]	298	622	2.0	52
		MeTHF[c]	77	583, 625	8.4	
4	228 (5.31), 257 (3.89), 279 (sh, 3.29), 341 (1.86), 387 (0.84), 471 (0.34)	CH_2Cl_2[b]	298	616	5.0	51
		MeTHF[c]	77	591, 622	6.0	
5a	236 (6.07), 283 (4.48), 387 (sh, 0.83), 456 (0.43)	CH_2Cl_2[b]	298	632	1.9	33
		MeTHF[c]	77	596, 634	5.6	
6	233 (8.29), 287 (5.67), 333 (3.94), 449 (0.59)	CH_2Cl_2[b]	298	627	2.0	39
		MeTHF[c]	77	586, 633	5.5	
7	239 (6.37), 281 (5.06), 342 (2.98), 444 (0.45)	CH_2Cl_2[b]	298	622	1.9	34
		MeTHF[c]	77	590, 636	4.4	
8	233 (6.61), 287(4.64), 322 (3.31), 453 (0.51)	CH_2Cl_2[b]	298	627	2.0	41
		MeTHF[c]	77	586, 633	6.8	

[a] UV – vis spectra were recorded in CH_2Cl_2 at a concentration of 10^{-5} M at 298 K. [b] PL spectra, lifetimes, and quantum yields were recorded in deaerated CH_2Cl_2 solutions at a concentration of 10^{-5} M at 298 K. [c] PL spectra and lifetimes were recorded in 2-methyltetrahydrofuran at a concentration of 10^{-5} M at 77 K. [d] Absolute quantum yields measured with an integrating sphere.

range tailing beyond 550 nm could be assigned to be metal-to-ligand charge transfer ($^{1/3}$MLCT) and ligand-to-ligand charge transfer ($^{1/3}$LLCT) transitions. Notably, the lowest-energy transition of complex **4** at 471 nm is red-shifted from that of complex **3** at 455 nm, which is in line with the electrochemical study mentioned above. Again, introduction of substituents by the Pd(II)-catalyzed C–H bond arylation of the C–N-ligands impart minor effects on the low-energy transitions of the series complexes, except increased molar extinction coefficients in the UV region. The HOMO-LUMO gaps estimated from the electronic absorption spectra are around 2.6 eV (475 nm), which is coincident with the energy gap estimated from the electrochemical measurements.

Complexes **3**–**8** in deoxygenated CH_2Cl_2 solutions emit intense orange-yellow light, upon photo-excited at 350 nm. Broad emission spectra (Figure 5b) were recorded for complexes **3**, **5a**, and **6**–**8** with emission maxima, quantum yields, and lifetimes of 622–627 nm, 33–52%, and 1.9–2.0 μs, respectively, which are slightly red-shifted, but comparable with the parameters recorded with the mono-fluorinated parent complex [IrC^N-pic-F)$_2$(acac)] (emission maximum at 600 nm in CH_2Cl_2 with quantum yield and lifetime of 33% and 1.2 μs, respectively).[17] As previously reported, the incorporation of aryl groups has no significant impact on the emission wavelength.[13] Complex **4** with F-substituents at 3,5-positions shows emission maximum at 616 nm but with a vibronically structured emission profile. The excitation spectrum (Figure S2) monitored at the emission maximum for each of the complexes are identical to their respective absorption spectrum, indicating that the emissions essentially came from the cyclometalated Ir(III) complexes. Interestingly, all these complexes under study show similar structured emission spectra (Figure S3) in the 77 K glassy 2-methyltetrahydrofuran solutions with peak maximum around 590/630 nm and lifetimes in the 4.4–8.4 μs, implying that the emission could be the same parentage most likely due to the difluorinated 2-arylisoquinoline ligands with little contribution from the metal and the aryl-substituents on the difluorinated phenyl-group.

In summary, Pd-catalyzed C–H bond arylation was successfully applied to the cyclometalated 2-(3,5-difluorophenyl) isoquinoline of neutral heteroleptic Ir(III) complexes giving rise to aryl-substituted complexes in good to excellent yields. The arylation regioselectively occurred at the C–H bond of the 3,5-difluorophenyl ring flanked by two fluorine atoms with a good functional group tolerance (i.e, trifluoromethyl, cyano, ketone, or ester). The arylation of the cyclometalated ligand seems to proceed faster than on the proligand due to the absence of interactions between the nitrogen atom of the isoquinoline unit and Pd complex. The introduced pendent aryl groups have a negligible impact on the emission properties, all post-functionalized complexes remain good red emitters. In addition, the incorporation of these aryl unit increases the intermetallic Ir···Ir distance (up to 3.8 Å) between two adjacent complexes in the crystal packing, an important parameter to reduce intermolecular quenching in optoelectronic devices. This *catalysis-on-the-complex* strategy based on aryl C–H bond arylation simplifies and opens new chemical space to design cyclometalated Ir(III) complexes featuring target functions that are essential for their applications in material science and biology especially for the chemical modulation of biological properties of metal complexes.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · post-synthetic modifications · iridium · luminescence · red emitters

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[18] Deposition numbers 2044887 (for **3**), 2044890 (for **4**), 2044888 (for **5a**), 2044889 (for **7**), 2044944 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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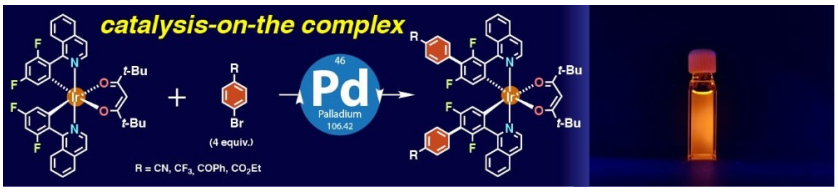

Catalysis-on-the-complex was developed to incorporate diversely substituted aryl group on the ligands of neutral cyclometalated Ir(III) complexes. The regioselectivity of Pd-catalyzed C–H bond arylation is not affected by C–Ir bond, as the reaction occurred at the C–H bond flanked by the two-fluorine atoms. All post-functionalized Ir(III) exhibit red phosphorescence with moderate to good efficiency.

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