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Supporting Information

Blue-Emitting Cationic Iridium(III) Complexes Featuring Pyridylpyrimidine Cyclometalating Ligands and their Use in Light-Emitting Electrochemical Cells (LEECs)

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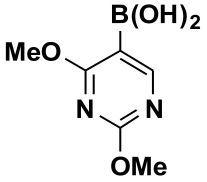
Experimental Section

General Synthetic Procedures. Commercial chemicals were used as supplied. The N^N ligand 1,1’-(α,α’-*o*-Xylylene)-2,2’-biimidazole (*o*-Xylbiim) was synthesized as reported previously.[1] All reactions were performed using standard Schlenk techniques under inert (N_2) atmosphere with reagent grade solvents. Flash column chromatography was performed using silica gel (60 Å, 40-63 μm). Analytical thin layer chromatography (TLC) was performed using silica plates with aluminum backings (250 μm with indicator F-254). Compounds were visualized under UV light. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance spectrometer at 400 MHz, 126 MHz and 376 MHz respectively. The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “p” for pentet and “m” for multiplet. Deuterated chloroform ($CDCl_3$), deuterated dichloromethane (CD_2Cl_2), deuterated acetonitrile (CD_3CN) and deuterated dimethylsulfoxide (DMSO-d_6) were used as the solvents of record. ^{1}H and ^{13}C NMR spectra were referenced to the solvent peak. High-resolution mass spectra were recorded at the EPSRC UK National Mass Spectrometry Facility at Swansea University on a quadrupole time-of-flight (ESI-Q-TOF), model ABSciex 5600 Triple TOF in positive electrospray ionization mode and spectra were recorded using sodium formate solution as the calibrant. Elemental analyses were performed by Mr. Stephen Boyer, London Metropolitan University.

2,4-Dimethoxypyrimidine-5-boronic acid

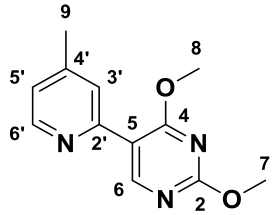


A 100 mL 2-neck round bottom flask fitted with a magnetic stirrer, septum and stopcock was flame dried under vacuum and filled with argon. 5-bromo-2,4-dimethoxypyrimidine (2.00 g, 9.13 mmol, 1 equiv.) and dry THF (30 mL) were added to the reaction vessel, and the resulting solution cooled to -78 ^{o}C. *n*-BuLi (2.5 M in hexanes, 4.75 mL, 11.9 mmol, 1.3 equiv.), was then added slowly dropwise to the stirred solution. The resulting dark red solution was stirred at -78 ^{o}C for 1 h before the addition of $B(OMe)_3$ (1.42 g, 13.7 mmol, 1.5 equiv.). The resulting solution was allowed to warm to rt, and was then stirred under argon for 16 h. HCl (3 M, 40 mL) was then added slowly dropwise and the solution stirred for further 16 h. The reaction mixture was then neutralised by careful addition of Na_2CO_3 (1 M). The organic phase was extracted and the aqueous phase extracted with EtOAc (3 x 100 mL). The organic phases were combined dried ($MgSO_4$) and solvent removed under reduced pressure to yield a crude yellow solid, which was carried forward without further characterization.

General synthesis of 5-(Pyridin-2-yl)pyrimidines

The relevant bromopyridine (1.0 equiv.), 2,4-dimethoxypyrimidyl-5-boronic acid (1.2 equiv.), and K_2CO_3 (3 equiv.) were combined along with 1,4-dioxane (20 mL) and H_2O (10 mL) to give a solution of with concentration of ~0.2M. The solvent was degassed by purging with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (5 mol %) was then added and the mixture degassed with argon again by purging for a further 10 min before stirring under argon at 80 ^{o}C for 16 h. After cooling to rt the solvent was removed under reduced pressure and CH_2Cl_2 (50 mL) and H_2O (50 mL) were added and the organic phase extracted. The aqueous phase was extracted with a further 2 portions of CH_2Cl_2 (50 mL). The organic phases were combined and dried ($MgSO_4$) and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography on silica.

5-(4-Methylpyridin-2-yl)-2,4-dimethoxypyrimidine (Mepypyrm).



2-Bromo-4-methylpyridine (779 mg, 4.53 mmol, 1 equiv.), boronic acid (1.00 g, 5.44 mmol, 1.2 equiv.), K_2CO_3 (1.88 g, 13.6 mmol, 3 equiv.) and $Pd(PPh_3)_4$ (523 mg, 0.453 mmol, 10 mol%). Purification: column chromatography on silica. (Et_2O:CH_2Cl_2 8:2) followed by a second silica column (hexane:EtOAc 8:2) afforded a white crystalline solid (728 mg, 3.15 mmol) **Yield:** 70%. ***R_f*:** 0.45 (Et_2O:CH_2Cl_2 8:2, on silica). **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)**: 8.82 (s, 1H, H_6), 8.50 (d, *J* = 5.0 Hz, 1H, $H_{6'}$), 7.59 (s, 1H, $H_{3'}$), 7.03 (d, *J* = 5.0 Hz, 1H, $H_{5'}$), 4.06 (s, 3H, H_8), 4.03 (s, 3H, H_7), 2.38 (s, 3H, H_9). **^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)**: 168.28 (C_4), 165.03 (C_2), 159.88 (C_6), 151.75 ($C_{2'}$), 149.37 ($C_{6'}$), 147.45 ($C_{4'}$), 124.91 ($C_{3'}$), 123.32 ($C_{5'}$), 114.89 (C_5), 55.06 (C_7), 54.27 (C_8), 21.36 (C_9)**. MS (TOF ES$^+$): *m/z* (%)**: 254.2 (100) $[M+Na]^+$. **HRMS (ES$^+$)**: $[M+H]^+$ **Calculated**: ($C_{12}H_{14}N_3O_2$) 232.1086; **Found:** 232.1088.

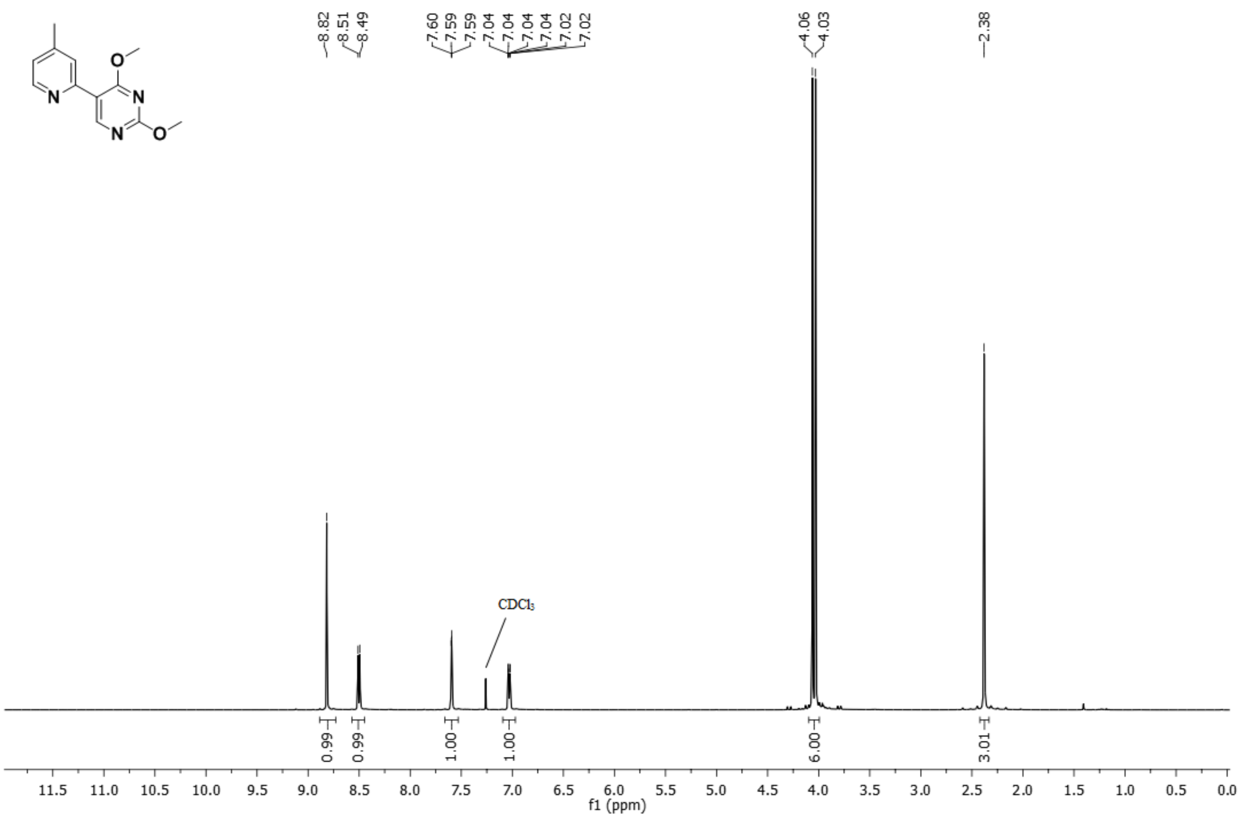


Figure **S1**. ^{1}H NMR spectrum of **5-(4-Methylpyridin-2-yl)-2,4-dimethoxypyrimidine (Mepypyrm)** in CDCl$_3$.

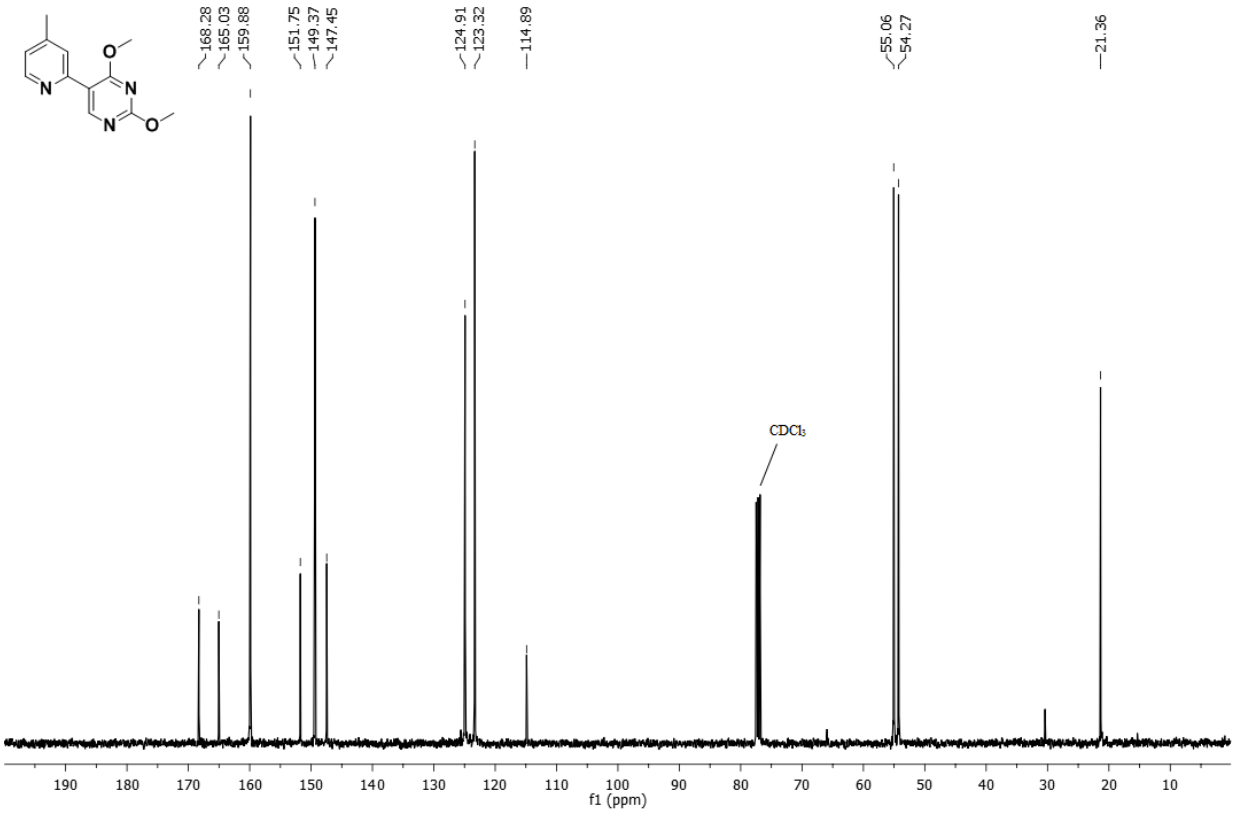
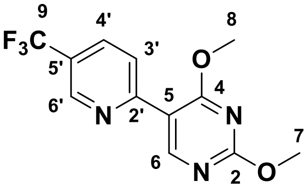


Figure **S2**. ^{13}C NMR spectrum of **5-(4-Methylpyridin-2-yl)-2,4-dimethoxypyrimidine (Mepypyrm)** in $CDCl_3$.

5-(5-(Trifluoromethyl)pyridin-2-yl)-2,4-dimethoxypyrimidine (CF$_3$pypyrm).



2-Bromo-5-(trifluoromethyl)pyridine (1.07 g, 4.53 mmol, 1 eq), boronic acid (1.00 g, 5.44 mmol, 1.2 eq), K_2CO_3 (1.88 g, 13.6 mmol, 3 eq) and $Pd(PPh_3)_4$ (262 mg, 227 µmol, 5 mol%). Purification: column chromatography on silica. (CH_2Cl_2:Et_2O 9:1) followed by a further silica column (hexane:EtOAc 9:1→8:2) afforded a white crystalline solid (1.09 g, 3.82 mmol, 84%). **Yield**: 84%. ***Rf***: 0.21 (hexane:EtOAc 9:2, on silica). **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.00 (s, 1H), 8.89 – 8.83 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.08 (s, 3H), 4.02 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):** 168.41 (s), 165.61 (s), 160.71 (q, *J* = 14.9 Hz), 155.18 (s), 146.33 (q, *J* = 3.8 Hz), 133.45 (q, *J* = 3.1 Hz), 124.70 (q, *J* = 32.9 Hz), 123.72 (q, *J* = 272.1 Hz), 123.24 (s), 113.26 (s), 55.20 (s), 54.38 (s). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -62.41 (s, *J* = 18.7 Hz). **MS (TOF EI$^+$): *m/z* (%):** 285.1 (100) $[M+H]^+$. **HRMS (EI$^+$):** $[M+H]^+$ **Calculated:** ($C_{12}H_{10}N_3O_2F_3$) 285.0725; **Found:** 285.0727.

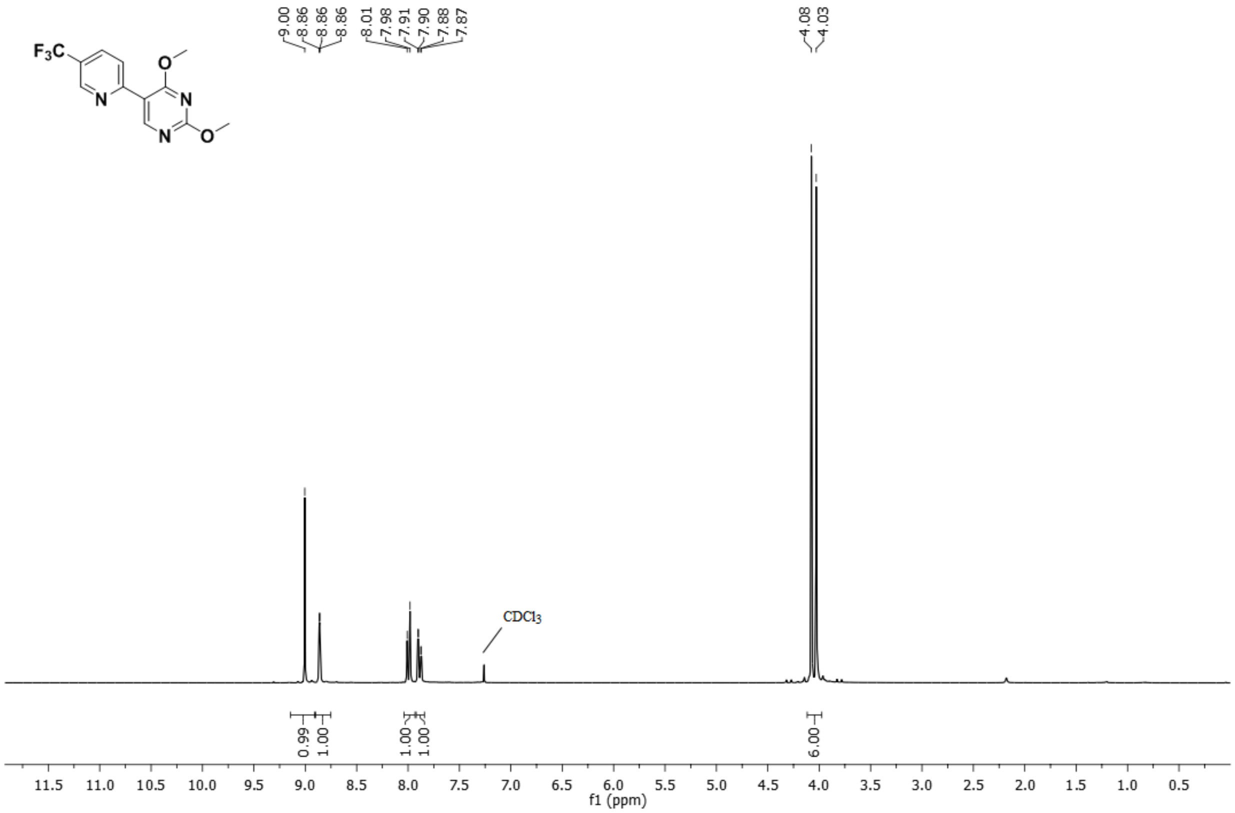


Figure **S3**. ^{1}H NMR spectrum of **5-(5-(Trifluoromethyl)pyridin-2-yl)-2,4-dimethoxypyrimidine (CF$_3$pypyrm)** in CDCl$_3$.

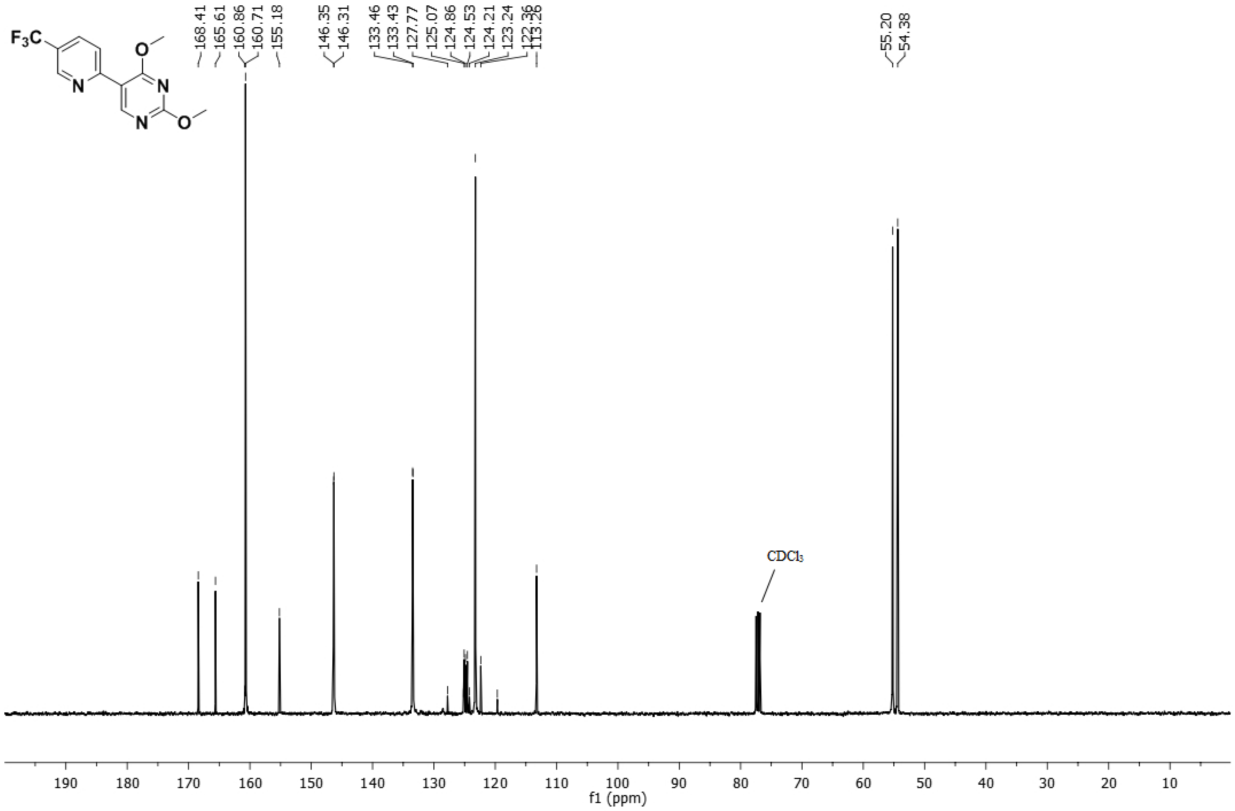


Figure **S4**. ^{13}C NMR spectrum of **5-(5-(Trifluoromethyl)pyridin-2-yl)-2,4-dimethoxypyrimidine (CF$_3$pypyrm)** in CDCl$_3$.

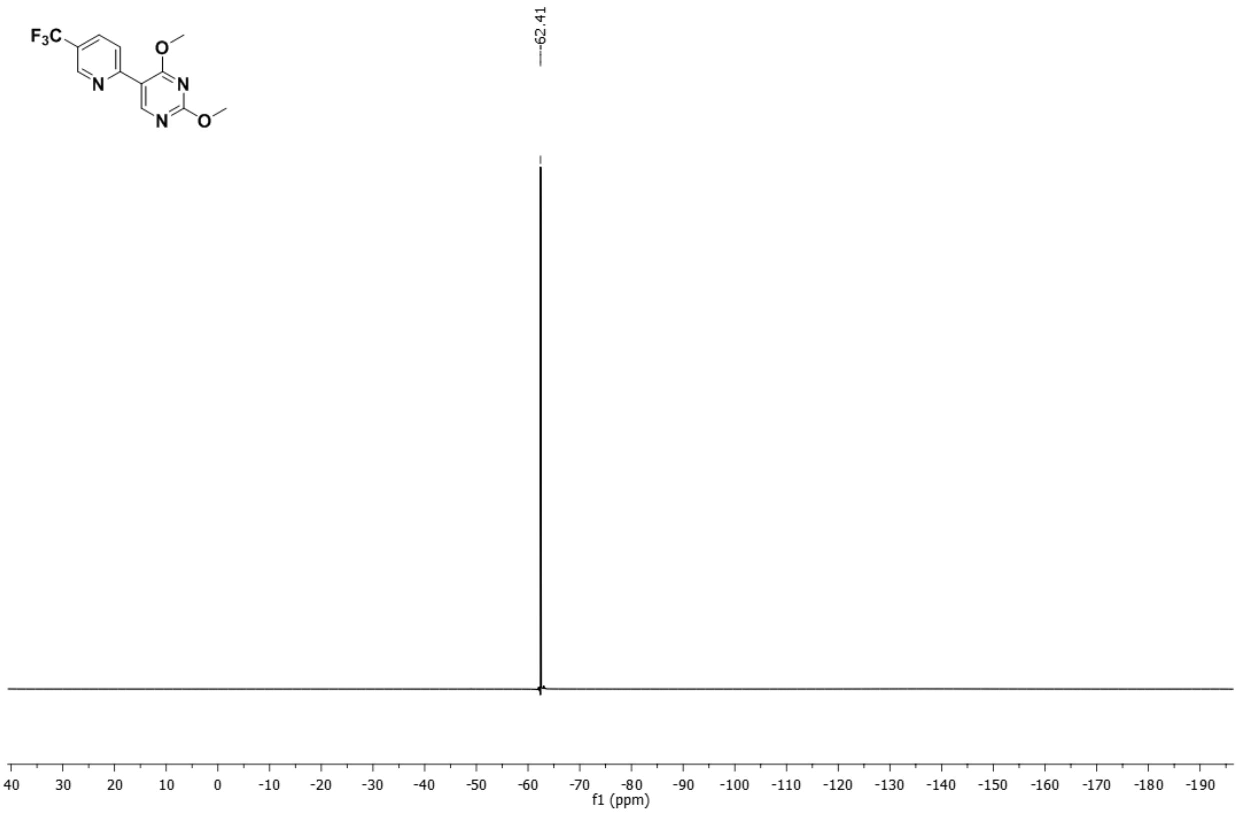
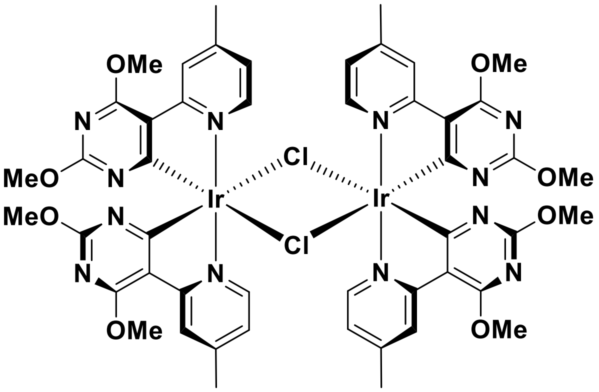


Figure **S5**. ^{19}F NMR spectrum of **5-(5-(Trifluoromethyl)pyridin-2-yl)-2,4-dimethoxypyrimidine (CF_3pypyrm)** in $CDCl_3$.

Synthesis of Iridium Dimers

The synthesis of both dimers was carried out in an analogous fashion to our previously reported synthesis of cyclometalated 2,3'-bipyridine dimers,[2] using a combination of [Ir(COD)(μ-Cl)]$_2$ (1.0 equiv.) and the cyclometalating ligand (4.0 equiv.) in refluxing 2-ethoxyethanol. Both dimers were used as isolated without further purification.

Tetrakis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-4-methylpyridinato-N,C$^{2'}$]-bis(μ-chloro)diiridium(III): [Ir(Mepypyrm)$_2$(μ-Cl)]$_2$.



Yellow solid. **^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ (ppm):** 8.83 (d, *J* = 6.0, Hz, 4H), 8.16 (s, 4H), 6.56 (dd, *J* = 9.6, 2.0 Hz, 4H), 3.98 (s, 12H), 3.41 (s, 12H), 2.60 (s, 12H).

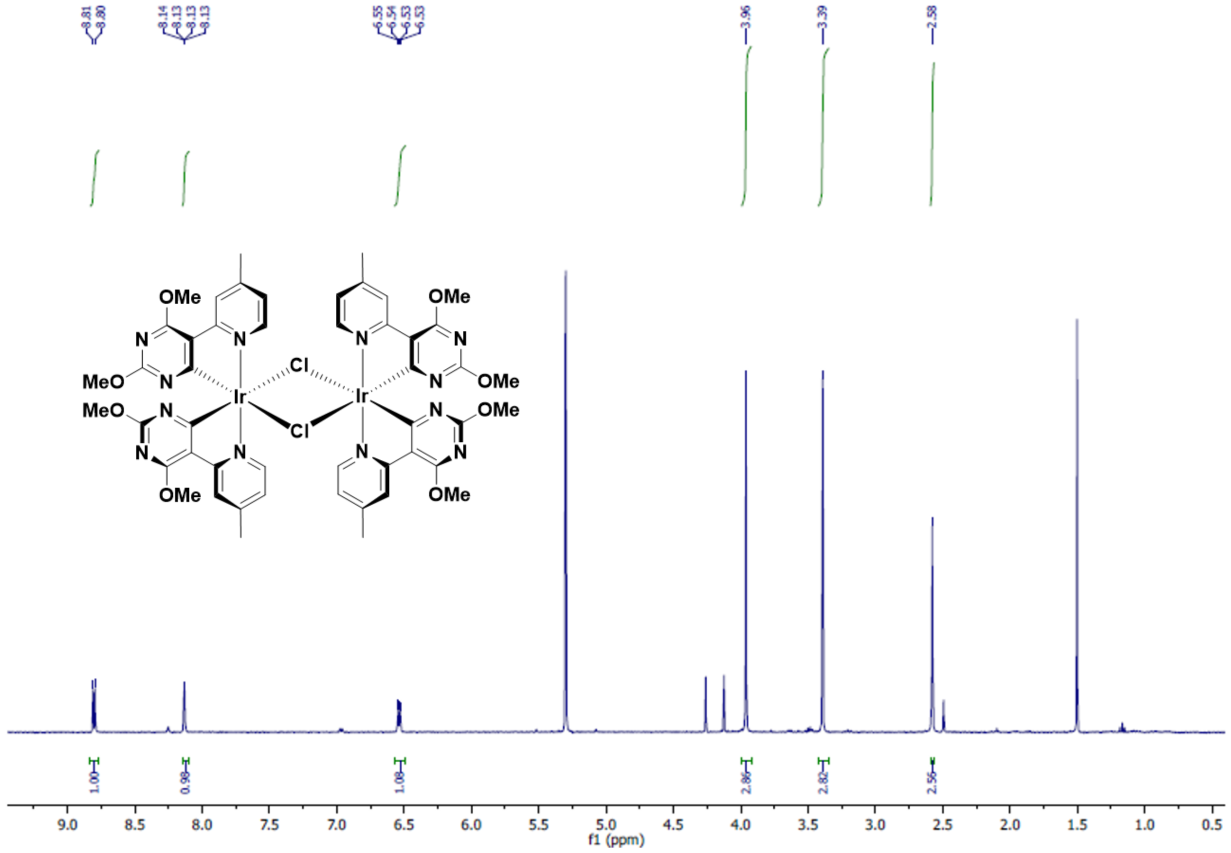
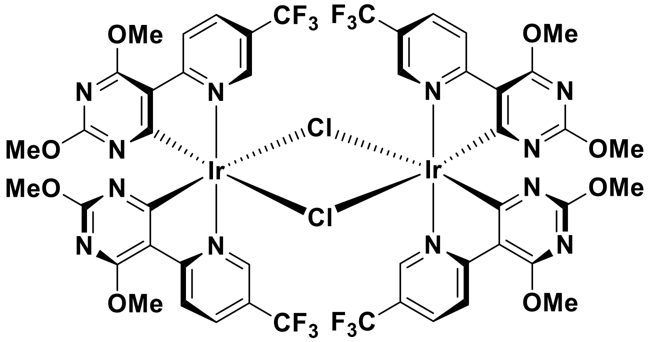


Figure **S6**. ^{1}H NMR spectrum of **tetrakis[2-(4',6’-dimethoxy-3’,5’-pyrimidyl)-4-methylpyridinato-N,C$^{2'}$]-bis(μ-chloro)diiridium(III) ([Ir(Mepypyrm)$_2$(μ-Cl)]$_2$)** in CD$_2$Cl$_2$.

Tetrakis[2-(4',6’-dimethoxy-3’,5’-pyrimidyl)-5-trifluoromethylpyridinato-N,C$^{2'}$]-bis(μ-chloro)diiridium(III): [Ir(CF_3pypyrm)$_2$(μ-Cl)]$_2$.



Yellow solid. **^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm):** 9.41 (dd, *J* = 1.6, 0.8 Hz, 4H), 8.46 (dd, *J* = 8.8, 0.4 Hz, 4H), 7.96 (dd, *J* = 9.2, 2.0 Hz, 4H), 4.00 (s, 12H), 3.33 (s, 12H). **^{19}F {^{1}H} NMR (371 MHz, CD_2Cl_2) δ (ppm):** -62.4 (s, 12F).

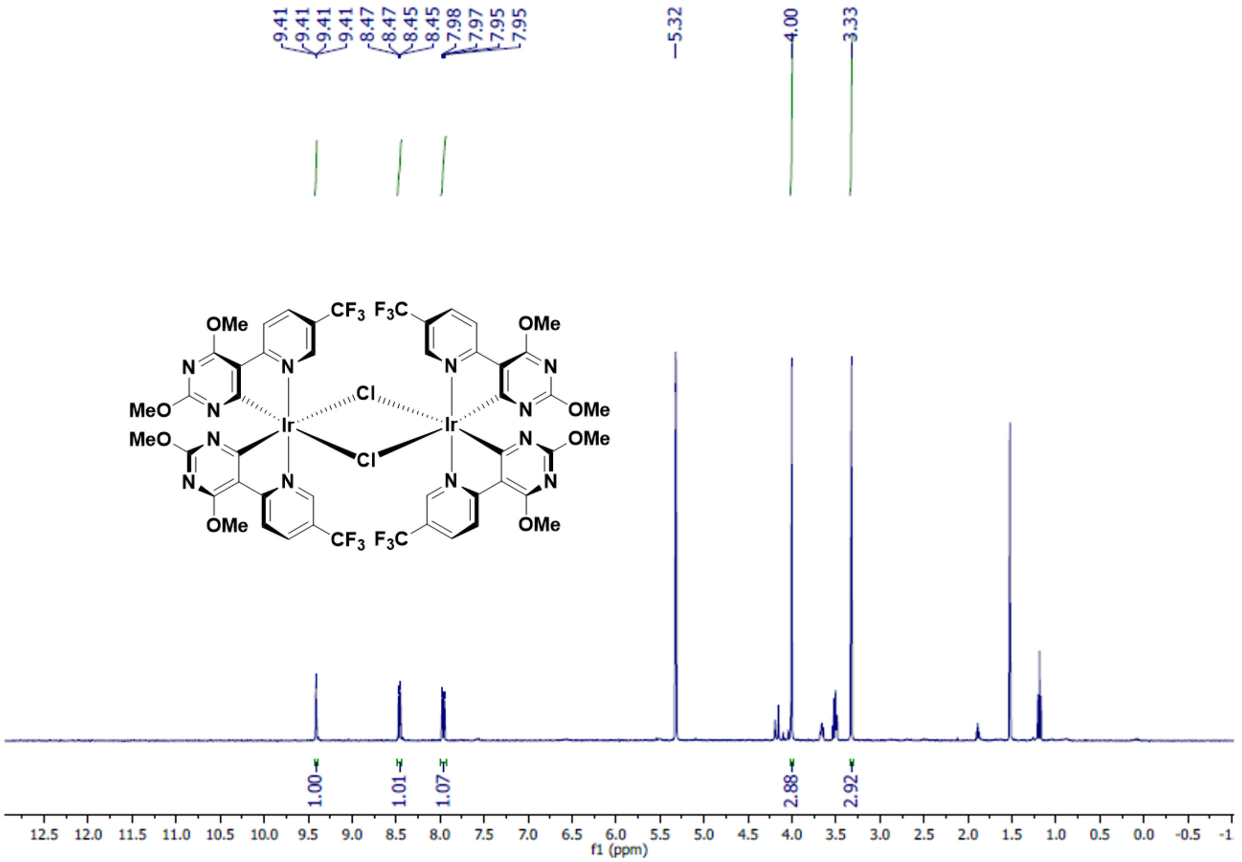


Figure **S7**. ^{1}H NMR spectrum of **tetrakis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-5-trifluoromethylpyridinato-N,C$^{2'}$]-bis(μ-chloro)diiridium(III) ([Ir(CF$_3$pypyrm)$_2$(μ-Cl)]$_2$)** in CD$_2$Cl$_2$.

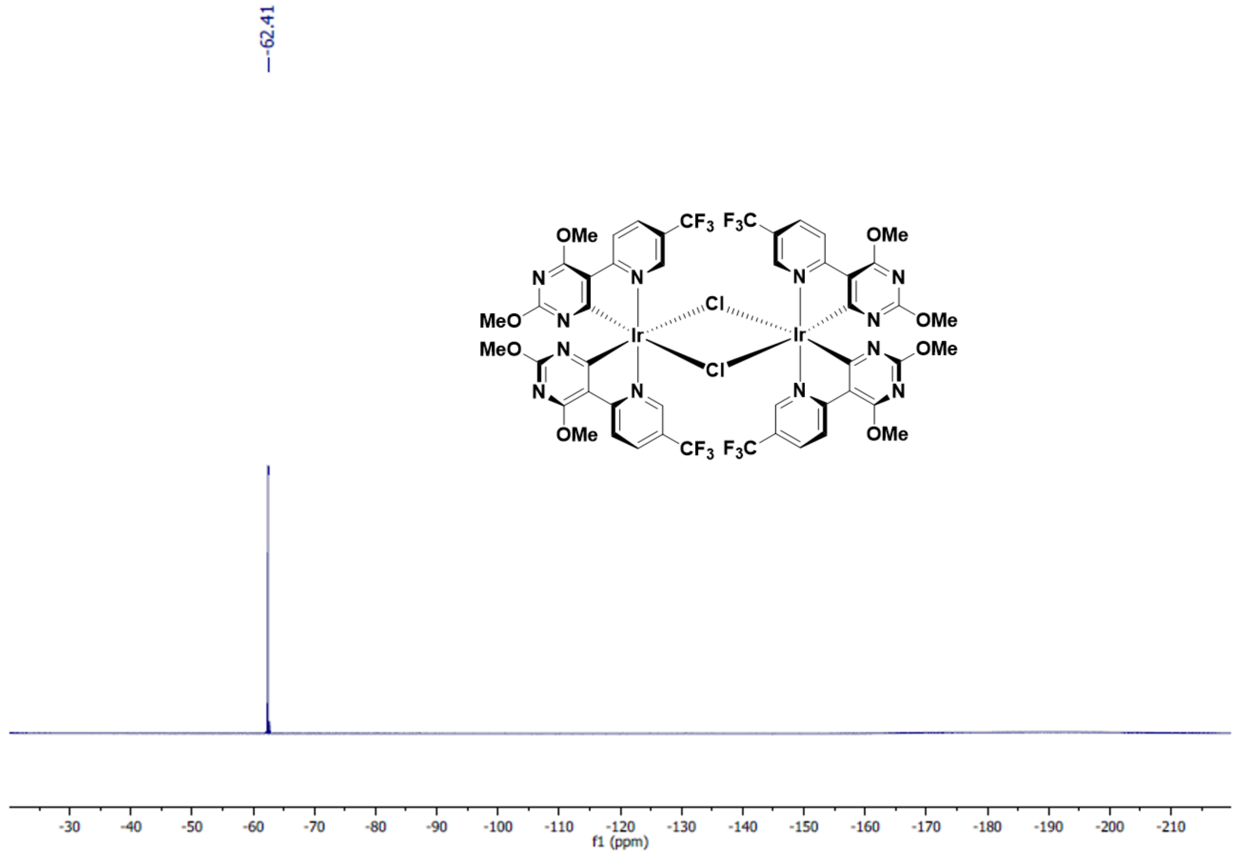
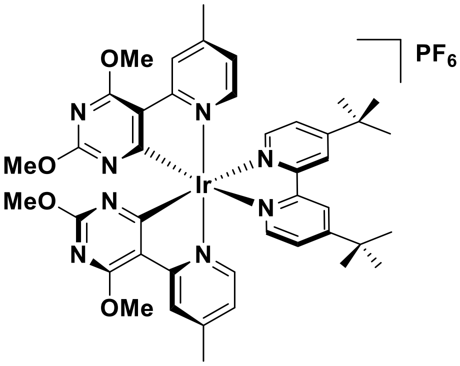


Figure **S8**. ^{19}F NMR spectrum of **tetrakis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-5-trifluoromethylpyridinato-N,C$^{2'}$]-bis(μ-chloro)diiridium(III) ([Ir(CF$_3$pypyrm)$_2$(μ-Cl)]$_2$)** in CD$_2$Cl$_2$.

Synthesis of Iridium(III) Complexes

To a round bottom flask containing the appropriate dichloro-bridged iridium dimer (1.0 equiv.) and N^N ligand (2.2 equiv.) were added DCM and MeOH (1:1 v/v) to give a suspension with a concentration of ca. 0.02 M. The mixture was degassed via bubbling with N_2 for 20 minutes, before the reaction vessel was sealed. The reaction mixture was heated to 40 °C for 19 h. Over the course of the reaction the mixture dissolved to give yellow to pale-yellow solutions. The solution was cooled to room temperature, and the solvent evaporated. DCM was added to dissolve the residue, before excess KPF_6 was added. The suspension was stirred at room temperature for 1 h, before filtering through celite. The DCM solution was taken and excess ether was added until a precipitate formed. This precipitate was filtered, before washing first with water to dissolve any salt residues, and then again with excess ether. The product was then dissolved in the minimum of MeCN, and crystallised from solution by slow evaporation of ether. The product was filtered and dried. If the product was impure, it was recrystallized again from either DCM/ether or MeCN/ether. Initial samples were prepared using NH_4PF_6 as the anion metathesis reagent, and although crystals of **3** and **4** were of sufficient quality to obtain for X-ray diffraction data, these samples were not analytically pure and thus KPF_6 was used instead.

Iridium (III) bis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-4-methylpyridinato-N,C$^{2'}$]-*N,N'*-(4,4'-di-*tert*-butyl-2,2'-bipyridine)hexafluorophosphate: [Ir(Mepypyrm)$_2$(d*t*Bubpy)](PF$_6$).



Off white solid (0.076 g). **Yield**: 98%. **^{1}H NMR (500 MHz, CD$_3$CN) δ (ppm):** 8.49 (d, *J* = 1.5, Hz, 2H), 8.20 (s, 2H), 7.97 (d, *J* = 6.0, Hz, 2H), 7.52 (dd, *J* = 6.0, 2.0 Hz, 2H), 7.39 (d, *J* = 6.0 Hz, 2H), 6.79 (dd, *J* = 6.0, 2.0 Hz, 2H), 4.06 (s, 6H), 3.61 (s, 6H), 2.45 (s, 6H), 1.41 (s, 18H). **^{13}C {^{1}H} NMR (126 MHz, CD$_3$CN) δ (ppm):** 189.84, 166.41, 165.51, 163.50, 155.97, 151.56, 149.35, 126.34, 122.84, 123.40, 122.91, 119.81, 118.26, 54.84, 54.23, 36.47, 30.34, 21.38. **HR-MS (**FTMS+**): [M-PF$_6$]$^+$ Calculated:** ($C_{42}H_{48}IrN_8O_4$) 921.3425; **Found:** 921.3402. **Anal.** Calcd for $C_{42}H_{48}N_8F_6O_4IrP$ (MW 1066.08): C, 47.32; H, 4.54; N, 10.51. Found: C, 47.14; H, 4.47; N, 10.40 (average of two runs).

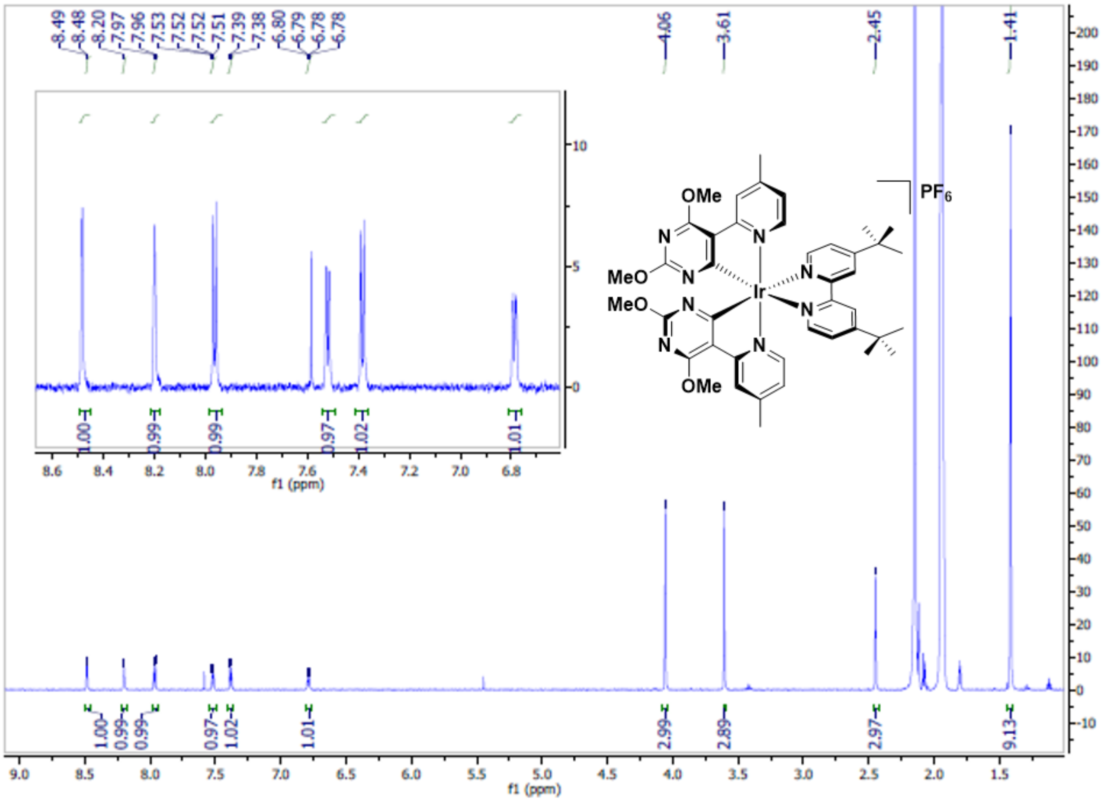


Figure **S9**. ^{1}H NMR spectrum of **[Ir(Mepypyrm)$_2$(d*t*Bubpy)](PF$_6$)** in CD$_3$CN.

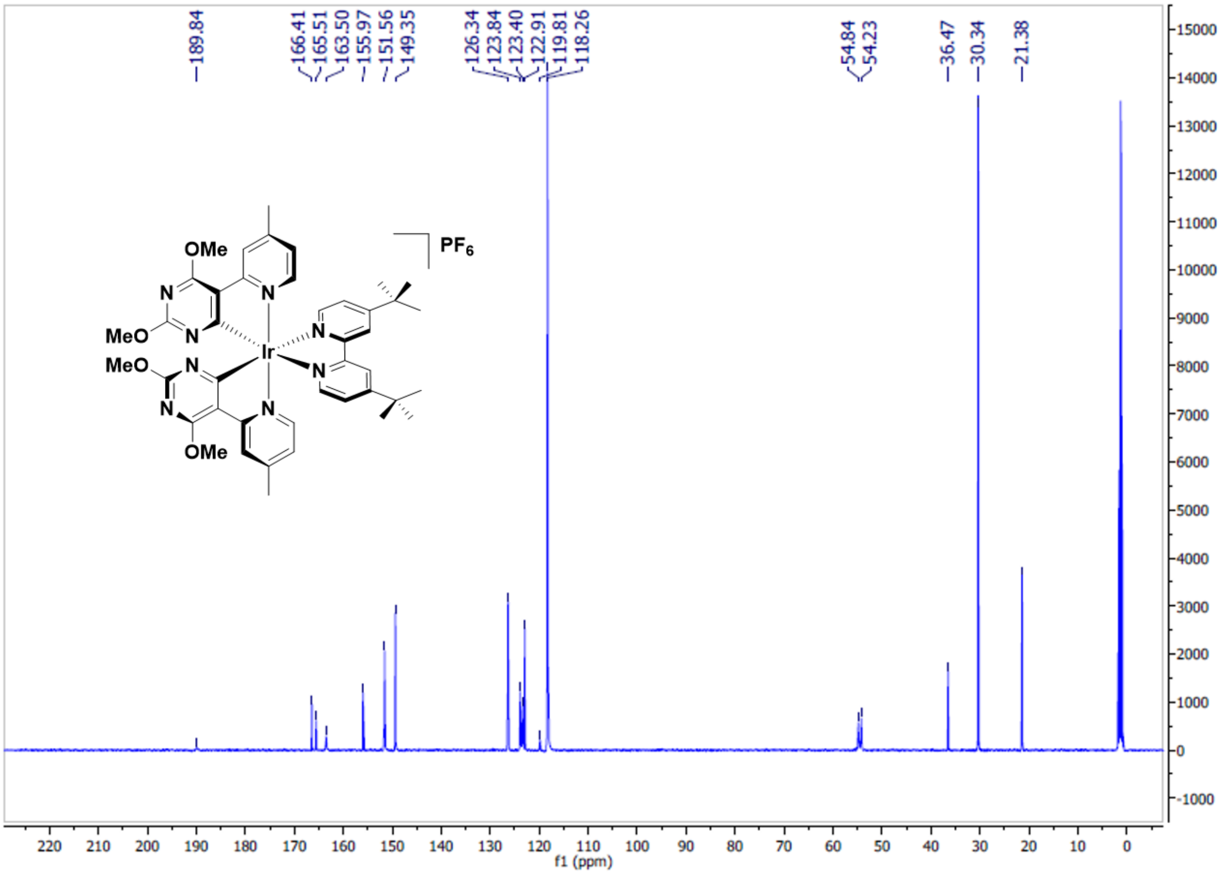
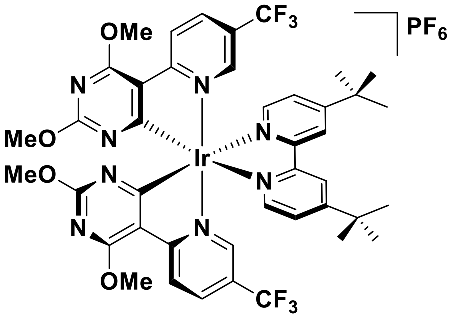


Figure **S10**. ^{13}C NMR spectrum of **[Ir(Mepypyrm)$_2$(d*t*Bubpy)](PF$_6$)** in CD$_3$CN.

Iridium (III) bis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-5-trifluoromethylpyridinato-N,C$^{2'}$]-*N,N'*-(4,4'-di-*tert*-butyl-2,2'-bipyridine)hexafluorophosphate: [Ir(CF$_3$pypyrm)$_2$(d*t*Bubpy)](PF$_6$).



Pale yellow solid (0.070 g). **Yield**: 95 %. **^{1}H {^{19}F} (500 MHz, CD$_3$CN) δ (ppm):** 8.52 (d, *J* = 2.0 Hz, 2H), 8.50 (s, 2H), 8.08 (dd, *J* = 2.0, 9.0 Hz, 2H), 8.04 (d, *J* = 5.5 Hz, 2H), 7.69 (s, 2H) 7.60 (dd, *J* = 1.6, 5.6 Hz, 2H), 4.06 (s, 6H), 3.54 (s, 6H), 1.43 (s, 18H). **^{13}C {^{1}H} NMR (126 MHz, CD$_2$Cl$_2$) δ (ppm):** 189.76, 167.32, 166.70, 165.21, 163.32, 155.48, 151.00, 145.90, 135.66, 125.55, 123.69, 123.07, 122.79, 122.40, 122.16, 121.53, 117.95, 54.08, 53.67, 35.64, 29.38. **^{19}F {^{1}H} NMR (371 MHz, CD$_3$CN) δ (ppm):** -63.30 (s, 6F), -72.92 (d, *J* = 697.48 Hz, 6F, PF$_6^-$). **HR-MS** (FTMS+)**: [M-PF$_6$]$^+$ Calculated:** (C$_{42}$H$_{42}$F$_6$IrN$_8$O$_4$) 1029.2859; **Found:** 1029.2863. **Anal.** Calcd for C$_{42}$H$_{42}$N$_8$F$_{12}$O$_4$IrP (MW 1174.02): C, 42.97; H, 3.61; N, 9.54. Found: C, 42.93; H, 3.44; N, 9.34 (average of two runs).

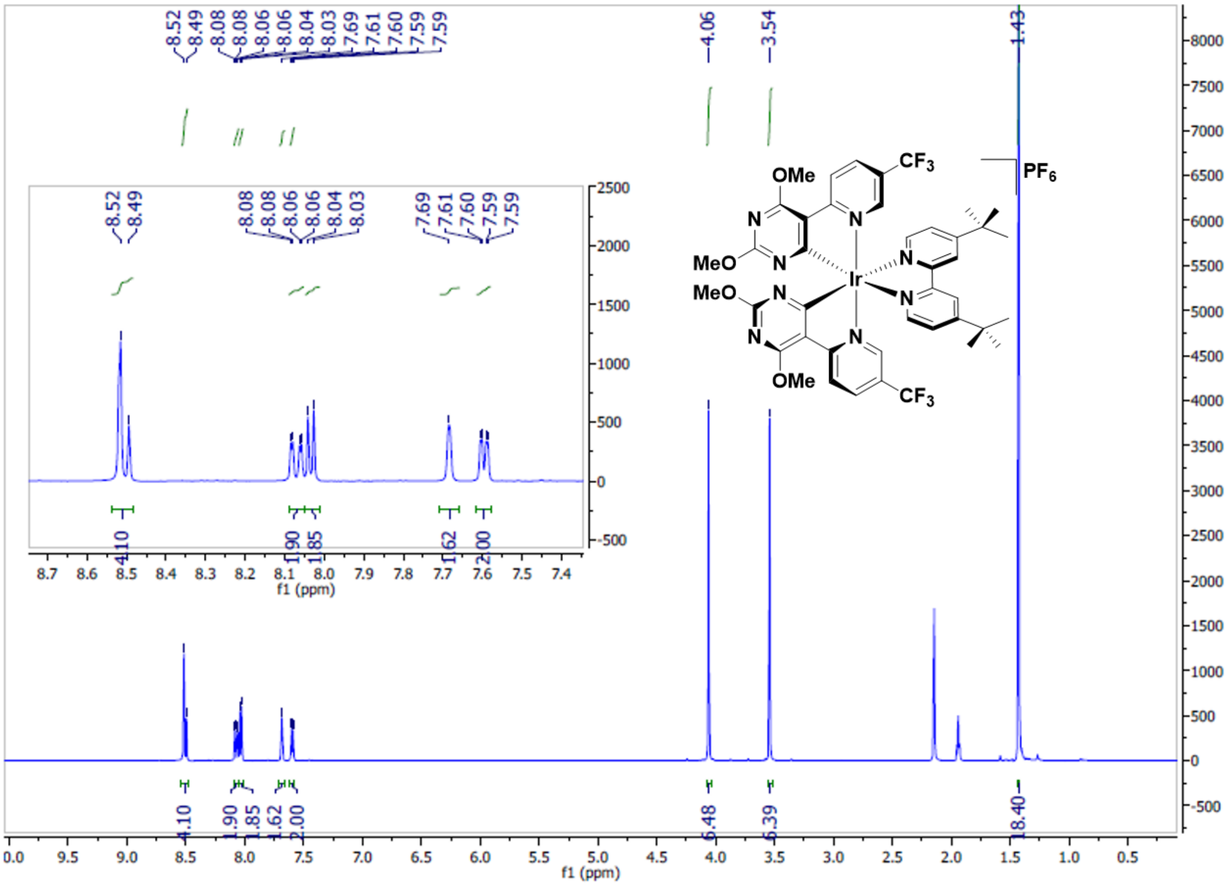


Figure **S11**. ^{1}H NMR spectrum of **[Ir(CF$_3$pypyrm)$_2$(d*t*Bubpy)](PF$_6$)** in CD$_3$CN.

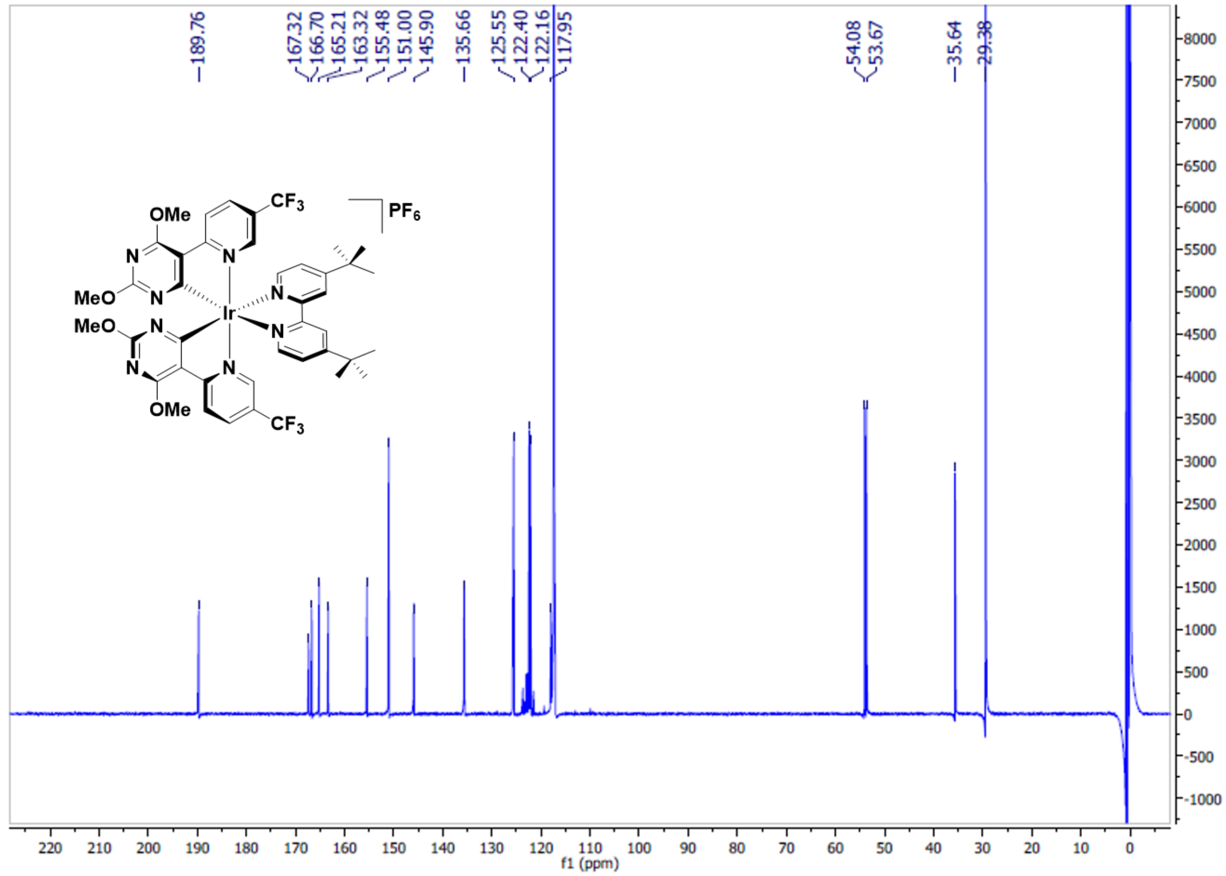


Figure **S12**. ^{13}C NMR spectrum of **[Ir(CF$_3$pypyrm)$_2$(d*t*Bubpy)](PF$_6$)** in CD$_3$CN.

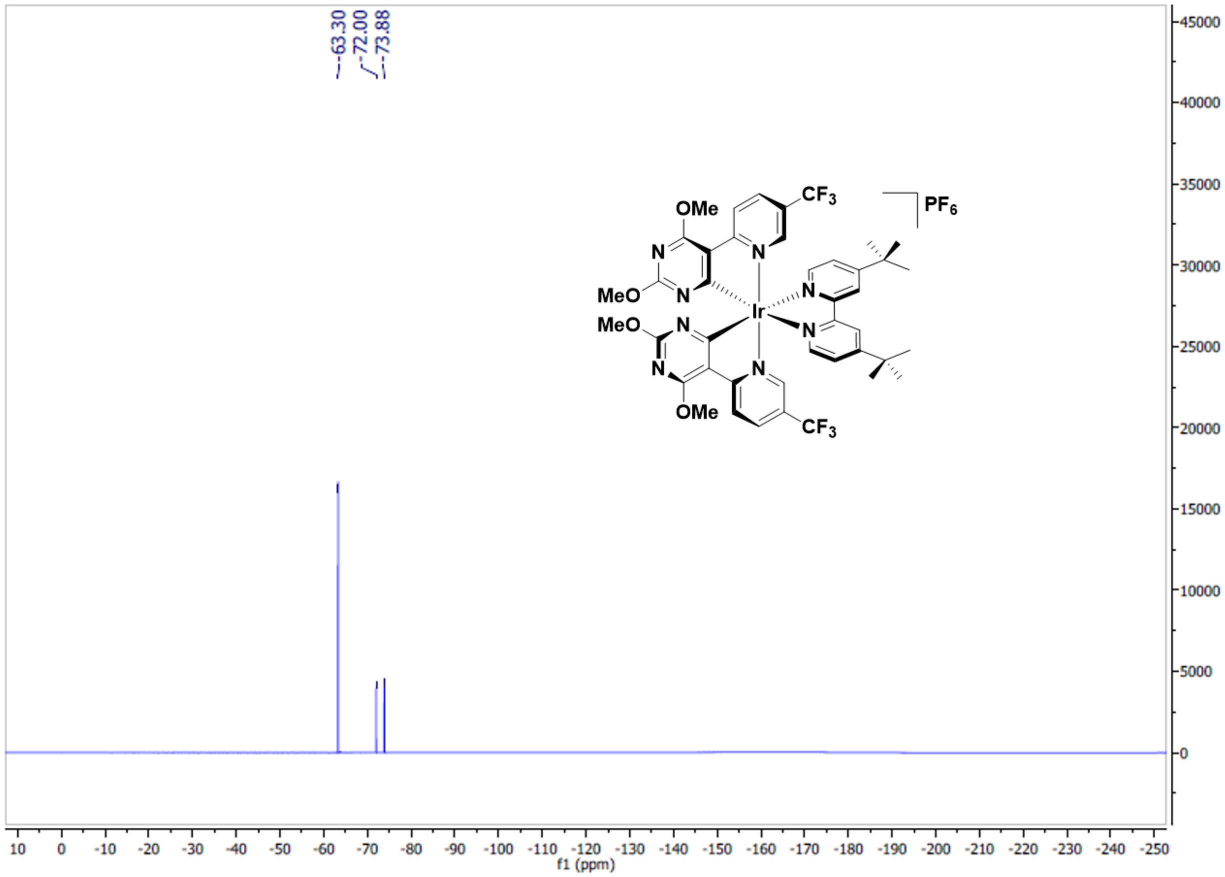
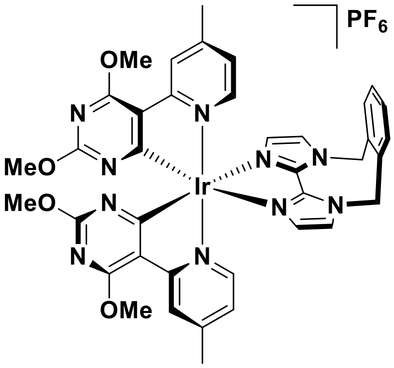


Figure **S13**. ^{19}F NMR spectrum of **[Ir(CF$_3$pypyrm)$_2$(d*t*Bubpy)](PF$_6$)** in CD$_3$CN.

Iridium (III) bis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-4-methylpyridinato-N,C$^{2'}$]- *N,N'*-(1,1'-(α,α'-*o*-Xylylene)-2,2-biimidazole)hexafluorophosphate: [Ir(Mepypyrm)$_2$(*o*-Xylbiim)](PF$_6$).



Off white powder (0.050 g). **Yield**: 67%. **^{1}H NMR (500 MHz, DMSO-*d*$_6$, 363 K) δ (ppm):** 8.08 (s, 2H), 7.76 (d, *J* = 1.5 Hz, 2H), 7.63 (t, *J* = 3.5 Hz, 2H), 7.46 (dd, *J* = 3.5, 5.5 Hz, 2H), 7.33 (br s, 2H), 6.85 (br s, 2H), 6.69 (br s, 2H), 5.85 (br s, 4H), 4.06 (s, 6H), 3.60 (s, 6H), 2.45 (s, 6H). **^{13}C {^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 298 K) δ (ppm):** 206.87, 187.80, 165.48, (d, 163.31, 163.07), 162.45, (d, 149.85, 149.72), (d, 149.10, 148.81), 139.67, (d, 133.92, 133.74), 131.60, 131.33, 128.04, (d, 125.98, 125.63), 122.88, (d, 122.68, 122.09), (d, 119.58, 119.48), 51.18, 30.99, 21.57. **HR-MS (**FTMS+**): [M-PF$_6$]$^+$ Calculated:** ($C_{38}H_{36}N_{10}O_4Ir$) 889.2545; **Found:** 889.2536. **Anal.** Calcd for $C_{38}H_{36}N_{10}F_6O_4IrP$ (MW 1033.95): C, 44.14; H, 3.51; N, 13.55 Found: C, 44.20; H, 3.45; N, 13.61 (average of two runs).

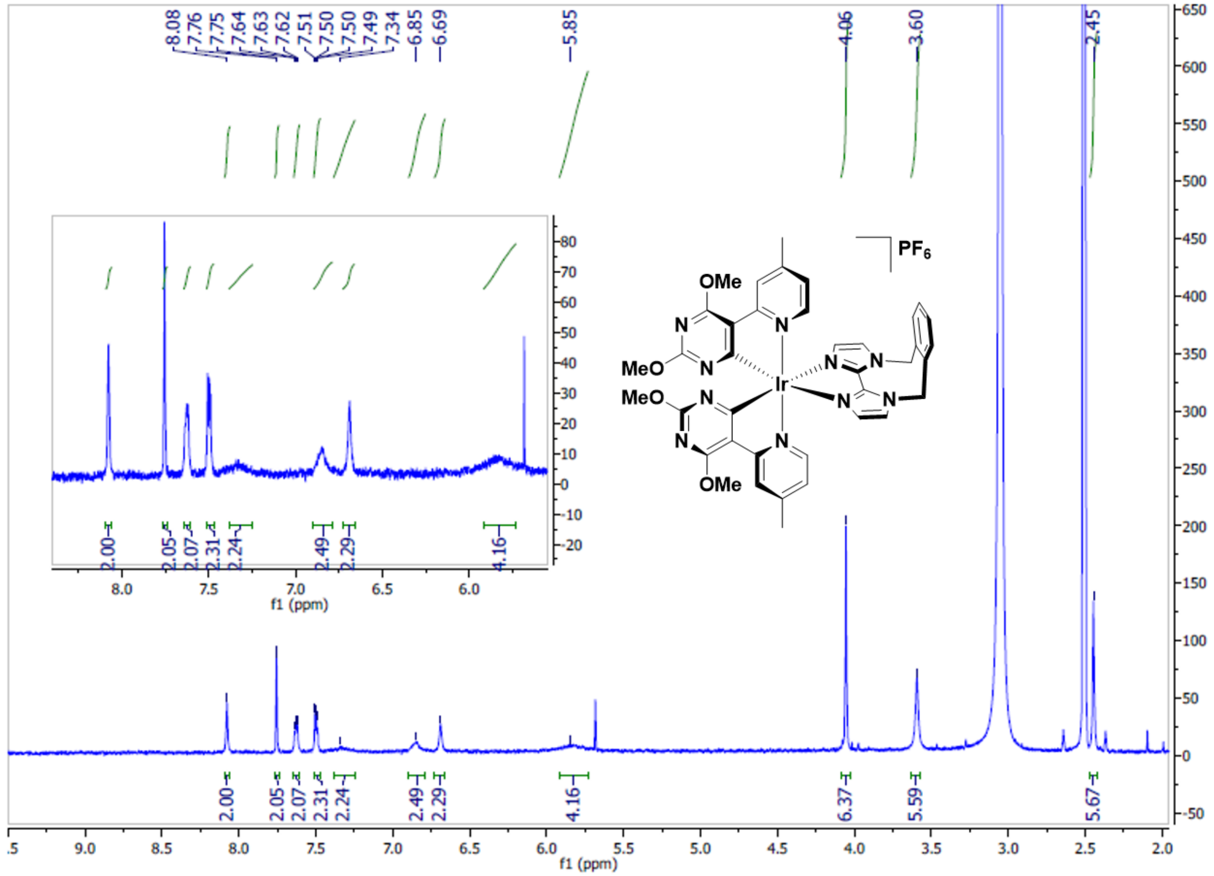


Figure **S14**. ^{1}H NMR spectrum of **[Ir(Mepypyrm)$_2$(*o*-Xylbiim)](PF$_6$)** in DMSO-d_6 at 363 K.

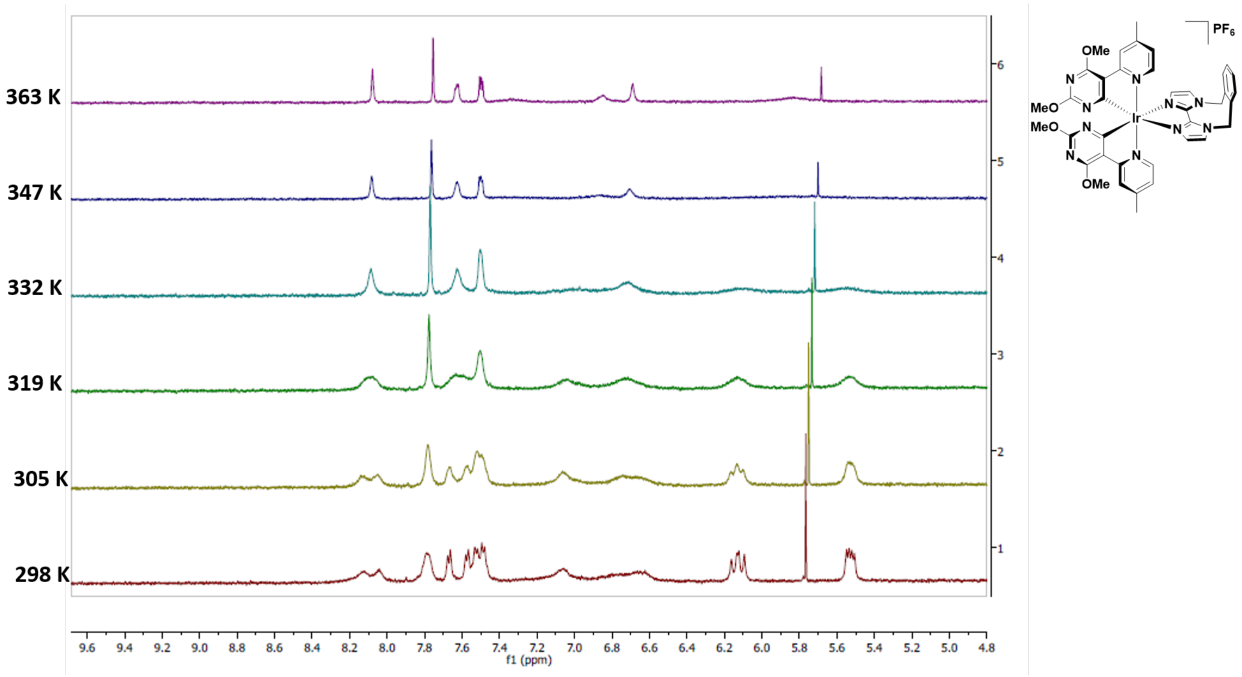
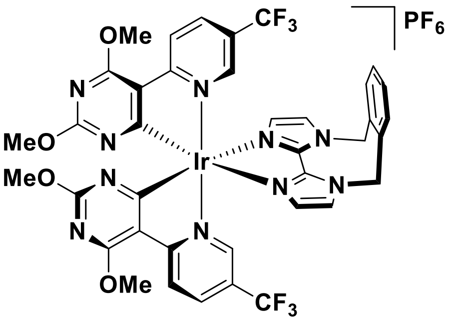


Figure **S15**. ^{1}H NMR temperature study of **[Ir(Mepypyrm)$_2$(*o*-Xylbiim)](PF$_6$)** in DMSO-*d*$_6$.

Iridium (III) bis[2-(4',6'-dimethoxy-3',5'-pyrimidyl)-5-trifluoromethylpyridinato-N,C$^{2'}$]-*N,N'*-(1,1'-(α,α'-*o*-Xylylene)-2,2-biimidazole)hexafluorophosphate: [Ir(CF_3pypyrm)$_2$(*o*-Xylbiim)](PF_6).



Pale yellow powder (0.050 g). **Yield**: 70%. **^{1}H NMR (500 MHz, DMSO-d_6, 372 K) δ (ppm):** 8.05 (s, 2H), 7.74 (d, *J* = 1.0 Hz, 2H), 7.62 (t, *J* = 4.0 Hz, 2H), 7.49 (dd, *J* = 5.5, 3.5 Hz, 2H), 7.38 (br s, 2H), 6.83 (br s, 2H), 6.64 (d, *J* = 1.5 Hz, 2H), 5.82 (br s, 4H), 4.01 (s, 6H), 3.53 (s, 6H). **^{13}C {^{1}H} NMR (126 MHz, CD_3CN, 298 K) δ (ppm):** 207.44, 189.78, (d, 168.27, 168.14), 167.35, 163.88, (d, 148.00, 146.89), (d, 141.08, 140.90), (d, 136.17, 135.95), 134.94, 131.77, 131.66, 128.22, (d, 127.83, 127.43), 126.83, 124.47, 122.48, 54.85, 54.42, 51.10. **^{19}F {^{1}H} NMR (371 MHz, CD_3CN) δ (ppm):** -62.97 (s, 3F), -63.39 (s, 3F), -72.92 (d, *J* = 697.48 Hz, 6F, PF_6^-)**. HR-MS** (FTMS+)**: [M-PF$_6$]$^+$ Calculated:** ($C_{38}H_{30}F_6N_{10}O_4Ir$) 997.1980; **Found:** 997.1955. **Anal.** Calcd for $C_{38}H_{30}N_{10}F_{12}O_4IrP$ (MW 1141.90): C, 39.97; H, 2.65; N, 12.27 Found: C, 40.25; H, 3.01; N, 12.40 (average of two runs).

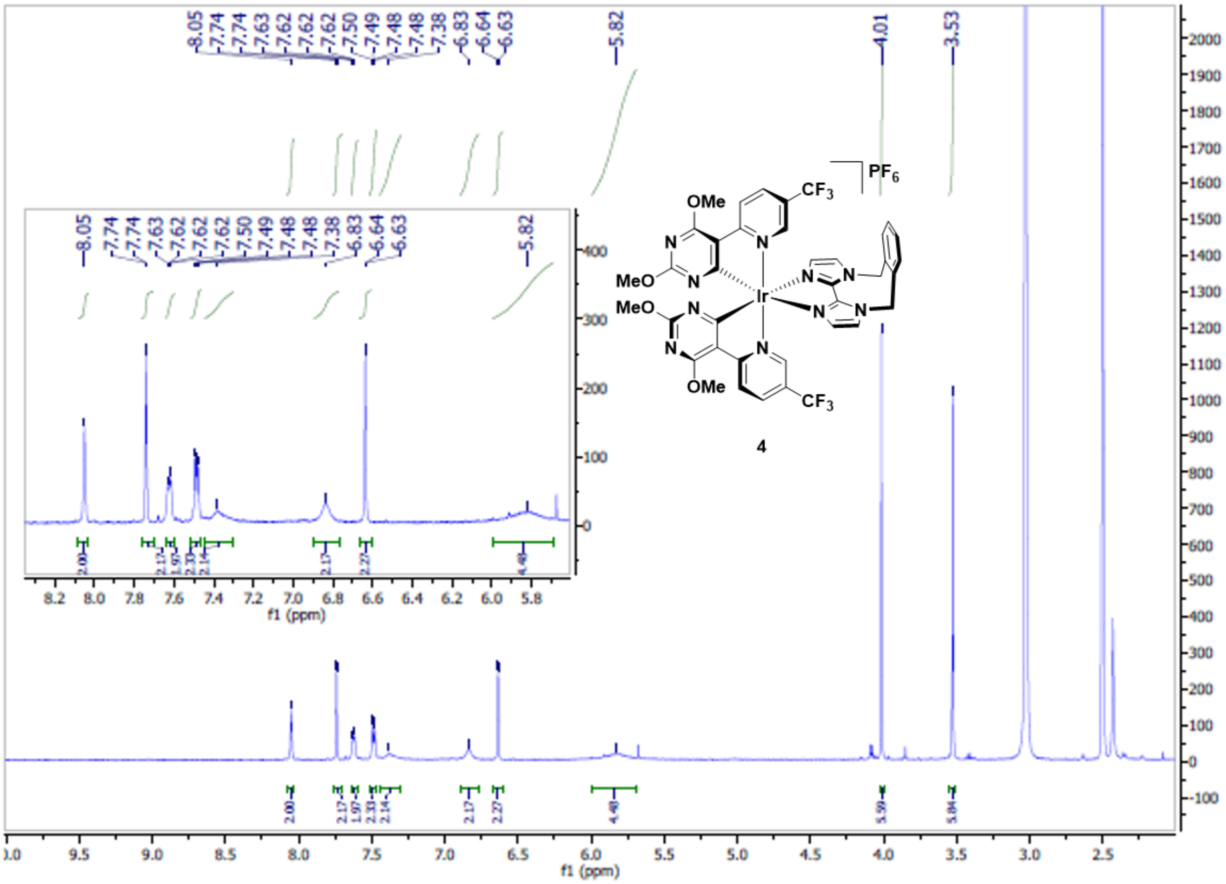


Figure **S16**. ^{1}H NMR spectrum of **[Ir(CF$_3$pypyrm)$_2$(*o*-Xylbiim)](PF$_6$)** in DMSO-d_6 at 363 K.

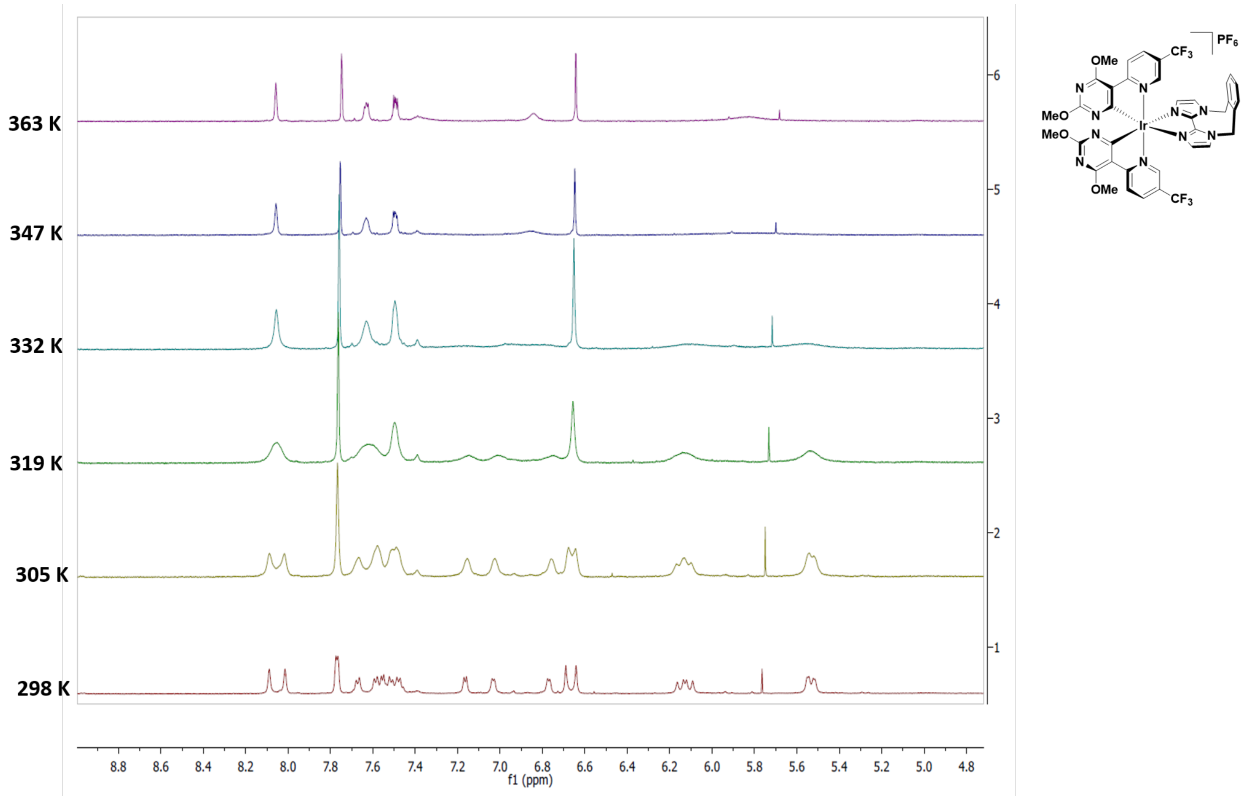


Figure **S17**. ^{1}H NMR temperature study of **[Ir(CF$_3$pypyrm)$_2$(*o*-Xylbiim)](PF$_6$)** in DMSO-d_6.

Photophysical measurements. All samples were prepared in HPLC grade acetonitrile (MeCN) with varying concentrations on the order of μM. Absorption spectra were recorded at RT using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least three independent solutions at varying concentrations with absorbance ranging from 1.62×10^{-4} to 9.02×10^{-6} M.

The sample solutions for the emission spectra were prepared in HPLC grade MeCN and degassed via vigorous bubbling with N_2 for 20 min. Steady state emission and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. All samples for steady state measurements were excited at 360 nm while samples for time-resolved measurements were excited at 378 nm using a PDL 800-D pulsed diode laser. Emission quantum yields were determined using the optically dilute method.[3] A stock solution with absorbance of ca. 0.5 was prepared and then four dilutions were prepared with dilution factors of 5, 6.6, 10 and 20 to obtain solutions with absorbances of ca. 0.1 0.075, 0.05 and 0.025, respectively. The Beer-Lambert law was found to be linear at the concentrations of the solutions. The emission spectra were then measured after the solutions were degassed by nitrogen purging for 20 min per sample prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor (R^2) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)_2$ was used to calculate the relative quantum yield of each of the sample, where Φ_r is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution of quinine sulfate in 0.5 M H_2SO_4 (Φr = 54.6%) was used as the external reference.[4]

Electrochemistry measurements. Cyclic voltammetry (CV) measurements were performed on an Electrochemical Analyzer potentiostat model 600D from CH Instruments. Solutions for cyclic voltammetry were prepared in MeCN and degassed with MeCN-saturated nitrogen bubbling for about 10 min prior to scanning. Tetra(*n*-butyl)ammoniumhexafluorophosphate ($TBAPF_6$; ca. 0.1 M in MeCN) was used as the supporting electrolyte. A Pt wire was used as the pseudoreference electrode; a Pt wire coil was used as the counter electrode and a Pt disk electrode was used for the working electrode. The redox potentials are reported relative to a saturated calomel electrode (SCE) electrode with a ferrocenium/ferrocene (Fc^+/Fc) redox couple as an internal reference (0.38 V vs SCE).[5]

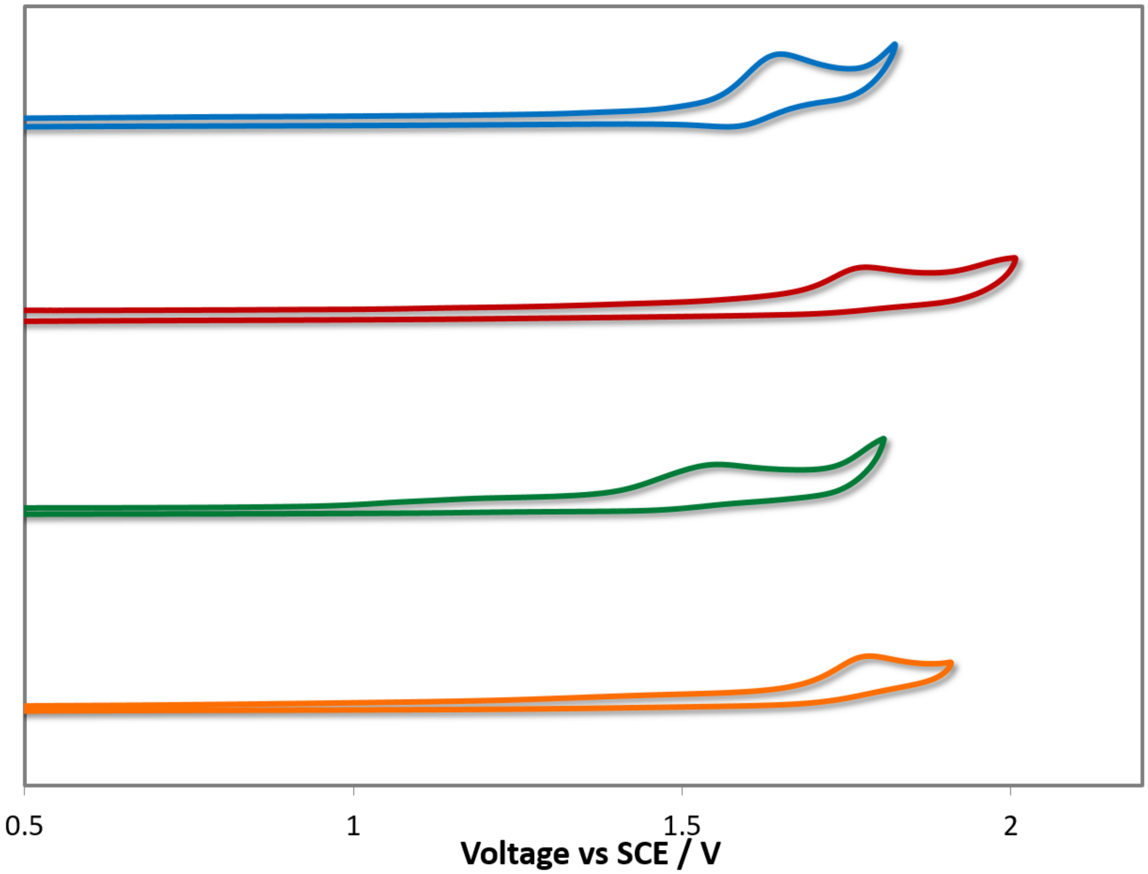


Figure **S18**. CV traces of first oxidations of complexes **1** – **4** in MeCN solution, reported versus SCE (Fc/Fc$^+$ = 0.38 V in MeCN).[5] Scan rates were at 100 mV s^{-1} and in the positive scan direction.

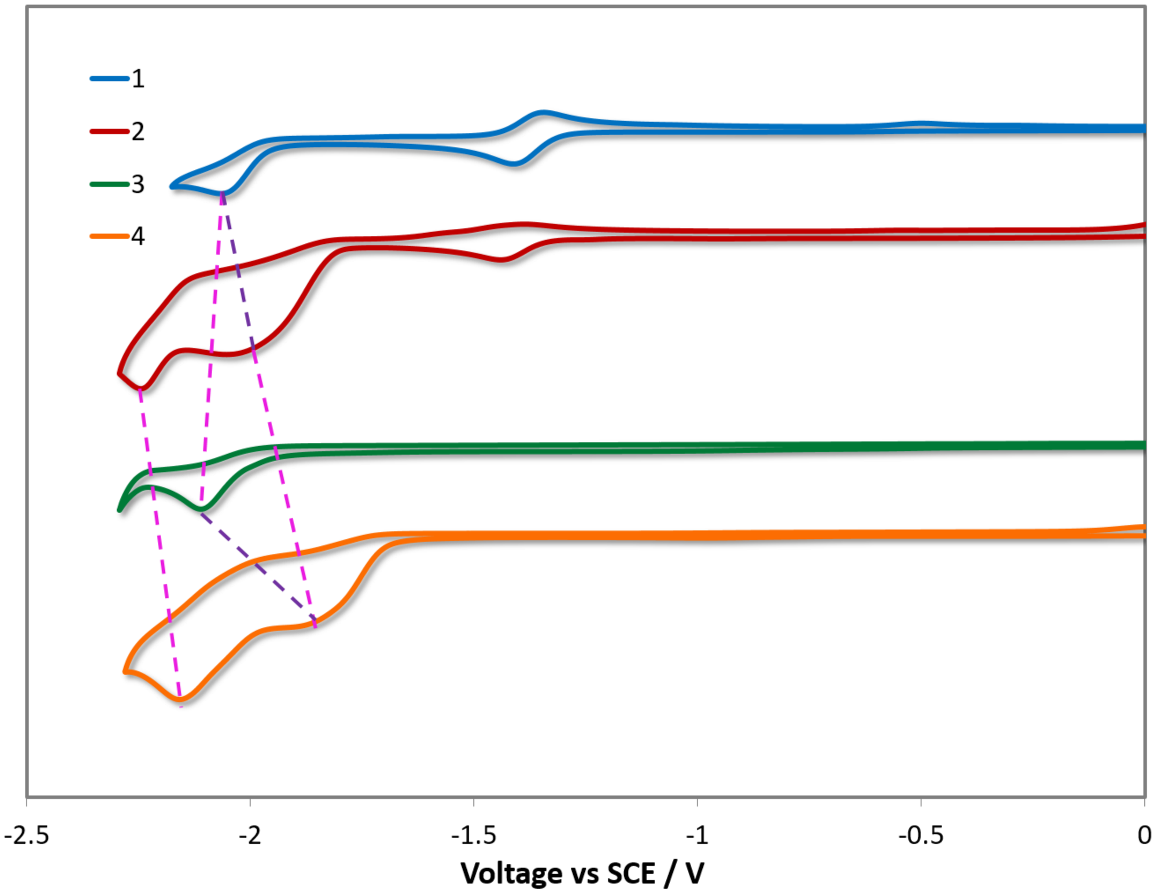


Figure **S19**. CV traces of reductions of complexes **1** – **4** in MeCN solution, reported versus SCE (Fc/Fc^+ = 0.38 V in MeCN).[5] Scan rates were at 100 mV s^{-1} and in the negative scan direction. Dashed pink lines show analogous reductions between complexes with the same C^N ligands. Dashed purple lines show analogous reductions between complexes with the same N^N ligands.

X-ray crystallography

Single crystals were grown by vapour diffusion of diethyl ether into either concentrated dichloromethane (**1** and **2**) or acetonitrile solutions (**3** and **4**). Data for compound **1** was collected at 173 K by using a Rigaku MM-007HF High brilliance RA generator/confocal optics and Rigaku XtaLAB P100 system, with Cu Kα radiation (λ = 1.54187 Å). Data for **2** - **4** were collected at 173 K by using a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics and Rigaku XtaLAB P200 system, with Mo Kα radiation (λ = 0.71075 Å). Intensity data were collected using ω and φ steps (**1**), or ω steps (**2** - **4**), accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using CrystalClear.[6] Structures were solved by Patterson (PATTY)[7] methods and refined by full-matrix least-squares against F^2 (SHELXL-2013).[8] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model, except for N-H hydrogens, which were located from the difference Fourier map, and refined subject to a distance restraint. All calculations were performed using the CrystalStructure interface.[9] Crystallographic data for the four structures are listed in Table **S1**.

Table S1. Crystal Data and Structure Refinement.

	1	**2**	**3**	**4**
empirical formula	$C_{46}H_{58}F_6IrN_8O_5P$	$C_{42}H_{42}F_{12}IrN_8O_4P$	$C_{47}H_{54.5}F_{12}IrN_{12.5}O_5P_2$	$C_{84}H_{77}F_{30}Ir_2N_{22}O_9P_3$
fw	1140.20	1174.02	1356.68	2585.99
crystal description	yellow platelet	yellow chip	yellow rod	yellow prism
crystal size [mm^3]	0.21×0.20×0.01	0.10×0.03×0.03	0.26×0.02×0.02	0.13×0.10×0.07
space group	$P\bar{1}$	$P\bar{1}$	$I2/a$	$P2_1/n$
a [Å]	11.876(3)	13.3398(14)	28.958(11)	13.7823(11)
b [Å]	15.659(3)	14.351(2)	13.786(6)	28.040(2)
c [Å]	17.043(5)	15.983(2)	30.357(9)	27.901(2)
α [°]	105.00(3)	80.569(13)		
β [°]	110.179(19)	67.093(10)	115.07(3)	97.757(2)
γ [°]	104.28(3)	74.566(12)		
vol [Å]^3	2668.9(15)	2710.6(6)	10978(8)	10683.8(14)
Z	2	2	8	4
ρ (calc) [g/cm^3]	1.419	1.438	1.642	1.608
μ [mm^{-1}]	5.614	2.584	2.595	2.654
F(000)	1152	1164	5432	5104
reflns collected	31358	21828	43322	171298
independent reflns (R_{int})	9020 (0.0850)	9455 (0.2372)	9801 (0.2646)	19713 (0.0629)
data/restraints/ params	9020/39/619	9455/633/620	9801/1/733	19713/32/1395
GOF on F^2	1.183	1.053	0.918	1.144
R_1 [$I > 2\sigma(I)$]	0.1146	0.1078	0.0485	0.0430
wR_2 (all data)	0.3194	0.3071	0.0966	0.1259
largest diff. peak/hole [e/Å^3]	7.30, -2.75	2.31, -1.02	1.48, -1.97	2.37, -0.68

DFT Calculations:

Computational details:

All calculations were performed with the Gaussian09, revision D.01[10] suite of programs employing the DFT method, the Becke three-parameter hybrid functional,[11] and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).[12] Singlet and triplet ground state geometry optimizations and single point energy calculations for [**1**]$^+$, [**2**]$^+$, [**3**]$^+$, [**4**]$^+$ were carried out at the (R)B3LYP and (U)B3LYP levels, using their respective crystallographic structures as starting points. All elements except Iridium were assigned the 6-31G(d,p) basis set.[13] The double-ζ quality SBKJC VDZ ECP basis set[14] with an effective core potential was employed for the Ir(III)-ion. Vertical electronic excitations based on (R)B3LYP-optimized geometries were computed for [**1**]$^+$, [**2**]$^+$, [**3**]$^+$ and [**4**]$^+$ using the TD-DFT formalism[15] in acetonitrile using conductor-like polarizable continuum model (CPCM).[16] Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. The electronic distribution and localization of the singlet excited states were visualized using the electron density difference maps (ED-DMs).[17] *Gausssum 2.2* and *Chemissian* v3.8[18] were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 cm^{-1}) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures and Kohn-Sham orbitals were visualized with ChemCraft.[19]

Table S2. Selected transitions from TD-DFT calculations of [**1**]$^+$ in the singlet ground state (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S], CPCM (MeCN)).

state	λ_{abs}/nm (TD-DFT)	λ_{abs}/nm (ε x10^4 M^{-1}cm^{-1}) [expt.]	f (TD-DFT)	Major transition(s)	character

38	259	264 (6.49)	0.3259	H-1->L+6 (55%), H->L+7 (23%)	Mepypyrm(π) to Mepypyrm(π*)(major) + Ir(dπ) to Mepypyrm(π*) (minor)
15	300	300 (3.45)	0.0635	H-2->L+1 (81%)	Mepypyrm(π) to Mepypyrm(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor)
12	310	311 (sh) (3.08)	0.0925	H-1->L+3 (81%)	Mepypyrm(π) to Mepypyrm(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor)
6	331	335 (1.71)	0.0438	H->L+3 (87%)	Mepypyrm(π) to Mepypyrm(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor)
4	344	361 (0.90)	0.1091	H->L+1 (88%)	Mepypyrm(π) to Mepypyrm(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor)

Table S3. Selected transitions from TD-DFT calculations of [**2**]$^+$ in the singlet ground state (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S], CPCM (MeCN)).

state	λ_{abs}/nm (TD-DFT)	λ_{abs}/nm (ε x10^4 M^{-1}cm^{-1}) [expt.]	f (TD-DFT)	Major transition(s)	character
42	255	261 (5.61)	0.1428	H-5->L+4 (15%), H-3->L+4 (18%), H-3->L+5 (45%)	CF$_3$pypyrm(π) to CF$_3$pypyrm(π*) (major) + CF$_3$pypyrm(π) to d*t*Bubpy(π*) (minor) + Ir(dπ) to CF$_3$pypyrm(π*) (minor) + Ir(dπ) to d*t*Bubpy(π*) (minor)
32	271	275 (sh) (4.63)	0.2389	H-7->L (15%), H-4->L+3 (47%), H-2->L+3 (19%)	Ir(dπ) to d*t*Bubpy(π*) (major) + CF$_3$pypyrm(π) to d*t*Bubpy(π*) (minor) + d*t*Bubpy(π) to d*t*Bubpy(π*) (minor)
24	289	297 (sh) (3.10)	0.1627	H->L+6 (62%)	CF$_3$pypyrm(π) to CF$_3$pypyrm(π*) (major) + Ir(dπ) to CF$_3$pypyrm(π*) (minor)
14	307	311 (2.50)	0.0283	H-4->L+1 (77%)	Ir(dπ) to CF$_3$pypyrm(π*) (major) + CF$_3$pypyrm(π) to CF$_3$pypyrm(π*) (minor)
3	357	350 (1.53)	0.1475	H->L+1 (88%)	CF$_3$pypyrm(π) to CF$_3$pypyrm(π*) (major) + Ir(dπ) to CF$_3$pypyrm(π*) (minor)
1	392	384 (0.69)	0.0005	H->L (97%)	CF$_3$pypyrm(π) to d*t*Bubpy(π*) (major) +

					Ir(dπ) to d*t*Bubpy(π*) (minor)

Table S3. Selected transitions from TD-DFT calculations of [**3**]$^+$ in the singlet ground state (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S], CPCM (MeCN)).

state	λ_{abs}/nm (TD-DFT)	λ_{abs}/nm (ε x10^4 M^{-1}cm^{-1}) [expt.]	f (TD-DFT)	Major transition(s)	character
30	262	268 (3.94)	0.2771	H-2->L+3 (27%), H-1->L+5 (35%), H->L+7 (12%)	Mepypyrm(π) to Mepypyrm(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor) + BIM(π*) to Mepypyrm(π*) (minor)
7	313	322 (sh) (1.46)	0.1179	H-2->L (27%), H-2->L+1 (12%), H-1->L+2 (32%)	Mepypyrm(π) to Mepypyrm(π*) (major) + *o*-Xylbiim(π) to *o*-Xylbiim(π*) (minor) + *o*-Xylbiim(π) to Mepypyrm(π*) (minor) + Ir(dπ) to Mepypyrm(π*) (minor) + Ir(dπ) to *o*-Xylbiim(π*) (minor)
3	332	339 (1.23)	0.0326	H->L+2 (87%)	Mepypyrm(π) to Mepypyrm(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor)
1	345	369 (0.41)	0.0938	H->L (48%), H->L+1 (40%)	Mepypyrm(π) to *o*-Xylbiim(π*) (major) + Ir(dπ) to Mepypyrm(π*) (minor) + Ir(dπ) to *o*-Xylbiim(π*) (minor)

Table S3. Selected transitions from TD-DFT calculations of [**4**]$^+$ in the singlet ground state (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S], CPCM (MeCN)).

state	λ_{abs}/nm (TD-DFT)	λ_{abs}/nm (ε x10^4 M^{-1}cm^{-1}) [expt.]	f (TD-DFT)	Major transition(s)	character
25	277	276 (4.05)	0.4359	H-2->L+4 (59%)	CF$_3$pypyrm(π) to CF$_3$pypyrm(π*)
13	303	315 (sh) (1.84)	0.1172	H-5->L (10%), H-3->L+1 (15%), H-1->L+2 (48%)	*o*-Xylbiim(π) to *o*-Xylbiim(π*) (major) + Ir(dπ) to CF$_3$pypyrm(π*) (minor)
2	348	352 (1.16)	0.0304	H->L+1 (86%)	CF$_3$pypyrm(π) to CF$_3$pypyrm(π*) (major) + Ir(dπ) to CF$_3$pypyrm(π*) (minor)
1	364	388 (0.42)	0.1327	H->L (87%)	CF$_3$pypyrm(π) to CF$_3$pypyrm(π*) (major) +

					Ir(dπ) to CF_3pypyrm(π*) (minor)

Table S4. Optimized Atomic coordinates obtained from DFT calculations of [**1**]$^+$.

			Coordinates (Angstroms)		
Center Number	Atomic Number	Atomic Type	X	Y	Z
1	77	0	0.318863	0.000003	-0.000003
2	8	0	3.876994	2.099077	3.286325
3	8	0	3.498809	4.154366	-0.726867
4	8	0	3.876922	-2.099178	-3.286339
5	8	0	3.498703	-4.154435	0.726862
6	7	0	0.474081	1.235324	-1.680149
7	7	0	2.334862	1.193818	1.829584
8	7	0	3.681688	3.104598	1.299172
9	7	0	0.474047	-1.235315	1.680138
10	7	0	2.334820	-1.193870	-1.829598
11	7	0	3.681608	-3.104675	-1.299175
12	7	0	-1.449703	-1.166103	-0.657477
13	7	0	-1.449693	1.166137	0.657428
14	6	0	1.418210	2.223478	-1.595856
15	6	0	1.633248	3.073447	-2.692790
16	1	0	2.383200	3.846814	-2.604065
17	6	0	0.905567	2.925252	-3.871660
18	6	0	-0.047583	1.895282	-3.923679
19	1	0	-0.641570	1.724171	-4.815472
20	6	0	-0.225772	1.082150	-2.818615
21	1	0	-0.942935	0.270450	-2.827610
22	6	0	2.116253	2.260040	-0.319393
23	6	0	1.760138	1.254897	0.616235
24	6	0	3.263378	2.115156	2.098813
25	6	0	3.112761	3.174182	0.105631
26	6	0	3.523993	1.063685	4.210826
27	1	0	3.712299	0.075546	3.783705
28	1	0	2.469539	1.130852	4.491720
29	1	0	4.159610	1.231277	5.080685
30	6	0	4.524678	5.055433	-0.265235
31	1	0	5.444666	4.510778	-0.044155
32	1	0	4.199864	5.581829	0.634408
33	1	0	4.677489	5.754009	-1.087703
34	6	0	1.124141	3.840293	-5.048340
35	1	0	0.252290	4.486372	-5.203916
36	1	0	1.267885	3.268375	-5.970849
37	1	0	1.996045	4.481414	-4.901795

38	6	0	1.418154	-2.223478	1.595849
39	6	0	1.633162	-3.073468	2.692787
40	1	0	2.383072	-3.846872	2.604049
41	6	0	0.905487	-2.925260	3.871648
42	6	0	-0.047680	-1.895291	3.923651
43	1	0	-0.641715	-1.724207	4.815419
44	6	0	-0.225831	-1.082147	2.818600
45	1	0	-0.943013	-0.270465	2.827571
46	6	0	2.116196	-2.260072	0.319389
47	6	0	1.760105	-1.254925	-0.616246
48	6	0	3.263316	-2.115231	-2.098823
49	6	0	3.112677	-3.174244	-0.105634
50	6	0	3.523988	-1.063743	-4.210823
51	1	0	3.712236	-0.075625	-3.783637
52	1	0	2.469561	-1.130919	-4.491817
53	1	0	4.159683	-1.231288	-5.080634
54	6	0	4.524563	-5.055515	0.265236
55	1	0	5.444557	-4.510872	0.044158
56	1	0	4.199745	-5.581911	-0.634407
57	1	0	4.677363	-5.754092	1.087706
58	6	0	1.124246	-3.840076	5.048469
59	1	0	1.993642	-4.484164	4.900093
60	1	0	0.250680	-4.483049	5.207129
61	1	0	1.272511	-3.267787	5.970061
62	6	0	-2.670359	-0.663134	-0.335290
63	6	0	-3.836062	-1.373872	-0.623041
64	1	0	-4.793734	-0.957117	-0.338686
65	6	0	-3.793693	-2.623514	-1.260376
66	6	0	-2.520286	-3.104876	-1.587326
67	1	0	-2.385437	-4.058212	-2.081752
68	6	0	-1.390850	-2.358064	-1.269397
69	1	0	-0.395712	-2.716892	-1.507629
70	6	0	-2.670355	0.663156	0.335283
71	6	0	-1.390828	2.358116	1.269314
72	1	0	-0.395684	2.716956	1.507504
73	6	0	-2.520259	3.104928	1.587259
74	1	0	-2.385401	4.058282	2.081648
75	6	0	-3.793673	2.623542	1.260375
76	6	0	-3.836054	1.373887	0.623065
77	1	0	-4.793733	0.957120	0.338753
78	6	0	-5.089811	3.390415	1.558641
79	6	0	-5.827102	3.670886	0.226192
80	1	0	-6.098581	2.748976	-0.297024
81	1	0	-5.210961	4.273789	-0.448295
82	1	0	-6.751620	4.222480	0.423060

83	6	0	-5.989173	2.528543	2.477802
84	1	0	-5.494018	2.314704	3.430331
85	1	0	-6.258296	1.574282	2.014689
86	1	0	-6.919040	3.063582	2.693762
87	6	0	-4.816463	4.733924	2.260151
88	1	0	-4.207418	5.402555	1.643161
89	1	0	-4.315819	4.598715	3.224376
90	1	0	-5.764866	5.242829	2.453737
91	6	0	-5.089835	-3.390390	-1.558618
92	6	0	-4.816499	-4.733890	-2.260147
93	1	0	-4.315925	-4.598668	-3.224407
94	1	0	-5.764902	-5.242822	-2.453669
95	1	0	-4.207395	-5.402507	-1.643200
96	6	0	-5.989217	-2.528507	-2.477749
97	1	0	-6.919076	-3.063556	-2.693720
98	1	0	-5.494073	-2.314629	-3.430275
99	1	0	-6.258354	-1.574266	-2.014603
100	6	0	-5.827099	-3.670878	-0.226158
101	1	0	-5.210958	-4.273818	0.448295
102	1	0	-6.751638	-4.222441	-0.423020
103	1	0	-6.098539	-2.748976	0.297092

Table S5. Optimized Atomic coordinates obtained from DFT calculations of [**2**]$^+$.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	77	0	-0.449070	0.000135	-0.000017
2	9	0	-0.402809	-5.950744	-0.266060
3	9	0	1.568591	-5.127432	-0.666146
4	9	0	0.480815	-6.181308	-2.239739
5	9	0	0.482321	6.181927	2.239136
6	9	0	1.572219	5.126622	0.667965
7	9	0	-0.398522	5.949751	0.264386
8	8	0	-3.823434	3.336995	-2.295816
9	8	0	-3.552577	-0.757806	-4.201894
10	8	0	-3.824862	-3.335101	2.296065
11	8	0	-3.551386	0.759348	4.202509
12	7	0	-0.645471	-1.717727	-1.170064
13	7	0	-2.388246	1.845150	-1.282638
14	7	0	-3.686913	1.309570	-3.227189
15	7	0	-0.644464	1.718071	1.170085
16	7	0	-2.389052	-1.843940	1.282760

17	7	0	-3.687043	-1.307846	3.227616
18	7	0	1.317076	-0.650673	1.172398
19	7	0	1.317288	0.650133	-1.172544
20	6	0	-1.579421	-1.638220	-2.173948
21	6	0	-1.844667	-2.775082	-2.959672
22	1	0	-2.565300	-2.696639	-3.760592
23	6	0	-1.206094	-3.973794	-2.685759
24	1	0	-1.416024	-4.857906	-3.278331
25	6	0	-0.287806	-4.035372	-1.632289
26	6	0	-0.033220	-2.880070	-0.908182
27	1	0	0.674404	-2.879040	-0.089797
28	6	0	-2.218382	-0.341318	-2.278237
29	6	0	-1.860652	0.610787	-1.288301
30	6	0	-3.269815	2.125366	-2.248525
31	6	0	-3.168717	0.092201	-3.239811
32	6	0	-3.482359	4.283101	-1.272178
33	1	0	-2.415810	4.520957	-1.287468
34	1	0	-3.745864	3.897561	-0.284228
35	1	0	-4.070469	5.171233	-1.502967
36	6	0	-4.526067	-0.289756	-5.159504
37	1	0	-4.143153	0.575188	-5.704155
38	1	0	-5.454506	-0.012179	-4.657171
39	1	0	-4.686147	-1.131697	-5.832272
40	6	0	0.346295	-5.329355	-1.207556
41	6	0	-1.578236	1.638945	2.174199
42	6	0	-1.842722	2.775860	2.960069
43	1	0	-2.563199	2.697719	3.761157
44	6	0	-1.203620	3.974299	2.686102
45	1	0	-1.412982	4.858465	3.278790
46	6	0	-0.285598	4.035519	1.632411
47	6	0	-0.031745	2.880128	0.908144
48	1	0	0.675705	2.878819	0.089603
49	6	0	-2.217816	0.342347	2.278521
50	6	0	-1.860782	-0.609866	1.288439
51	6	0	-3.270594	-2.123767	2.248782
52	6	0	-3.168190	-0.090757	3.240250
53	6	0	-3.484511	-4.281288	1.272262
54	1	0	-2.418102	-4.519788	1.287361
55	1	0	-3.747935	-3.895474	0.284398
56	1	0	-4.073114	-5.169098	1.503037
57	6	0	-4.524942	0.291716	5.160256
58	1	0	-4.142413	-0.573531	5.704696
59	1	0	-5.453647	0.014749	4.658076
60	1	0	-4.684396	1.133649	5.833182
61	6	0	0.349177	5.329119	1.207511

62	6	0	2.537860	-0.338584	0.661566
63	6	0	3.704981	-0.643954	1.362071
64	1	0	4.662878	-0.371544	0.938513
65	6	0	3.666154	-1.288777	2.608045
66	6	0	2.392960	-1.604139	3.097622
67	1	0	2.260096	-2.104611	4.048017
68	6	0	1.261726	-1.269924	2.361559
69	1	0	0.268248	-1.504796	2.726680
70	6	0	2.537966	0.337490	-0.661799
71	6	0	1.262135	1.269414	-2.361702
72	1	0	0.268738	1.504749	-2.726745
73	6	0	2.393470	1.603107	-3.097847
74	1	0	2.260769	2.103664	-4.048220
75	6	0	3.666554	1.287127	-2.608380
76	6	0	3.705175	0.642307	-1.362397
77	1	0	4.662974	0.369441	-0.938907
78	6	0	4.965318	1.608324	-3.360456
79	6	0	5.841113	2.536070	-2.483259
80	1	0	6.771579	2.771287	-3.008905
81	1	0	6.110254	2.070221	-1.530331
82	1	0	5.328280	3.478414	-2.266531
83	6	0	5.724838	0.288222	-3.640522
84	1	0	5.994993	-0.236518	-2.719093
85	1	0	6.651954	0.502602	-4.180938
86	1	0	5.125742	-0.391888	-4.254169
87	6	0	4.694505	2.313534	-4.702535
88	1	0	4.100583	1.691896	-5.380492
89	1	0	5.644882	2.522734	-5.201280
90	1	0	4.180033	3.270361	-4.566764
91	6	0	4.964831	-1.610669	3.359978
92	6	0	4.693787	-2.315625	4.702145
93	1	0	4.100270	-1.693609	5.380111
94	1	0	4.178792	-3.272189	4.566515
95	1	0	5.644108	-2.525299	5.200801
96	6	0	5.725193	-0.291021	3.639861
97	1	0	5.995550	0.233525	2.718382
98	1	0	5.126599	0.389478	4.253567
99	1	0	6.652255	-0.505946	4.180154
100	6	0	5.839930	-2.539008	2.482706
101	1	0	6.109235	-2.073366	1.529723
102	1	0	6.770312	-2.774805	3.008243
103	1	0	5.326459	-3.481028	2.266081

Table S6. Optimized Atomic coordinates obtained from DFT calculations of [**3**]$^+$.

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         77           0        0.202869   -0.085988   -0.097775
      2          8           0        3.030572    0.873059    4.158601
      3          8           0        4.313128   -2.829288    1.759532
      4          8           0        3.845395    1.270317   -3.665373
      5          8           0        1.944771    4.714966   -1.427343
      6          7           0        1.056588   -1.827283   -0.880623
      7          7           0        1.868822    0.402319    2.296320
      8          7           0        3.704457   -0.980755    2.976609
      9          7           0       -0.352004    1.759735    0.708136
     10          7           0        2.261345    0.700731   -2.088340
     11          7           0        2.897795    2.963831   -2.553363
     12          7           0       -1.576177   -0.028965   -1.440433
     13          7           0       -3.676912   -0.544777   -1.929904
     14          7           0       -1.383676   -1.294569    0.894758
     15          7           0       -3.404803   -2.203844    0.949133
     16          6           0        2.141034   -2.306998   -0.197145
     17          6           0        2.811825   -3.446593   -0.670841
     18          1           0        3.663688   -3.811016   -0.114149
     19          6           0        2.398404   -4.093108   -1.833562
     20          6           0        1.290095   -3.563620   -2.514558
     21          1           0        0.925136   -4.016958   -3.430501
     22          6           0        0.659221   -2.440580   -2.009358
     23          1           0       -0.189819   -1.995203   -2.513741
     24          6           0        2.476849   -1.529732    0.986245
     25          6           0        1.669272   -0.380490    1.231594
     26          6           0        2.874035    0.059550    3.108283
     27          6           0        3.503250   -1.769052    1.922908
     28          6           0        4.097227    0.594878    5.073525
     29          1           0        5.066092    0.628266    4.568370
     30          1           0        3.972690   -0.387912    5.536238
     31          1           0        4.037729    1.378645    5.828879
     32          6           0        5.358227   -3.033080    2.726645
     33          1           0        4.939889   -3.183096    3.724371
     34          1           0        6.037471   -2.178212    2.749162
     35          1           0        5.882184   -3.928867    2.393402
     36          6           0        3.112820   -5.315504   -2.348750
     37          1           0        3.478511   -5.154342   -3.368770
     38          1           0        2.437064   -6.177422   -2.383377
     39          1           0        3.965576   -5.578004   -1.718909
     40          6           0        0.293446    2.846351    0.183368
```

41	6	0	0.013238	4.127937	0.681976
42	1	0	0.530831	4.972587	0.249689
43	6	0	-0.900408	4.312109	1.717502
44	6	0	-1.532340	3.172552	2.239131
45	1	0	-2.246638	3.248999	3.052338
46	6	0	-1.228612	1.929609	1.713252
47	1	0	-1.684789	1.026807	2.100213
48	6	0	1.244527	2.510582	-0.866332
49	6	0	1.399552	1.129542	-1.150023
50	6	0	2.962973	1.638186	-2.728307
51	6	0	2.046957	3.391209	-1.632428
52	6	0	4.014695	-0.129528	-3.910990
53	1	0	3.082769	-0.584218	-4.257649
54	1	0	4.343780	-0.649547	-3.007575
55	1	0	4.779080	-0.191817	-4.686244
56	6	0	2.790170	5.577429	-2.211941
57	1	0	2.584216	5.456243	-3.277372
58	1	0	3.843565	5.356477	-2.028218
59	1	0	2.545207	6.587613	-1.883900
60	6	0	-1.186643	5.681954	2.275277
61	1	0	-0.735602	6.466724	1.663954
62	1	0	-0.786783	5.774972	3.291657
63	1	0	-2.264128	5.867599	2.335246
64	6	0	-2.661888	-0.700184	-1.025867
65	6	0	-3.194430	0.260853	-2.942957
66	1	0	-3.810012	0.533030	-3.785966
67	6	0	-1.897824	0.571840	-2.625336
68	1	0	-1.187404	1.180577	-3.162898
69	6	0	-2.549009	-1.408110	0.239134
70	6	0	-1.490861	-2.027626	2.043627
71	1	0	-0.677670	-2.095361	2.749561
72	6	0	-2.737694	-2.595271	2.093252
73	1	0	-3.204540	-3.235925	2.824870
74	6	0	-4.790996	-2.600860	0.634169
75	1	0	-5.108210	-3.250948	1.450706
76	1	0	-4.776862	-3.216380	-0.269388
77	6	0	-5.732703	-1.424381	0.511878
78	6	0	-5.846114	-0.707221	-0.693603
79	6	0	-6.716940	0.386364	-0.762031
80	1	0	-6.812295	0.936248	-1.694529
81	6	0	-7.470393	0.770897	0.346048
82	1	0	-8.146928	1.616488	0.273766
83	6	0	-7.359179	0.058639	1.540691
84	1	0	-7.949022	0.344980	2.405603
85	6	0	-6.494063	-1.031808	1.618624

86	1	0	-6.414872	-1.590514	2.547403
87	6	0	-5.045798	-1.098442	-1.915420
88	1	0	-4.980813	-2.183459	-2.035649
89	1	0	-5.530493	-0.713120	-2.813443

Table S7. Optimized Atomic coordinates obtained from DFT calculations of [**4**]$^+$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	0.371609	-0.083190	-0.024894
2	9	0	-4.815497	-4.196093	0.525118
3	9	0	-4.577100	-2.489298	-0.815973
4	9	0	-3.570550	-4.365820	-1.249788
5	9	0	2.417834	5.073508	0.408903
6	9	0	4.296272	5.238988	-0.692170
7	9	0	4.240170	4.220353	1.228857
8	8	0	4.438607	-0.242672	3.321123
9	8	0	1.120693	-3.202327	4.161871
10	8	0	1.097431	-4.465741	-2.857494
11	8	0	3.981169	-1.090774	-3.736166
12	7	0	-0.871182	-1.595461	0.696986
13	7	0	2.671632	-0.224319	1.841867
14	7	0	2.794906	-1.701743	3.727770
15	7	0	1.895012	1.161727	-0.715569
16	7	0	0.830933	-2.556160	-1.594866
17	7	0	2.519160	-2.794042	-3.282630
18	7	0	-0.747015	1.466986	1.113871
19	7	0	-2.317524	3.023165	1.271457
20	7	0	-1.093621	0.801839	-1.442609
21	7	0	-2.720647	2.222235	-1.940011
22	6	0	-0.385629	-2.281525	1.783080
23	6	0	-1.116772	-3.371069	2.292003
24	1	0	-0.736830	-3.892400	3.158427
25	6	0	-2.287340	-3.773673	1.669579
26	1	0	-2.848751	-4.621257	2.047997
27	6	0	-2.737896	-3.078733	0.541997
28	6	0	-2.000685	-1.991155	0.096383
29	1	0	-2.311384	-1.420058	-0.768727
30	6	0	0.889970	-1.789451	2.263224
31	6	0	1.485922	-0.751243	1.499074
32	6	0	3.259092	-0.727809	2.931871
33	6	0	1.626845	-2.226250	3.394720

34	6	0	5.053948	0.775569	2.519152
35	1	0	6.008633	0.977498	3.004844
36	1	0	4.445733	1.683020	2.489421
37	1	0	5.212979	0.421754	1.497559
38	6	0	1.899512	-3.631435	5.298276
39	1	0	2.053746	-2.803757	5.993073
40	1	0	2.870823	-4.011234	4.976094
41	1	0	1.309200	-4.421234	5.761993
42	6	0	-3.933229	-3.533235	-0.244936
43	6	0	2.725251	0.604060	-1.656921
44	6	0	3.830774	1.339742	-2.122179
45	1	0	4.466049	0.900381	-2.877356
46	6	0	4.102835	2.592935	-1.597078
47	1	0	4.961002	3.159922	-1.941768
48	6	0	3.260535	3.120448	-0.612768
49	6	0	2.164822	2.371320	-0.208479
50	1	0	1.482544	2.738902	0.546788
51	6	0	2.351859	-0.742458	-2.039942
52	6	0	1.261445	-1.312653	-1.331295
53	6	0	1.482077	-3.226069	-2.551020
54	6	0	2.948536	-1.568798	-3.027428
55	6	0	0.023298	-5.050251	-2.107358
56	1	0	-0.084309	-6.057972	-2.508656
57	1	0	-0.906203	-4.490429	-2.237025
58	1	0	0.268817	-5.088217	-1.043178
59	6	0	4.567433	-1.956459	-4.730713
60	1	0	3.827568	-2.230492	-5.485067
61	1	0	4.956590	-2.864918	-4.267285
62	1	0	5.373321	-1.371619	-5.173175
63	6	0	3.556003	4.421115	0.077363
64	6	0	-1.704945	2.126142	0.441990
65	6	0	-1.713667	2.909559	2.507600
66	1	0	-2.020829	3.520268	3.342030
67	6	0	-0.747153	1.944135	2.395354
68	1	0	-0.063330	1.569369	3.141092
69	6	0	-1.886304	1.770795	-0.956474
70	6	0	-1.422447	0.629569	-2.758798
71	1	0	-0.922528	-0.098593	-3.378534
72	6	0	-2.430699	1.500674	-3.080455
73	1	0	-2.959137	1.672883	-4.004950
74	6	0	-3.771118	3.259836	-1.875071
75	1	0	-4.205314	3.305508	-2.874645
76	1	0	-3.289913	4.225204	-1.697145
77	6	0	-4.846667	2.955702	-0.857407
78	6	0	-4.679074	3.288846	0.499543

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    79          6           0       -5.694998    2.982081    1.412031
    80          1           0       -5.571984    3.247373    2.458695
    81          6           0       -6.865675    2.351666    0.992876
    82          1           0       -7.647134    2.127371    1.711808
    83          6           0       -7.031648    2.021216   -0.352529
    84          1           0       -7.942853    1.537158   -0.688955
    85          6           0       -6.025618    2.323633   -1.268963
    86          1           0       -6.160438    2.073005   -2.317767
    87          6           0       -3.419471    3.966792    0.987804
    88          1           0       -3.054094    4.720879    0.285534
    89          1           0       -3.615516    4.483706    1.928053
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Device preparation and characterization

LEEC preparation. LEECs were prepared on top of a patterned indium tin oxide (ITO, 15 Ω sq^{-1}) coated glass substrate (www.naranjosubstrates.com) previously cleaned as follows: a) sonication with soap, b) deionized water, c) isopropanol, and d) UV–O_3 lamp for 20 min. The thickness of the films was determined with an Ambios XP-1 profilometer. Prior to the deposition of the emitting layer, 80 nm of poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) (CLEVIOS™ P VP AI 4083, aqueous dispersion, 1.3–1.7% solid content, Heraeus) was coated in order to avoid the formation of pinholes and to increase the reproducibility of the cells. The emitting layer (100 nm) was prepared by spin-coating of an acetonitrile solution consisting of the iTMC (**1-4**) with the addition of the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] (> 98.5%, Sigma-Aldrich) in a 4:1 molar ratio (iTMC:IL). The devices were then transferred to an inert atmosphere glovebox (< 0.1 ppm O_2 and H_2O, MBraun) and annealed during 1 hour at 100 °C. Finally, a layer (70 nm) of aluminium (the top electrode) was thermally evaporated onto the devices using an Edwards Auto500 evaporator integrated in the inert atmosphere glovebox. The area of the device was 6.5 mm^2. The devices were not encapsulated and were characterized inside the glovebox at room temperature.

LEEC characterization: The device lifetime was measured by applying a pulsed current and monitoring the voltage and the luminance versus time by a True Colour Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System. The average current density, due to the duty cycle of 50%, corresponds to one-half of the peak current density. The average luminance was directly obtained by taking the average of the obtained photodiode results and correlating it to the value obtained from a luminance meter. The current efficiency was obtained by dividing the average luminance by the average current density. The electroluminescent (EL) spectra were measured using an Avantes AvaSpec-2048 Fiber Optic Spectrometer during device lifetime measurement.

OLED preparation: For the OLED preparation, the following materials were purchased from Luminescence Technology Corporation (Lumtec) and used as received: *N*4,*N*4'-di(naphthalen-1-yl)-*N*4,*N*4'-bis(4-vinylphenyl)biphenyl-4,4'-diamine (VNPB), 4,4',4"-tris(carbazol-9-yl)triphenylamine (TcTa), 2,7-bis(diphenylphosphoryl)-9,9'-spirobifluorene (SPPO13) and 1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (BmPyPhB). The OLED device was prepared using patterned indium-tin-oxide (ITO) glass substrates sequentially cleaned with soap, de-ionized water, isopropanol and UV-O_3 lamp for 20 min. The hole injection layer (HIL), hole transport layer (HTL) and emissive layer (EML) were added by spin-coating while the electron transport layer (ETL) and top electrode were thermally evaporated using an Edwards Auto500 evaporator integrated in the glovebox. The thickness of films was determined with an Ambios XP-1 profilometer. First, a 30 nm of poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) (CLEVIOS™ P VP CH8000, aqueous dispersion, 2.4 – 3.0% solids, Heraeus) was coated and dried in air (70ºC, 5 minutes). Then, the substrates were transferred to inert atmosphere and annealed at 170ºC during 30 minutes. A VNPB HTL (35nm) was spin-coated from 10 mg mL^{-1} toluene solution. After VNPB coating, the substrates were annealed inside a glovebox at 180 ºC for 30 minutes to make the HTL resistant to toluene. Then, the EML (30 nm) were spin-coated from 10 mg mL^{-1} anisole solution inside the glovebox. The EML consisted on a mixture of TcTa, SPPO13 and **1**, where the concentration of the emitter was 10 wt% (solids). Subsequently, 40 nm of BmPyPhB ETL, 5 nm of barium and silver (70nm) top electrode was thermally evaporated.

OLED characterization: The devices were characterized in inert atmosphere without encapsulation. The current versus voltage (J-V) and luminance versus voltage (L-V) curves were obtained using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 picoampmeter using a Minolta LS100 to calibrate the photocurrent. The electroluminescent spectra were measured using an Avantes AvaSpec-2048 Fiber Optic Spectrometer.

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