ORGANOMETALLICS

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Soluble Phosphorescent Iridium(III) Complexes from *Cinchonine*-Derived Ligands

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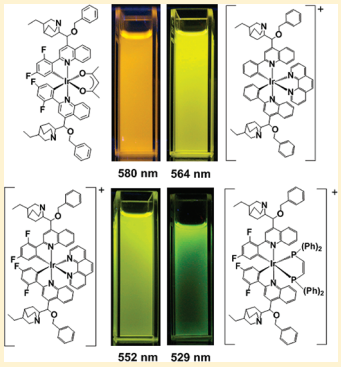
Supporting Information

ABSTRACT: *Cinchonine*-derived complexes Ir(**L2**)$_2$(acac) (**3**), Ir(**L2**)$_2$(dbm) (**4**), [Ir(**L1**)$_2$(bipy)][PF$_6$] (**5**), [Ir(**L1**)$_2$(phen)][PF$_6$] (**6**), [Ir(**L1**)$_2$(dppe)][PF$_6$] (**7**), [Ir(**L2**)$_2$(bipy)][PF$_6$] (**8**), [Ir(**L2**)$_2$(phen)][PF$_6$] (**9**), and [Ir(**L2**)$_2$(dppe)][PF$_6$] (**10**) (**L1** = 2′-phenyl-9-*O*-benzyl-10,11-dihydrocinchonine-*N*,*C*; **L2** = 2′-(2,4-difluorophenyl)-9-*O*-benzyl-10,11-dihydrocinchonine-*N*,*C*; acac = acetylacetonate; dbm = dibenzoylmethane; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; dppe = (*Z*)-1,2-bis(diphenylphosphino)ethene) are highly soluble in common organic solvents and phosphoresce with emission wavelengths from orange to green (583−529 nm) and internal quantum efficiencies from 4 to 24%. The emission is blue-shifted for the neutral auxiliary ligands and/or by incorporation of fluorine into the alkaloid-based chromophore. An unprecedented regiospecific monohydrodefluorination of **L2**, giving 2′-(4-fluorophenyl)-9-*O*-benzyl-10,11-dihydrocinchonine (**L2′**), occurred during the synthesis of **3** and **4**.

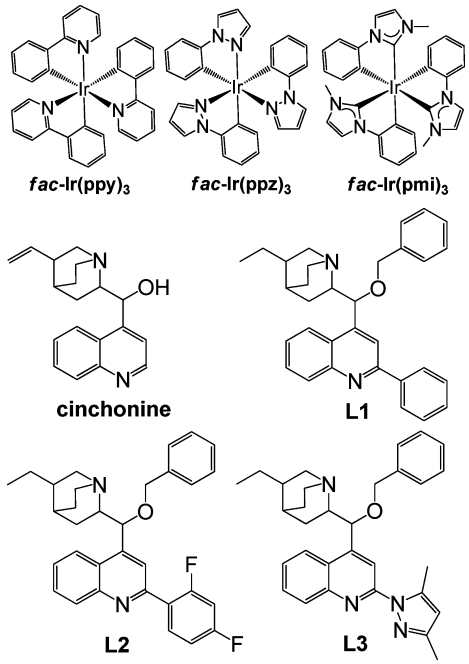


INTRODUCTION

Third-row transition metal based phosphors have been developed for organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) because of the spin−orbit interaction that allows spin-forbidden electronic transitions and thereby higher quantum efficiencies in these organometallic complexes.[1−3] Well-studied examples include Ir(ppy)$_3$ (ppy = 2-phenylpyridinato-C_2,N), Ir(ppz)$_3$ (ppz = 1-phenylpyrazolato-N,$C^{2'}$), and Ir(pmi)$_3$ (pmi = 1-phenyl-3-methylimidazolin-2-ylidene-C,$C^{2'}$) (Chart 1) and their derivatives, which exhibit a wide range of emission colors. Ligands with dendritic peripheries reduce triplet−triplet annihilation of the emissive iridium cores, improve processability, and avoid the necessity of a polymer host.[1d,4,5] We have recently reported that, with relatively straightforward synthetic modifications, *Cinchona* alkaloid derivatives (Chart 1) function as novel cyclometalating and coordinating ligands for phosphorescent iridium complexes.[6] The bulky 1-azabicyclo[2.2.2]octane and benzyl moieties impart higher quantum efficiencies to the resulting bis-cyclometalated complexes relative to simple quinoline congeners, thereby serving a similar, albeit reduced, function relative to more elaborate dendritic ligands.[4,5]

In an attempt to improve solubility and broaden the range of emissive wavelengths of these compounds, we have prepared the dinuclear complexes [Ir(**L1**)$_2$Cl]$_2$ (**1**) and fluorinated analogue [Ir(**L2**)$_2$Cl]$_2$ (**2**) and reacted them with a series of neutral and anionic auxiliary ligands to yield the corresponding cationic and neutral heteroleptic mononuclear complexes. In some cases the reaction of these alkaloid-based complexes leads

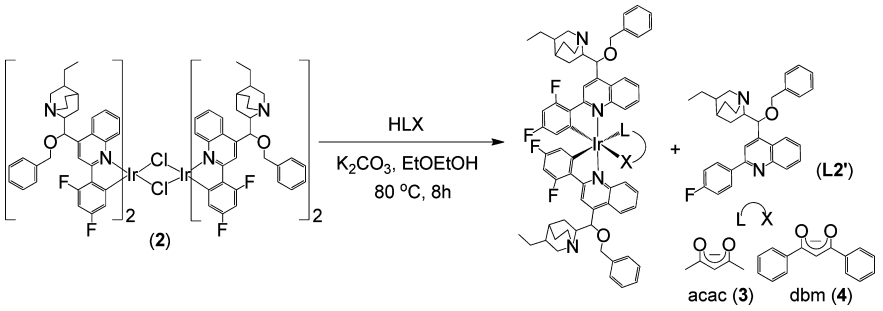
Chart 1



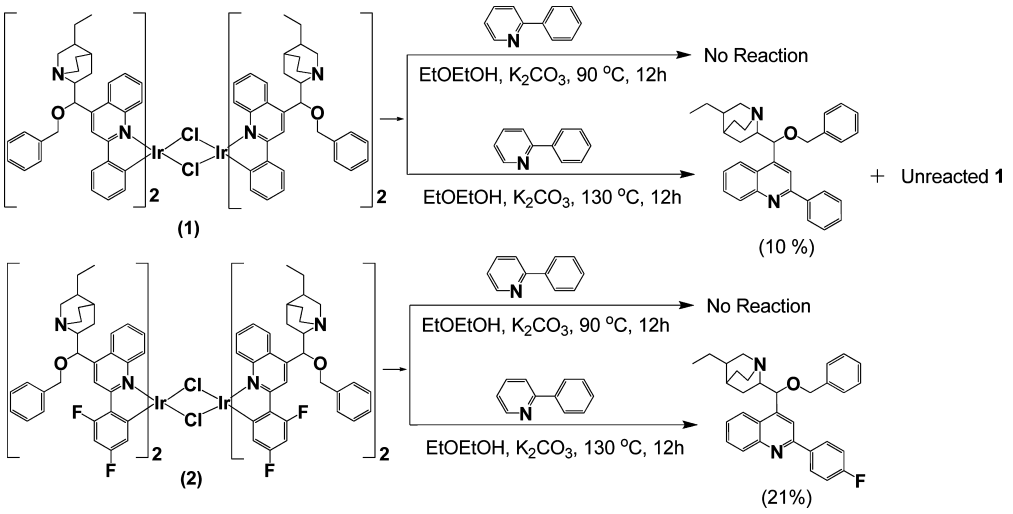
Received: August 13, 2011
Published: December 30, 2011

   dx.doi.org/10.1021/om200759d | *Organometallics* 2012, 31, 553−559

Scheme 1. Synthesis of Complexes 3 and 4



Scheme 2. Reaction of 1 and 2 with 2-Phenylpyridine (ppy)



to an unexpected hydrodefluorination. Herein we report the improved solubility and blue shift of emission for a series of eight new *Cinchonine*-based mononuclear Ir(III) complexes.

RESULTS AND DISCUSSION

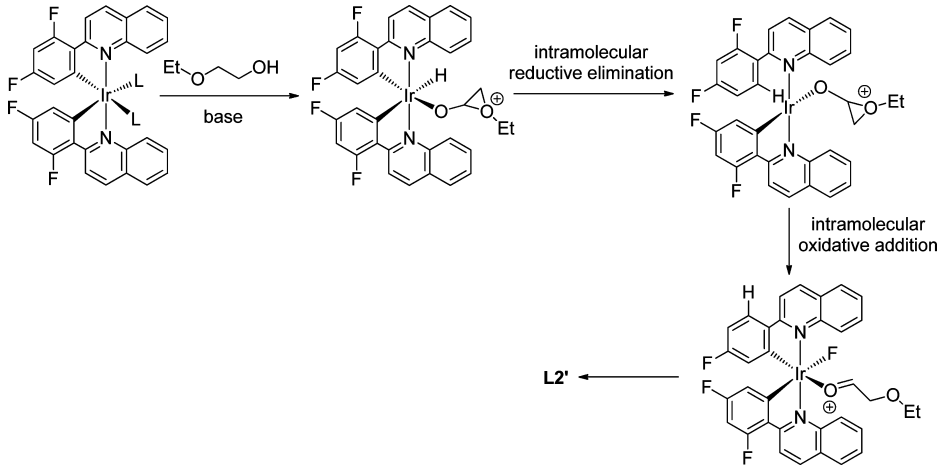
Dinuclear complexes **1** and **2** were synthesized by the well-established Nonoyama method[7] of heating a mixture of $IrCl_3 \cdot xH_2O$ with 3 equiv of **L1** or **L2** in 2-ethoxyethanol/water (3/1 v/v) under an inert atmosphere. During the preparation of **2**, a trace amount of a hydrodefluorinated Ir(III) complex was also observed in the ESI mass spectrum. A molecular ion of m/z 1169.5 corresponds to the substitution of a proton for one fluorine atom in $[Ir(\mathbf{L2})_2]^+$ (m/z 1187.5). The facile reaction of **1** and ancillary ligands acetylacetone (acacH) and dibenzoylmethane (dbm) in the presence of base yielded the two targeted neutral complexes $Ir(\mathbf{L1})_2$(acac) and $Ir(\mathbf{L1})_2$(dbm) in high yield.[6] Analogous reactions of **2** also yielded the target complexes $Ir(\mathbf{L2})_2$(acac) (**3**) and $Ir(\mathbf{L2})_2$(dbm) (**4**) (Scheme 1). In the preparation of **3** and **4**, however, the regiospecific formation of the hydrodefluorinated ligand 2′-(4-fluorophenyl)-9-*O*-benzyl-10,11-dihydrocinchonine (**L2′**) was observed as a side product (Scheme 1). The proportion of **L2′** correlated with the reaction temperature. At an elevated temperature of 120 °C, **L2′** was isolated in ca. 20% yield for both reactions, while **3** and **4** were only formed in trace amounts. However, at 80 °C, complexes **3** and **4** were isolated in moderate yield (58% and 45%, respectively).

Motivated by these observations, we further scrutinized the reactivity of **1** and **2** toward 2-phenylpyridine (ppy), which is often utilized to form cyclometalated Ir(III) complexes. Heating a mixture of **1**, ppy, and K_2CO_3 in 2-ethoxyethanol at 90 °C for 12 h resulted in none of the anticipated product with ca. 90% of the starting material recycled (Scheme 2). At a higher temperature (130 °C), the starting material **1** partially decomposed and liberated the free ligand **L1** (Scheme 2). The corresponding reaction of **2** with ppy at 90 °C also resulted in none of the expected product. However, when the reaction was carried out at 130 °C, **L2′** was formed in 21% isolated yield and the liberation of **L2** was not observed (Scheme 2). The formation of mixed-chelate complexes **3** and **4** (Scheme 1) is driven by displacement of HCl and stable chelate formation. The absence of $[Ir(\mathbf{L})_2(ppy)]$ (L = **L1**, **L2**) can be explained by the nature of ppy, which is a monodentate ligand but can serve as a chelating ligand upon an energetically demanding C−H activation.

More interestingly, however, is the regiospecific monohydrodefluorination of coordinated **L2** to **L2′** (Scheme 1). The C−F bond is the strongest single bond connected to carbon,[8] and dehydrofluorination[9] usually requires either a reactive substrate[10] and/or a highly reducing, electron-rich metal (e.g. low-valent niobium[11]) reacting through an oxidative-addition or a single-electron-transfer step or a Lewis acid abstraction of fluoride by a highly electrophilic silylium cation.[12] The iridium(I)-mediated cleavage of hexafluorobenzene with $(Et_3P)_3IrMe$ to yield the unusual $(Et_2FP)(Et_3P)_2IrC_6F_5$ with evolution of methane most likely proceeds via an electron-transfer process.[13] We are unaware of any reports of Ir(III)-mediated hydrodefluorination, although a Rh(III) catalyst generated from $[(Cy_3P)_2Rh(H)Cl_2]$, molecular hydrogen, and base (in the absence of oxygen) efficiently hydrodefluorinates

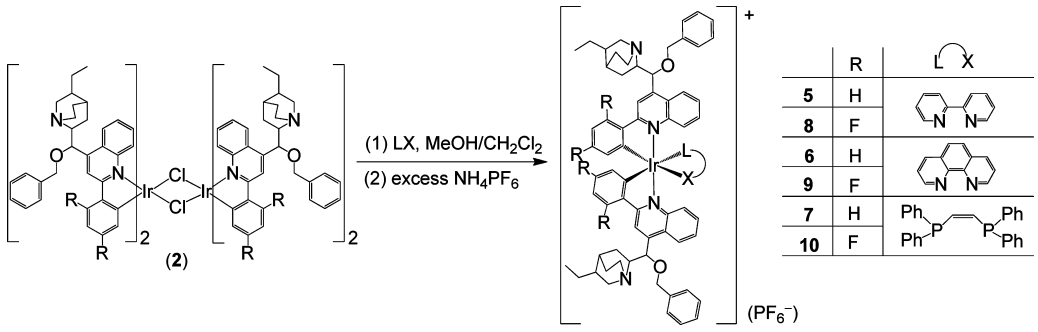
dx.doi.org/10.1021/om200759d | *Organometallics* 2012, 31, 553−559

Scheme 3. Proposed Hydrodefluorination Mechanism[a]



[a]The quinuclidine moiety on C4 is omitted for clarity.

Scheme 4. Synthesis of Complexes 5−10



some unreactive monofluoroarenes such as 1-fluoronaphthalene to yield naphthalene.[14] A possible mechanism in the present case is the formation of a hydrido iridium species by hydrogen transfer[15] from solvent (ethoxyethanol) followed by reductive elimination and iridium insertion into the C−F bond of the cyclometalated ligand (Scheme 3).

Treatment of **1** or **2** with the neutral chelating ligands 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and (*Z*)-1,2-bis(diphenylphosphino)ethene (dppe) in refluxing CH_2Cl_2/MeOH (2/1 v/v) followed by anion exchange with excess NH_4PF_6 at room temperature yielded the six ionic complexes $[Ir(\mathbf{L1})_2(bipy)][PF_6]$ (**5**), $[Ir(\mathbf{L1})_2(phen)][PF_6]$ (**6**), $[Ir(\mathbf{L1})_2(dppe)][PF_6]$ (**7**), $[Ir(\mathbf{L2})_2(bipy)][PF_6]$ (**8**), $[Ir(\mathbf{L2})_2(phen)][PF_6]$ (**9**), and $[Ir(\mathbf{L2})_2(dppe)][PF_6]$ (**10**), which were separated by chromatography on neutral alumina in moderate to high yields (Scheme 4).

These complexes (**3**−**10**) are highly soluble in CH_2Cl_2, DMF, and DMSO and readily soluble in $CHCl_3$, MeCN, MeOH, and toluene. Molecular ions $[M + H]^+$ (neutral complexes) and $[M - PF_6]^+$ (charged complexes) were observed in the ESI mass spectra at *m*/*z* 1286.9 (**3**), 1411.1 (**4**), 1271.5 (**5**), 1295.5 (**6**), 1511.4 (**7**), 1343.4 (**8**), 1367.5 (**9**), and 1583.5 (**10**). The corresponding cationic fragments $[Ir(\mathbf{L1})_2]^+$ and $[Ir(\mathbf{L2})_2]^+$ (**3**−**10**) and dicationic species $[M + 2H]^{2+}$ (**3**, **4**) and $[Ir(\mathbf{L1})_2 + H]^{2+}$ and $[Ir(\mathbf{L2})_2 + H]^{2+}$ (**5**−**10**) were also observed. ^1H and ^{13}C NMR spectra for these complexes were rather complex, but the protons ortho to the cyclometalated carbon appeared characteristically at ca. 6.5 ppm.[16] Complexes **3**−**10** were further characterized by FT-IR spectra and their bulk purity confirmed by elemental analysis.

The UV−vis absorption and emission data for complexes **3**−**10** are given in Figures 1−3 and Table 1. The intense bands in

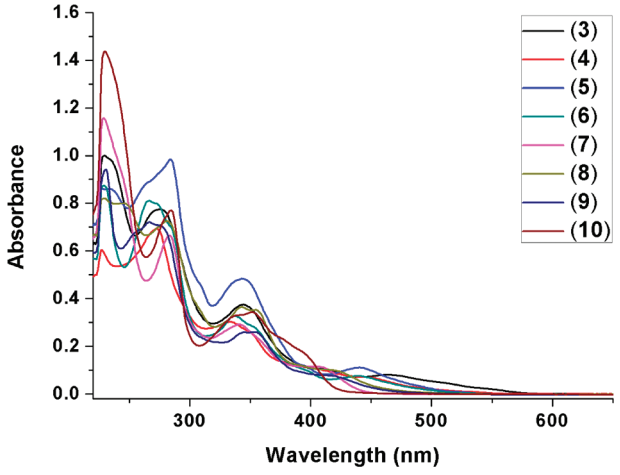


Figure 1. UV−vis spectra of **3**−**10** recorded in degassed CH_2Cl_2 solutions at room temperature.

the UV−vis spectra for all complexes in the high-energy portion of the spectra between 230 and 350 nm can be assigned to the spin-allowed $^1(\pi-\pi^*)$ ligand transition. The weaker, low-energy bands at wavelengths longer than 440 nm suggests substantial mixing of spin-forbidden ^{3}MLCT and higher lying

dx.doi.org/10.1021/om200759d | *Organometallics* 2012, 31, 553−559

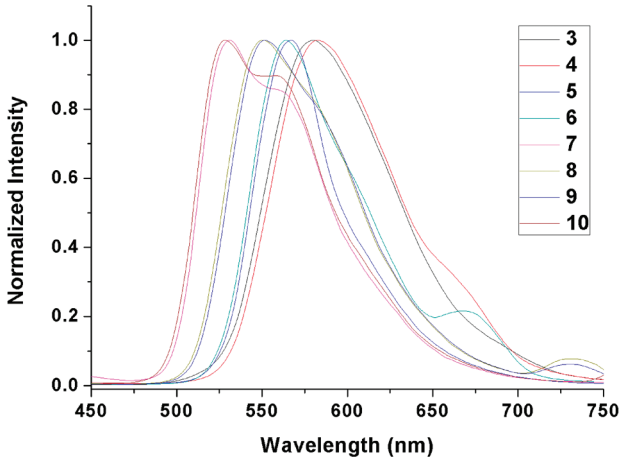


Figure 2. Normalized luminescence spectra of **3**–**10** recorded in degassed CH_2Cl_2 solutions at room temperature.

^{1}MLCT transitions facilitated by the strong spin–orbit coupling of the Ir(III) center.[17]

Complexes **3**–**10** give emissions in a broad color range from green (529 nm, **10**) to orange-red (583 nm, **4**) (Figure 3) with phosphorescence quantum yields between 0.04 and 0.24 and lifetimes in the range 0.26–0.73 μs. The quantum yields for these complexes are relatively low compared to those of well-established examples such as Ir(ppy)$_2$(acac) (0.34, 2-MeTHF solution, room temperature),[17a] *fac*-Ir(ppy)$_3$ (0.40, 2-MeTHF solution, room temperature),[17b] [(dfbmb)$_2$Ir(fptz)] (0.73, CH_2Cl_2, room temperature; dfbmb = 1-(2,4-difluorobenzyl)-3-methylbenzimidazolium; fptz = 2-(5-(trifluoromethyl)-2*H*-1,2,4-triazol-3-yl)pyridine),[17e] and the dendrimer complex *fac*-tris[1-methyl-5-(4-fluorophenyl)-3-*n*-propyl-1*H*-[1,2,4]-triazolyl]iridium(III) (0.94, toluene, room temperature).[4b] The lifetimes of complexes **3**–**10** are, however, very short and are similar to those found in *mer*-Ir(ppy)$_3$ (0.15 μs, CH_2Cl_2, room temperature),[17b] *mer*-Ir(46dfppy)$_3$ (0.21 μs, CH_2Cl_2, room temperature; 46dfppy = 2-(4,6-difluorophenyl)pyridinato-*N*,$C^{2'}$),[17b] *fac*-Ir(tiq)$_3$ (0.74 μs, toluene, room temperature; tiq = 1-thiophen-2-ylisoquinolinato-C^3,*N*),[17c] and [(dfbmb)$_2$Ir-(fptz)] (0.38 μs, CH_2Cl_2, room temperature)[17e] and are shorter than those of *fac*-tris[1-methyl-5-(4-fluorophenyl)-3-*n*-propyl-1*H*-[1,2,4]triazolyl]iridium(III) (3.6 μs, toluene, room temperature),[4b] and *fac*-tris[5-(4-fluorophenyl)-1-methyl-3-propyl-[1,2,4]-triazolyl]iridium(III) (1.25 μs, toluene, room temperature).[4g]

Table 1. Photophysical Data for 3–10 in Degassed CH_2Cl_2 at Room Temperature

	UV–vis (nm) (ε, 10^3 L mol^{-1} cm^{-1})	λ_{max} (nm)	Φ^a	τ (μs)
3	228 (100.0), 277 (98.6), 345 (40.9), 411 (12.4), 469 (8.5)	580	0.10	0.30
4	226 (68.0), 272 (86.0), 334 (37.4), 451 (8.6), 483 (3.9)	583	0.05	0.26
5	233 (81.1), 284 (92.9), 344 (36.4), 422 (45.6)	567	0.23	0.63
6	228 (83.7), 268 (77.5), 338 (31.4), 442 (7.1)	564	0.24	0.46
7	227 (106.0), 282 (61.3), 341 (27.1), 408 (10.9)	531	0.04	0.73
8	228 (61.6), 249 (61.3), 283 (56.1), 343 (28.5), 426 (7.4)	551	0.14	0.38
9	229 (65.3), 267 (47.9), 353 (17.8), 423 (5.5)	552	0.13	0.43
10	229 (87.5), 284 (46.9), 351 (21.1), 398 (9.7)	529	0.04	0.53

^{a}With respect to Rhodamine 6G (Φ = 0.95 in ethanol).

The introduction of two fluorine atoms on the 2,4-position of the phenyl ring stabilizes the energy of the HOMO orbitals, resulting in a blue shift of **3** (580 nm) and **4** (583 nm) compared to Ir(**L1**)$_2$(acac) (597 nm) and Ir(**L1**)$_2$(dbm) (608 nm).[6] The triplet energy levels of the acac of complex **3** lie above the energies of **L2** and MLCT excited states, and the luminescence is thus dominated by **L2** and MLCT transitions. The slightly longer emission wavelength and relatively low quantum efficiency of complex **4** can be attributed to the lower triplet-state energy of dbm relative to **L2** or the ^{1}MLCT in this complex. The emission wavelengths of **5** (567 nm) and **6** (564 nm) are further blue-shifted relative to those of **3** and **4**, suggesting that, for these cationic Ir(III) complexes, the HOMO consists mainly of a mixture of Ir d and phenyl π orbitals, while the LUMO has significant chelating ligand character. Such an explanation is further supported by the observation that using the higher triplet energy dppe as the chelating ligand results in a more significant blue shift to 531 nm (**7**). Not surprisingly, the use of auxiliary ligands bipy and phen in complexes **5** and **6** resulted in similar emission wavelengths and quantum yields. The contribution of two fluorine atoms at the 2,4-position of the phenyl ring blue-shifted the phosphorescence wavelength by 2–16 nm (Table 1).

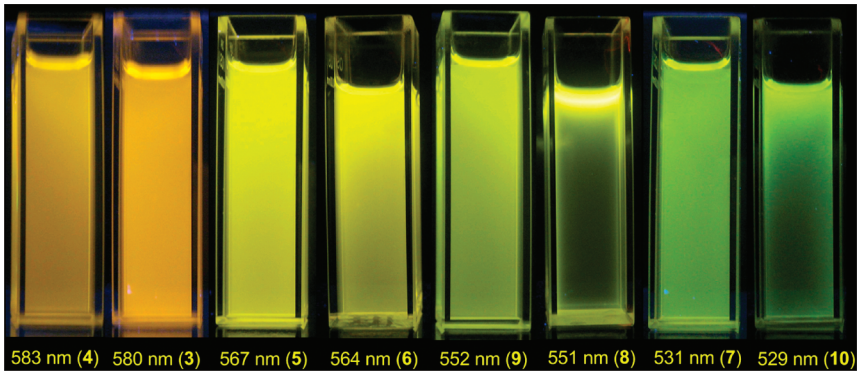


Figure 3. Emission of **3**–**10** recorded in degassed CH_2Cl_2 solutions at room temperature excited at 365 nm.

dx.doi.org/10.1021/om200759d | *Organometallics* 2012, 31, 553–559

CONCLUSION

We have prepared two neutral and six ionic Ir(III) phosphorescent complexes from alkaloid-derived ligands. These complexes phosphoresce at wavelengths from orange to green with internal quantum efficiencies from 0.04 to 0.24. The extra functionality of the natural products enables the resultant cationic complexes to be dissolved in a range of common organic solvents. In this respect, it serves a similar function to the elaborate dendrimer architectures of Burn and co-workers.[4] This enhanced solubility has prompted us to investigate their potential advantages in device fabrication. The unusual regiospecific monohydrodefluorination suggests the possibility of Ir(III)-catalyzed C−F activation, and we are investigating the mechanism and scope of this reaction.

EXPERIMENTAL SECTION

All synthetic procedures involving $IrCl_3{\cdot}xH_2O$ and other Ir(III) species were carried out in the dark and under a N_2 atmosphere using standard Schlenk techniques. Elemental analyses were performed on a Perkin−Elmer PE 2400 CHNS Elemental Analyzer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 500 MHz spectrometer, and their chemical shifts were referenced to Me_4Si (TMS). The ^{19}F NMR spectra were recorded on a Bruker ACF 300 spectrometer. IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer using KBr pellets. UV−vis spectra were recorded on a UVIKON spectrometer. Electrospray mass spectra were obtained in positive ion mode with a Finnigan/MAT LCQ mass spectrometer. Peaks were assigned from the m/z values and the isotope distribution patterns. Photoluminescence was measured using a Perkin-Elmer LS55 luminescence spectrometer, and the quantum yield was determined using Rhodamine 6G (quantum yield 0.96 in ethanol) as reference.[18] The phosphorescence lifetime was measured using an Edinburgh FL920P Lifetime Spectrometer.

Synthesis of 3. A mixture of **2** (0.25 g, 0.1 mmol), acetylacetone (0.025 g, 0.25 mmol), and K_2CO_3 (0.14 g, 1 mmol) were dissolved in 2-ethoxyethanol (5 mL), which was then degassed, flushed three times with N_2, and heated to 80 °C for 8 h. The mixture was then cooled to room temperature, the solvent was removed in vacuo, and CH_2Cl_2 (50 mL) was added. The organic phase was washed with brine (3 × 50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the crude product was dried under vacuum and purified by chromatography on a neutral Al_2O_3 column using ethyl acetate/MeOH (10/1 v/v) as eluent to give an orange-red solid (**3**). Yield: 0.15 g (58% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.69 (br, 1H), 8.62 (br, 1H), 8.38−8.41 (m, 2H), 8.20−8.34 (m, 3H), 7.36−7.62 (m, 18H), 6.53−6.58 (m, 2H), 6.15−6.17 (m, 2H), 5.48 (br, 1H), 4.49−4.74 (m, 6H), 3.34−3.38 (m, 1H), 3.19−3.20 (m, 1H), 2.65−3.01 (m, 11H), 1.98−2.12 (m, 5H), 1.75−1.79 (m, 3H), 1.31−1.64 (m, 28H), 0.91−0.95 (m, 10H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 186.1, 185.9, 166.8, 163.3 (d, J_{C-F} = 15.0 Hz), 162.7 (d, J_{C-F} = 13.9 Hz), 161.3 (d, J_{C-F} = 15.2 Hz), 160.6 (d, J_{C-F} = 14.1 Hz), 153.4, 153.4, 153.3, 150.5, 150.2, 148.8, 148.7, 137.9, 131.7, 131.7, 130.2, 130.1, 128.3, 128.3, 128.1, 127.8, 127.8, 126.8, 126.8, 126.3, 126.2, 125.5, 123.6, 118.1, 118.1, 117.9, 100.1, 100.0, 97.8, 97.6, 97.4, 71.9, 71.6, 61.4, 61.1, 50.9, 50.7, 50.1, 50.0, 37.7, 37.6, 27.8, 27.7, 27.5, 27.5, 26.6, 26.5, 25.4, 25.3, 11.8 ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ −34.14 ppm. MS (ESI; CH_2Cl_2, 180 °C): m/z 644.2 $[M + 2H]^{2+}$; 1187.5 $[Ir(\mathbf{L2})_2]^+$; 1286.9 $[M + H]^+$. Anal. Calcd for $C_{69}H_{69}F_4IrN_4O_4$: C, 64.42; H, 5.41; N, 4.35. Found: C, 63.76; H, 5.89; N, 4.03. IR (KBr pellet): 3067 (w), 3030 (w), 2932 (s), 2865 (m), 2038 (w), 1599 (s), 1581 (s), 1543 (m), 1516 (m), 1499 (w), 1453 (m), 1397 (m), 1360 (w), 1325 (w), 1287 (w), 1250 (w), 1201 (w), 1158 (m), 1104 (s), 1067 (w), 1042 (w), 1025 (w), 988 (s), 935 (w), 853 (m), 833 (m), 760 (m), 698 (m), 611 (w), 588 (w), 530 (w), 519 (w), 497 (w), 424 (w) cm^{-1}.

Characterization data for **L2′** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.2 Hz, 1H), 8.15−8.18 (m, 2H), 7.97 (s, 1H), 7.72−7.75 (m, 1H), 7.54−7.58 (m, 1H), 7.35−7.38 (m, 4H), 7.30−7.33 (m, 1H), 7.19−7.22 (m, 2H), 5.40 (br, 1H), 4.46−4.52 (AB quartet, 2H), 3.47−3.73 (m, 1H), 3.06−3.10 (m, 2H), 2.88−2.93 (m, 1H), 2.81−2.85 (m, 1H), 2.69−2.75 (m, 1H), 2.07−2.12 (m, 1H), 1.69 (br, 1H), 1.40−1.50 (m, 5H), 1.20−1.29 (m, 3H), 0.89 (t, J = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 164.8, 162.8, 155.9, 148.8, 147.5, 138.0, 136.0, 136.0, 130.7, 129.5, 129.4, 129.4, 128.5, 128.3, 128.0, 127.9, 127.8, 126.4, 125.6, 123.1, 115.8, 115.7, 71.7, 60.7, 51.1, 50.3, 37.6, 27.4, 26.5, 25.4, 12.0 ppm. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ −36.4 ppm. MS (ESI): m/z 481.3 $[M + H]^+$.

Synthesis of 4. Complex **4** was synthesized using the same procedure described for **3**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate as eluent. Yield: 0.13 g (45% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.71−8.75 (m, 2H), 8.47−8.48 (m, 2H), 8.12 (br, 2H), 7.15−7.50 (m, 25H), 6.59−6.64 (m, 2H), 6.27−6.29 (m, 1H), 5.91−5.94 (m, 1H), 5.34−5.42 (m, 3H), 4.28−4.63 (m, 5H), 2.61−3.25 (m, 11H), 1.97−2.19 (m, 3H), 1.77 (br, 1H), 1.12−1.63 (m, 25H), 0.90−0.97 (m, 12H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 180.9, 180.6, 166.7 (m), 163.4, 163.3, 162.9, 162.8, 161.4, 161.3, 160.8, 160.7, 153.6, 153.5, 150.7, 150.2, 148.8, 148.7, 140.5, 140.4, 138.0, 131.7, 130.2, 130.2, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.7, 126.9, 127.4, 126.3, 126.1, 125.1, 123.7, 117.9 (br), 97.7, 94.6, 71.9, 71.4, 61.4, 60.9, 50.9, 50.1, 50.0, 37.7, 37.7, 29.7, 27.4, 26.7, 26.6, 25.3, 11.8 ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ −34.3 to −34.2 (m) ppm. MS (ESI): m/z 706.5 $[M + 2H]^{2+}$; 1187.5 $[Ir(\mathbf{L2})_2]^+$; 1411.1 $[M + H]^+$. Anal. Calcd for $C_{79}H_{73}F_4IrN_4O_4$: C, 67.26; H, 5.22; N, 3.97. Found: C, 67.14; H, 5.34; N, 3.73. IR (KBr pellet): 3063 (w), 2955 (m), 2932 (m), 2869 (w), 2037 (m), 1598 (s), 1575 (m), 1544 (m), 1518 (w), 1455 (w), 1424 (w), 1402 (w), 1359 (w), 1326 (w), 1287 (w), 1251 (w), 1199 (w), 1159 (w), 1106 (m), 1059 (w), 1024 (w), 988 (m), 936 (w), 839 (m), 758 (m), 699 (m), 611 (w), 529 (w) cm^{-1}.

Synthesis of 5. A mixture of **1** (0.23 g, 0.1 mmol) and 2,2′-bipyridine (0.032 g, 0.21 mmol) in a double-necked flask was flushed three times with N_2. A CH_2Cl_2/MeOH mixture (20 mL/10 mL) was added under N_2, and the mixture was heated to reflux for 12 h. The mixture was cooled to room temperature, and NH_4PF_6 (0.16 g, 1.0 mmol) in MeOH (5 mL) was added under N_2. The mixture was stirred for another 5 h and the solvent evaporated. The resulting orange-red residue was dried under vacuum, and CH_2Cl_2 (5 mL) was added. NH_4Cl was removed by filtration. The solvent was removed and the product purified by chromatography on neutral Al_2O_3 column using ethyl acetate/MeOH (30/1 v/v) as eluent to give an orange-red solid. Yield: 0.18 g (63.5% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.26−8.34 (m, 2H), 8.01−8.13 (m, 3H), 7.91−7.94 (m, 1H), 7.36−7.46 (m, 8H), 7.23−7.27 (m, 1H), 6.98−7.03 (m, 1H), 6.91−6.94 (m, 1H), 6.69−6.73 (m, 1H), 5.36 (s, 1H), 4.54−4.59 (m, 1H), 4.38−4.45 (m, 1H), 3.00−3.01 (m, 1H), 2.74−2.88 (m, 2H), 2.61−2.64 (m, 2H), 1.96−2.00 (m, 1H), 1.76−1.78 (m, 2H), 1.45−1.52 (m, 5H), 1.25−1.31 (m, 2H), 0.91−0.97 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 169.0, 155.5, 152.1, 152.0, 150.5, 150.4, 147.7, 147.6, 147.3, 146.0, 139.1, 137.7, 134.8, 134.8, 130.6, 130.3, 130.3, 128.5, 128.2, 128.0, 127.9, 127.4, 127.1, 126.6, 125.6, 125.5, 124.9, 124.7, 123.8, 123.7, 123.0, 72.2, 71.7, 61.6, 61.6, 50.9, 50.9, 50.1, 49.9, 37.6, 37.5, 27.4, 27.4, 26.4, 26.4, 25.4, 25.3, 11.8 ppm. MS (ESI; CH_2Cl_2, 180 °C): m/z 558 $[Ir(\mathbf{L1})_2 + H]^{2+}$; 636.6 $[Ir(\mathbf{L1})_2(bipy) + H]^{2+}$; 1115.6 $[Ir(\mathbf{L1})_2]^+$; 1271.5 $[Ir(\mathbf{L1})_2(\mathbf{bipy})]^+$. Anal. Calcd for $C_{74}H_{74}F_6IrN_6O_2P$: C, 62.74; H, 5.27; N, 5.93; found: C, 62.61; H, 5.50; N, 5.64. IR (KBr pellet): 3032 (w), 2930 (m), 2863 (w), 1601 (s), 1581 (m), 1541 (m), 1515 (w), 1451 (m), 1367 (m), 1314 (w), 1288 (w), 1203 (w), 1162 (w), 1114 (w), 1066 (w), 1028 (w), 939 (w), 841 (s), 764 (m), 736 (w), 699 (m), 612 (w), 557 (m) cm^{-1}.

Synthesis of 6. Complex **6** was synthesized using the same procedure described for **5**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/MeOH (8/1 v/v) as eluent. Yield: 0.21 g (72.9% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.61−8.63 (m, 2H), 8.45−8.47 (m, 2H), 8.32−8.38 (m, 2H), 8.14−8.19 (m, 2H), 7.99−8.01 (m, 1H), 7.88−7.93 (m, 3H), 7.81−7.84 (m, 1H), 7.73−7.76 (m, 1H), 7.21−7.46 (m, 15H), 6.96−6.99 (m, 2H), 6.75−6.84 (m, 4H), 5.36 (s, 1H), 5.17−5.18 (m, 1H), 4.54 (s, 2H), 4.35−4.42 (m, 2H), 3.13−3.18 (m, 1H), 2.94−2.96 (m,

dx.doi.org/10.1021/om200759d | Organometallics 2012, 31, 553−559

1H), 2.76−2.89 (m, 4H), 2.58−2.63 (m, 4H), 1.96−2.02 (m, 5H), 1.75 (br, 2H), 1.56−1.62 (m, 2H), 1.46−1.52 (m, 9H), 0.92−0.96 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 169.1, 151.8, 150.3, 150.2, 150.1, 148.1, 147.6, 146.8, 146.7, 146.2, 138.3, 138.2, 137.7, 137.7, 135.9, 135.2, 135.1, 130.8, 130.7, 130.7, 130.6, 130.0, 130.0, 128.5, 128.5, 128.2, 128.0, 127.9, 127.9, 127.9, 127.2, 127.1, 126.6, 126.5, 126.3, 126.3, 126.1, 125.9, 125.0, 125.0, 124.8, 124.5, 123.1, 123.0, 72.1, 71.7, 61.4, 50.8, 50.0, 49.9, 37.6, 37.5, 27.4, 27.3, 26.4, 26.4, 25.3, 25.3, 11.8 ppm. MS (ESI; CH_2Cl_2, 180 °C): *m/z* 648.5 $[Ir(\mathbf{L1})_2(phen) + H]^{2+}$; 1115.6 $[Ir(\mathbf{L1})_2]^+$; 1295.5 $[Ir(\mathbf{L1})_2(phen)]^+$. Anal. Calcd for $C_{76}H_{74}F_6IrN_6O_2P$: C, 63.36; H, 5.18; N, 5.83. Found: C, 62.78; H, 5.28; N, 5.63. IR (KBr pellet): 3057 (w), 2930 (m), 2863 (w), 1601 (s), 1580 (m), 1541 (m), 1515 (w), 1453 (m), 1429 (w), 1366 (m), 1288 (w), 1260 (w), 1224 (w), 1204 (w), 1162 (m), 1112 (w), 1028 (w), 939 (m), 841 (s), 764 (w), 726 (m), 699 (m), 613 (w), 557 (m) cm^{-1}.

Synthesis of 7. Complex **7** was synthesized using the same procedure described for **5**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/MeOH (25/1 v/v) as eluent. Yield: 0.08 g (24.1% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.95−9.06 (m, 1H), 7.87−7.95 (m, 3H), 7.59−7.68 (m, 3H), 7.19−7.48 (m, 12H), 6.90−6.92 (m, 1H), 6.50−6.59 (m, 6H), 5.84−5.86 (m, 1H), 5.16 (br, 1H), 4.37−4.43 (m, 2H), 2.66−2.99 (m, 5H), 1.95−2.04 (m, 2H), 1.73−1.78 (m, 1H), 1.26−1.57 (m, 11H), 0.85−0.94 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 170.4, 157.1, 156.4, 151.1, 149.7, 149.7, 149.4, 149.2, 147.1, 145.2, 137.5, 135.0, 134.7, 133.2, 133.2, 132.2, 132.2, 132.2, 132.1, 130.9, 130.7, 129.6, 129.5, 128.9, 128.8, 128.5, 128.2, 128.0, 127.0, 126.9, 126.8, 126.8, 125.9, 124.2, 124.1, 71.9, 60.8, 50.7, 50.0, 37.6, 29.7, 27.7, 26.6, 25.4, 11.8, 11.8 ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 11.1, −143.7 (hept) ppm. MS (ESI; CH_2Cl_2, 180 °C): *m/z* 756.6 $[Ir(\mathbf{L1})_2(dppe) + H]^{2+}$; 1511.4 $[Ir(\mathbf{L1})_2(dppe)]^+$. Anal. Calcd for $C_{90}H_{88}F_6IrN_4O_2P_3$: C, 65.24; H, 5.35; N, 3.38. Found: C, 65.04; H, 5.53; N, 3.12. IR (KBr pellet): 3054 (w), 2928 (s), 2859 (m), 1720 (w), 1607 (s), 1579 (m), 1544 (s), 1519 (w), 1454 (m), 1434 (m), 1368 (m), 1291 (w), 1261 (w), 1214 (w), 1162 (w), 1098 (m), 1067 (w), 1026 (w), 998 (m), 937 (w), 840 (s), 747 (s), 736 (s), 696 (s), 612 (w), 555 (s), 526 (w), 504 (w), 474 (w) cm^{-1}.

Synthesis of 8. Complex **8** was synthesized using the same procedure described for **5**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/MeOH (20/1 v/v) as eluent. Yield: 0.13 g (43.2% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.71 (s, 1H), 8.61 (s, 1H), 8.30−8.34 (m, 2H), 8.15−8.23 (m, 3H), 8.04−8.06 (m, 2H), 7.34−7.51 (m, 17H), 7.00−7.06 (m, 2H), 6.78−6.82 (m, 2H), 6.28−6.30 (m, 2H), 5.36−5.37 (m, 2H), 5.15 (br, 1H), 4.37−4.61 (m, 4H), 3.16−3.21 (m, 1H), 2.57−2.95 (m, 10H), 1.93−2.37 (m, 8H), 1.75−1.78 (m, 2H), 1.13−1.69 (m, 25H), 0.90−0.95 (m, 11H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 166.0−166.1 (m), 164.6 (d), 163.4−163.6 (m), 162.6 (d), 161.4−161.5 (m), 155.4, 155.3, 153.3, 153.3, 152.8, 152.8, 147.5, 147.5, 147.3, 147.2, 129.8, 139.7, 137.6, 137.5, 130.6, 130.6, 130.2, 130.1, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.6, 127.6, 127.0, 126.9, 126.1, 125.9, 125.4, 125.3, 125.1, 124.7, 124.5, 124.3, 117.3, 117.2, 99.4−99.9 (m), 72.3, 71.7, 61.5, 61.2, 50.8, 50.6, 50.0, 49.9, 37.5, 37.4, 31.9, 29.7, 29.4, 27.3, 27.2, 26.4, 26.3, 25.4, 25.3, 23.1, 23.0, 22.7, 13.9, 11.8, 11.7 ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ 3.49 (s), 0.96 (s), −30.41 to −30.38 (m), −31.73 (d), −32.00 (d) ppm. MS (ESI; CH_2Cl_2, 180 °C): *m/z* 672.5 $[Ir(\mathbf{L2})_2(bipy) + H]^{2+}$; 1343.4 $[Ir(\mathbf{L2})_2(bipy)]^+$. Anal. Calcd for $C_{74}H_{70}F_{10}IrN_6O_2P$: C, 59.71; H, 4.74; N, 5.65. Found: C, 59.98; H, 5.00; N, 4.82. IR (KBr pellet): 2930 (s), 2860 (m), 1737 (w), 1599 (s), 1573 (m), 1544 (s), 1515 (w), 1448 (m), 1411 (m), 1361 (m), 1289 (w), 1254 (m), 1201 (w), 1162 (m), 1109 (s), 1065 (w), 1027 (w), 991 (s), 938 (w), 909 (w), 842 (s), 763 (w), 726 (m), 699 (m), 613 (w), 557 (m), 530 (w), 497 (w) cm^{-1}.

Synthesis of 9. Complex **9** was synthesized using the same procedure described for **5**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/MeOH (20/1 v/v) as eluent. Yield: 0.13 g (42.2%). ^1H NMR (500 MHz, CD_2Cl_2): δ 9.16−9.17 (m, 2H), 8.67−8.76 (m, 6H), 8.50−8.52 (m, 3H), 8.33−8.34 (m, 2H), 8.11−8.15 (m, 2H), 7.88−7.94 (m, 9H), 7.77−7.80 (m, 2H), 7.68−7.70 (m, 2H), 7.22−7.52 (m, 25H), 6.78−6.88 (m, 6H), 6.39−6.42 (m, 2H), 5.36 (br, 2H), 5.16−5.22 (m, 1H), 4.54 (br, 3H), 4.32−4.43 (m, 3H), 3.10−3.15 (m, 1H), 2.76−2.90 (m, 8H), 2.34−2.40 (m, 16H), 1.94−1.98 (m, 3H), 1.76 (br, 3H), 1.19−1.64 (m, 43H), 0.74−0.97 (m, 23H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 166.2, 166.2, 164.7, 164.6, 163.6, 163.3, 162.6, 162.5, 161.5, 161.4, 153.0, 152.9, 152.9, 152.6, 152.5, 150.0, 148.1, 148.0, 147.5, 147.4, 146.5, 146.4, 146.3, 139.0, 138.9, 137.6, 137.5, 136.0, 130.9, 130.8, 130.3, 128.8, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 126.9, 126.8, 126.6, 126.1, 126.1, 125.8, 125.6, 125.0, 124.8, 124.7, 124.6, 123.0, 117.7, 117.6, 99.8 (m), 72.3, 71.7, 61.3, 61.0, 50.7, 50.6, 50.0, 49.8, 37.5, 37.3, 32.0, 29.7, 29.4, 29.1, 27.2, 27.1, 26.4, 25.3, 25.3, 25.3, 23.0, 22.7, 13.9, 11.8, 11.7 ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ 3.45 (s), 0.94 (s), −30.29−(−31.94) (m) ppm. MS (ESI; CH_2Cl_2, 180 °C): *m/z* 684.5 $[Ir(\mathbf{L2})_2(phen) + H]^{2+}$; 1367.5 $[Ir(\mathbf{L2})_2(phen)]^+$. Anal. Calcd for $C_{76}H_{70}F_{10}IrN_6O_2P$: C, 60.35; H, 4.66; N, 5.56. Found: C, 62.73; H, 5.24; N, 5.40. IR (KBr pellet): 2928 (s), 2858 (m), 1735 (w), 1599 (s), 1574 (m), 1543 (s), 1515 (w), 1499 (w), 1455 (m), 1414 (m), 1360 (m), 1325 (w), 1289 (m), 1254 (m), 1227 (w), 1200 (w), 1162 (m), 1108 (s), 1026 (w), 991 (s), 938 (w), 909 (w), 841 (s), 760 (w), 726 (m), 699 (w), 613 (w), 557 (m), 530 (w), 495 (w), 439 (w) cm^{-1}.

Synthesis of 10. Complex **10** was synthesized using the same procedure described for **5**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/MeOH (25/1 v/v) as eluent. Yield: 0.035 g (10% based on Ir). ^1H NMR (500 MHz, CD_2Cl_2): δ 9.13−9.15 (m, 1H), 9.05−9.06 (m, 1H), 8.54 (br, 1H), 8.42 (br, 1H), 7.82−8.01 (m, 3H), 7.55−7.75 (m, 8H), 7.26−7.48 (m, 24H), 6.52−6.76 (m, 14H), 5.10−5.26 (m, 4H), 4.36−4.47 (m, 4H), 2.63−3.03 (m, 11H), 1.90−2.01 (m, 2H), 1.73−1.77 (m, 2H), 1.33−1.57 (m, 17H), 0.88−0.93 (m, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 167.7 (br), 164.3 (br), 163.3 (br), 162.3 (br), 161.2 (br), 160.2 (br), 159.8 (br), 159.4 (br), 159.1 (br), 159.8, 159.4, 159.1, 152.4, 152.2, 149.5, 149.3, 149.0, 149.0, 144.9, 144.8, 143.7, 143.7, 142.9, 142.9, 137.5, 137.5, 134.2, 133.8, 133.8, 132.3, 132.2, 132.2, 131.9, 131.9, 131.8, 131.2, 131.2, 131.1, 131.0, 129.5, 129.5, 129.4, 129.3, 129.2, 129.1, 129.1, 128.5, 128.4, 128.0, 128.0, 127.4, 127.2, 127.1, 127.0, 126.9, 125.8, 125.6, 124.2, 123.9, 115.7, 115.5, 115.3, 115.1, 100.9, 100.7, 100.4, 71.7, 71.6, 61.3, 61.0, 60.2, 50.8, 50.5, 50.0, 49.8, 37.5, 37.5, 29.7, 29.1, 27.6, 27.3, 26.6, 26.5, 25.3, 25.3, 20.8, 14.0, 11.8, 11.7, 11.7 ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 19.3, 12.0, 11.3, −143.6 (hept) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ 3.91, 1.39, −29.27 (br), −31.1 (br) ppm. MS (ESI; CH_2Cl_2, 180 °C): *m/z* 792.6 $[Ir(\mathbf{L2})_2(dppe) + H]^{2+}$; 1583.5 $[Ir(\mathbf{L2})_2(dppe)]^+$. Anal. Calcd for $C_{90}H_{84}F_{10}IrN_4O_2P_3$: C, 62.53; H, 4.90; N, 3.24. Found: C, 62.33; H, 4.87; N, 3.04. IR (KBr pellet): 3057 (w), 2932 (m), 2867 (w), 2038 (m), 1596 (s), 1579 (m), 1546 (m), 1519 (w), 1484 (w), 1453 (w), 1436 (m), 1412 (m), 1361 (m), 1288 (w), 1257 (w), 1198 (w), 1163 (w), 1164 (m), 1069 (m), 1027 (w), 995 (w), 841 (s), 749 (m), 738 (m), 697 (m), 595 (w), 558 (m), 502 (w), 475 (w) cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ESI mass, ^1H NMR, and ^{13}C NMR spectra for **L2′** and **3**−**10**, ^{19}F NMR for **L2′**, **3**, **4**, and **8**−**10**, and ^{31}P NMR spectra for **7** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

This work was supported by the National University of Singapore (NUS) (R143-000-323-112). D.J.Y. and A.L.T.

gratefully acknowledge funding from the Universiti Brunei Darussalam.

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