Supplementary Information

for

1,12-Diazaperylene and 2,11-Dialkylated-1,12-Diazaperylene Iridium(III) Complexes $[Ir(C^\wedge N)_2(N^\wedge N)]PF_6$: New Supramolecular Assemblies by π-π Stacking and CH-π Interactions in the Solid State, and Photophysical and Electrochemical Properties and Stability Measurements in the Gas Phase

Stefan Kammer,[a] Ines Starke,[b] Andreas Pietrucha,[a] Alexandra Kelling,[a] Wulfhard Mickler,[a] Uwe Schilde,[a] Carsten Dosche,[c] Erich Kleinpeter[b] and Hans-Jürgen Holdt*[a]

[a] Universität Potsdam, Institut für Chemie, Anorganische Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany.
Fax:+49 3319775055; Tel: +49 3319775180; E-mail: holdt@chem.uni-potsdam.de
[b] Universität Potsdam, Institut für Chemie, Analytische Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam , Germany.
[c] Carl von Ossietzky Universität Oldenburg, Institut für Reine und Angewandte Chemie, Postfach 2503, 26111 Oldenburg.

1 General

All reagents and chemicals were procured from commercial sources and used without further purification. NMR spectra were recorded with an Avance 300 spectrometer. IR spectra were recorded with a Thermo Nicolet NEXUS FTIR instrument. UV/VIS measurements were carried out with a Perkin Elmer UV/VIS Spectrometer Lambda 2 using sealed quartz cuvettes. The ESI spectra were recorded using a Micromass Q-TOF$_{micro}$ mass spectrometer in positive electrospray mode. Elemental analyses (C, H, N, S) were performed with an Elementar Vario EL elemental analyzer. For room-temperature luminescence measurements, a Spectronics Instrument 8100 spectrofluorometer with T-optics configuration was employed, allowing for the detection of luminescence in the wavelength ranges 300–750 and 650–1100 nm. Luminescence measurements at 77 K were performed with a Perkin Elmer LS50B fluorometer equipped with a low-temperature accessory unit (detection range 250–850 nm). Solutions adjusted to optical densities of 0.05, 0.1 and 0.3 at the MLCT absorption maximum were employed. Electrochemical measurements were performed with a BAS 100B system using a glassy carbon electrode as working electrode, a platinum wire as auxiliary electrode and a $Ag/AgNO_3$ electrode as working electrode. The experiments were conducted in degassed CH_3CN solutions using 0.1 M $[nBu_4N][PF_6]$ as the supporting electrolyte and the ferrocene/ferrocinium (Fc/Fc^+) couple as a reference. 2-Phenylpyrine, 1-phenylpyrazole were obtained from Merck, 2-(p-tolyl)pyridine,2-(2,4-difluorophenyl)pyridine, benzo[*h*]quinoline, 2-(2,4-difluorophenyl)pyridine from Aldrich and 2-(2-thienyl)pyridine, 1-phenylisoqinoline and $IrCl_3 \cdot xH_2O$ from ABCR. All reactions were carried out in dry solvents under an argon or nitrogen atmosphere. The cyclometalated iridium(III) chlorobridged dimers

$[Ir(C^\wedge N)_2Cl]_2$ (C^N = ppy, meppy, bzq, thpy),[1] $[Ir(ppz)_2Cl]_2$,[2] $[Ir(dfppy)_2Cl]_2$[3] and $[Ir(piq)_2Cl]_2$[4] were prepared according to literature methods.[5] The synthesis of α,α-diimin ligands dmedap and dipdap were synthesized by our previously reported procedure.[6] 1,12-Diazaperylen was prepared by the method reported by Thummel et al.[7]

2 Synthesis of the Ir(III) complexes

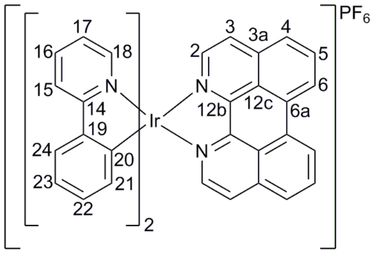
The iridium(III) complexes $[Ir(C^\wedge N)_2(dap)]PF_6$ (C^N = ppy, meppy, dfppy, thpy, ppz) were prepared by the same procedure. For these complexes only the synthesis of $[Ir(C^\wedge N)_2(dap)]PF_6$ is describe in detail.

Method A: The solution of $[Ir(C^\wedge N)_2Cl]_2$ (0.2 mmol, C^N = ppy, meppy, ppz, thpy,dfppy) and dap or dmedap (0.4 mmol, N^N = dap, dmedap) in CH_2Cl_2-MeOH (30 mL, 2:1 v/v) was heated to reflux. After 6 h, the solution was cooled to room temperature, and then a 10-fold excess of potassium hexafluorophosphate (0.736 g, 4 mmol) was added. The suspension was stirred for 2 h, and then it was filtered to remove insoluble inorganic salts. The solution was evaporated to dryness under reduce pressure. It was chromatographed with CH_2Cl_2/ acetone (3:1) on neutral Al_2O_3 to produce a green solid.

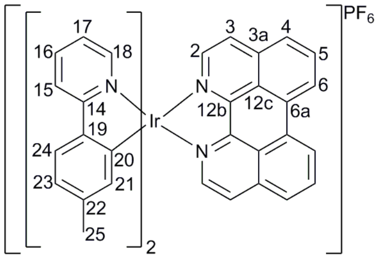
Method B: $[Ir(C^\wedge N)_2Cl]_2$ (0.2 mmol, C^N = bzq, piq) and dap or dipdap (0.4 mmol) were suspended in 10 mL degassed ethylene glycol. The mixture was heated to 150°C and stirred for 20 h at this temperature. After cooling to room temperature the reaction mixture is poured into 200 mL water and the solids were separated by filtration. The filtrate was extracted with CH_2Cl_2 (8 x 50 mL) and after that the combined organic phases were evaporated to dryness. After the solids were dissolved in CH_2Cl_2-MeOH (30 mL, 2:1 v/v) a 10-fold excess of potassium hexafluorophosphate (0.736 g, 4 mmol) was added. The suspension was stirred for 2 h, and then it was filtered to remove insoluble inorganic salts. The solution was evaporated to dryness under reduce pressure. First, It was chromatographed with THF on neutral Al_2O_3 to remove uncoordinated 1,12-diazaperylene and then with CH_2Cl_2/ acetone (3:1) to produce a green solid.

---

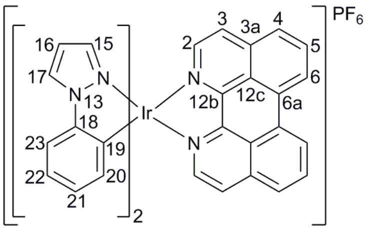
[1] M. S. Lowry, W. R. Hudson, R. A. Pascal, S. Bernhard, *J. Am. Chem. Soc.*, 2004, **126**, 14129.
[2] B. Geiß, C. Lambert, *Chem. Commun.*, 2009, 1670.
[3] Y. You, S. Y. Park, *J. Am. Chem. Soc.*, 2005, **127**, 12438.
[4] C.-H. Yang, C.-C. Tai, I.-W. Sun, *J. Mater. Chem.*, 2004, **14**, 947.
[5] K. Nonoyama, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 467.
[6] S. Kammer, A. kelling, H. Baier, W. Mickler, C. Dosche, K. Rurack, A. Kapp, F. Lisdat, H.-J. Holdt, *Eur. J. Inorg. Chem.*, 2009, **31**, 4648.
[7] A. Chouai, S. E. Wicke, C. Turro, J. Bacsa, K. R. Dunbar, D. Wang, R. P. Thummel, *Inorg. Chem.*, 2005, **44**, 5996.



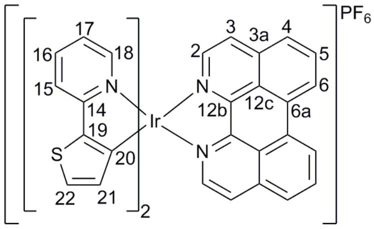
[Ir(ppy)$_2$(dap)]PF$_6$. As describe in method A from [Ir(ppy)$_2$Cl]$_2$ (0.214 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.325 g (90%). M. p.: >360°C. ^{1}H-NMR (300 MHz, CD$_3$CN): δ = 8.74 (dd, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.6 Hz, 2H, 4-H), 8.07-7.99 (m, 6H, 5-H, 6-H, 15-H), 7.95-7.89 (m, 4H, 18-H, 24-H), 7.86-7.76 (m, 4H, 3-H, 16-H), 7.61 (dd, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 0.6 Hz, 2H, 2-H), 7.09 (dt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.3 Hz, 2H, 22-H), 6.98 (dt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.3 Hz, 2H, 23-H), 6.91 (dt, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 1.4 Hz, 2H, 17-H), 6.37 (dd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 0.9 Hz, 2H, 21-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ□ = 168.5, 157.0, 156.7, 151.5, 150.2, 144.3, 139.4, 138.4, 134.3, 132.4, 131.0, 130.7, 128.0, 126.8, 125.7, 125.5, 125.0, 124.2, 123.2, 120.8 ppm. ESI-MS: m/z calcd. for [Ir(ppy)$_2$(dap)]$^+$ (C$_{40}$H$_{26}$N$_4$Ir): 755.1783, found 755.1781 and m/z calcd. for [Ir(ppy)$_2$]$^+$ (C$_{22}$H$_{16}$N$_2$Ir): 501.0943, found 501.0962. Elemental analysis (%) calcd. for C$_{40}$H$_{26}$F$_6$IrN$_4$P (899.86): C 53.39 H 2.91 N 6.23, found: C 53.46 H 2.93 N 6.37. IR (KBr pellet): v~ = 848 (s, P-F), 563 (m, P-F) cm^{-1}.



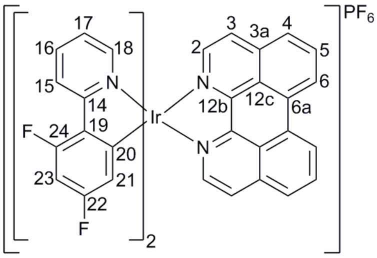
[Ir(meppy)$_2$dap]PF$_6$. As describe in method A from [Ir(meppy)$_2$Cl]$_2$ (0.226 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.364 g (98%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD$_3$CN): δ= 8.70 (dd, $^3J_{H,H}$ = 6.7, $^4J_{H,H}$ = 1.7 Hz, 2H, 4-H), 8.06-7.98 (m, 6H, 5-H, 6-H, 15-H), 7.94-7.89 (m, 4H, 18-H, 24-H), 7.78-7.72 (m, 4H, 3-H, 16-H), 7.56 (d, $^3J_{H,H}$ = 5.8 Hz, 2H, 2-H), 6.93-6.84 (m, 4H, 17-H, 23-H), 6.19 (s, 2H, 21-H), 2.16 (s, 6H, 25-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ = 168.5, 155.0, 151.7, 150.8, 143.9, 142.4, 141.6, 139.2, 137.5, 134.4, 133.1, 131.4, 128.9, 127.9, 126.7, 126.5, 125.8, 124.7, 123.9, 120.3, 21.8 ppm. ESI-MS: m/z calcd. for [Ir(meppy)$_2$(dap)]$^+$ (C$_{42}$H$_{30}$N$_4$Ir): 783.2100, found 783.2083 and m/z calcd. for [Ir(meppy)$_2$]$^+$ (C$_{24}$H$_{20}$N$_2$Ir): 529.1256, found 529.1266. Elemental analysis (%) calcd. for C$_{42}$H$_{30}$F$_6$IrN$_4$P (927.91): C 54.37 H 3.26 N 6.04, found: C 54.43 H 3.31 N 6.10. IR (KBr pellet): v~ = 850 (s, P-F), 562 (m, P-F) cm^{-1}.



[Ir(ppz)$_2$dap]PF$_6$. As describe in method A from [Ir(ppz)$_2$Cl]$_2$ (0.206 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.313 g (89%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD$_3$CN): δ = 8.75 (dd, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, 2H, 4-H), 8.36 (d, $^3J_{H,H}$ = 2.9 Hz, 2H, 17-H), 8.09-8.00 (m, 6H, 3-H, 5-H, 23-H), 7.94 (d, $^3J_{H,H}$ = 6.1 Hz, 2H, 6-H), 7.51 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 0.9 Hz, 2H, 2-H), 7.11 (dt, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.3 Hz, 2H, 21-H), 7.03 (d, $^3J_{H,H}$ = 2.3 Hz, 2H, 15-H), 6.94 (dt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.3 Hz, 2H, 22-H), 6.49 (t, $^3J_{H,H}$ = 2.3 Hz, 2H, 16-H), 6.38 (dt, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.2 Hz, 2H, 20-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ = 155.6, 144.4, 144.2, 140.3, 137.6, 134.4, 133.9, 133.2, 131.3, 128.9, 128.8, 127.6, 127.3, 126.6, 126.4, 124.4, 112.9, 109.1 ppm. ESI-MS: m/z calcd. for [Ir(ppz)$_2$(dap)]$^+$ (C$_{36}$H$_{24}$N$_6$Ir): 733.1692, found 733.1655 and m/z calcd. for [Ir(ppz)$_2$]$^+$ (C$_{18}$H$_{14}$N$_4$Ir): 479.0848, found 479.0856. Elemental analysis (%) calcd. for C$_{36}$H$_{24}$F$_6$IrN$_6$P (877.81): C 49.26 H 2.76 N 9.57, found: C 49.34 H 2.82 N 9.68. IR (KBr pellet): v~ = 856 (s, P-F), 567 (m, P-F) cm^{-1}.

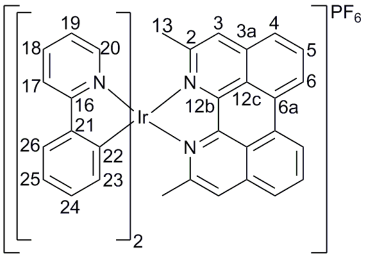


[Ir(thpy)$_2$dap]PF$_6$. As describe in method A from [Ir(thpy)$_2$Cl]$_2$ (0.219 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.357 g (98%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD$_3$CN): δ = 8.68 (dd, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.1 Hz, 2H, 4-H), 8.07-7.96 (m, 6H, 5-H, 6-H, 15-H), 7.86 (d, $^3J_{H,H}$ = 6.3 Hz, 2H, 18-H), 7.70-7.61 (m, 4H, 3-H, 22-H), 7.56-7.52 (m, 4H, 2-H, 16-H), 6.73 (dt, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 2.0 Hz, 2H, 17-H), 6.36 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, 21-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ = 164.5, 155.2, 153.3, 151.6, 144.4, 139.9, 137.8, 137.5, 134.5, 131.5, 131.4, 131.3, 128.9, 128.0, 126.6, 126.5, 121.6, 119.1 ppm. ESI-MS: m/z calcd. for [Ir(thpy)$_2$(dap)]$^+$ (C$_{36}$H$_{22}$N$_4$S$_2$Ir): 767.0915, found 767.0882 and m/z calcd. for [Ir(thpy)$_2$]$^+$ (C$_{18}$H$_{12}$N$_4$S$_2$Ir): 513.0071, found 513.0078. Elemental analysis (%) calcd. for C$_{36}$H$_{22}$F$_6$IrN$_4$PS$_2$ (911.9): C 47.42 H 2.43 N 6.14 S 7.03, found: C 47.51 H 2.49 N 6.28 S 7.12. IR (KBr pellet): v~ = 848 (s, P-F), 560 (m, P-F) cm^{-1}.

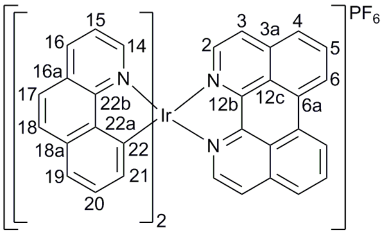


[Ir(dfppy)$_2$dap]PF$_6$. As describe in method A from [Ir(dfppy)$_2$Cl]$_2$ (0.243 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.319 g (82%). M.p.: >360°C. ^{1}H-NMR (300 MHz, C$_2$D$_2$Cl$_4$): δ = 8.69 (dd, $^3J_{H,H}$ = 5.6, $^4J_{H,H}$ = 2.7 Hz, 2H, 4-H), 8.33 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, 14-H), 8.15-8.048 (m, 4H, 18-H, 23-H), 8.01 (d, $^3J_{H,H}$ = 6.1 Hz, 2H, 3-H), 7.89 (d, $^3J_{H,H}$ = 6.1 Hz, 2H, 2-H), 7.79 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, 5-H), 7.43 (d, $^3J_{H,H}$ = 5.4 Hz, 2H, 6-H), 7.00 (t, $^3J_{H,H}$ = 6.6 Hz, 2H, 16-H), 6.66 (dt, $^3J_{H,H}$ = 10.6, $^4J_{H,H}$ = 2.0 Hz, 2H, 17-H), 5.78 (dd, $^3J_{H,F}$ = 8.2, $^4J_{H,F}$ = 2.2 Hz, 2H, 21-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ = 164.5, 155.2, 153.3, 151.6, 144.4, 139.9, 137.8, 137.5, 134.5, 131.5, 131.4, 131.3, 128.9, 128.0, 126.6, 126.5, 121.6, 119.1 ppm. ^{13}C-NMR (75 MHz, C$_2$D$_2$Cl$_4$): δ = 173.4, 165.9 (d, $J_{C\text{-}F}$ = 13 Hz), 164.7 (d,

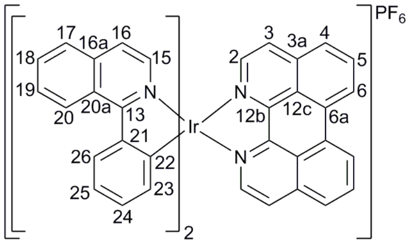
$J_{C\text{-}F}$ = 7 Hz), 163.7 (d, $J_{C\text{-}F}$ = 13 Hz), 162.5 (d, $J_{C\text{-}F}$ = 12 Hz), 160.2 (d, $J_{C\text{-}F}$ = 12 Hz), 153.7, 149.2, 143,1 139.8, 137.1, 134.7, 130.7, 128.9, 128.3, 128.0, 126.6, 126.0, 124.5, 124.4, 124.3, 114.3 (d, $J_{C\text{-}F}$ = 18 Hz), 100.2 (d, $J_{C\text{-}F}$ = 27 Hz) ppm. ESI-MS: m/z calcd. for $[Ir(dfppy)_2(dap)]^+$ ($C_{40}H_{22}F_4N_4Ir$): 827.1410, found 827.1385 and m/z calcd. for $[Ir(dfppy)_2]^+$ ($C_{22}H_{12}F_4N_2Ir$): 573.0566, found 573.0587. Elemental analysis (%) calcd. for $C_{40}H_{22}F_{10}IrN_4P$ (971.8): C 49.44 H 2.28 N 5.77, found: C 49.65 H 2.34 N 5.81. IR (KBr pellet): v~ = 845 (s, P-F), 561 (m, P-F) cm^{-1}.



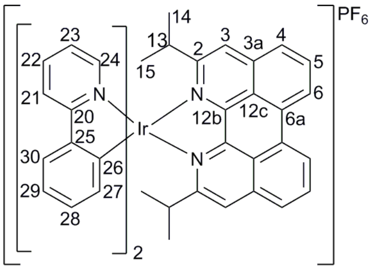
$[Ir(ppy)_2(dmedap)]PF_6$. As describe in method A from $[Ir(ppy)_2Cl]_2$ (0.214 g, 0.2 mmol) and dmedap (0.113 g, 0.4 mmol). Yield: 0.319 g (86%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD_3CN): δ = 8.58 (dd, $^3J_{H,H}$ = 6.9, $^4J_{H,H}$ = 0.9 Hz, 2H, 4-H), 8.04 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, 17-H), 7.94-7.86 (m, 4H, 20-H, 26-H), 7.81 (dt, $^4J_{H,H}$ = 1.4, $^3J_{H,H}$ = 7.8 Hz, 2H, 18-H), 7.74-7.70 (m, 6H, 3-H, 5-H, 6-H), 6.98-6.92 (m, 4H, 24-H, 25-H), 6.78 (dt, $^4J_{H,H}$ = 1.4, $^3J_{H,H}$ = 7.4 Hz, 2H, 19-H), 6.12 (dd, $^4J_{H,H}$ = 0.8, $^3J_{H,H}$ = 7.7 Hz, 2H, 23-H), 1.97 (s, 6H, 13-H) ppm. ^{13}C-NMR (75 MHz, CD_3CN): δ□ = 168.5, 157.0, 156.7, 151.5, 150.2, 144.3, 139.4, 138.4, 134.3, 132.4, 131.0, 130.7, 128.0, 126.7, 125.7, 125.5, 125.0, 124.2, 123.2, 120.8 ppm. ESI-MS: m/z calcd. for $[Ir(ppy)_2(dmedap)]^+$ ($C_{42}H_{30}N_4Ir$): 783.2100, found 783.2065 and m/z calcd. for $[Ir(ppy)_2]^+$ ($C_{22}H_{16}N_2Ir$): 501.0943, found 501.0960. Elemental analysis (%) calcd. for $C_{42}H_{30}F_6IrN_4P$ (927.9): C 54.37 H 3.26 N 6.04, found: C 54.30 H 3.32 N 5.94. IR (KBr pellet): v~ = 842 (s, P-F), 552 (m, P-F) cm^{-1}.



$[Ir(bzq)_2dap]PF_6$. As describe in method B from $[Ir(bzq)_2Cl]_2$ (0.234 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.364 g (96%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD_3CN): δ = 8.67 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.9 Hz, 2H, 4-H), 8.36 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.0 Hz, 2H, 16-H), 8.05 (dd, $^3J_{H,H}$ = 5.4, $^4J_{H,H}$ = 1.0 Hz, 2H, 17-H), 7.98-7.92 (m, 6H, 5-H, 6-H, 18-H), 7.87-7.77 (m, 6H, 3-H, 2-H, 19-H), 7.56 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, 14-H), 7.37-7.33 (m, 2H, 20-H), 7.22 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, 15-H), 6.39 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, 21-H) ppm. ^{13}C-NMR (75 MHz, CD_3CN): δ□ = 157.8, 155.4, 150.6, 148.2, 144.4, 141.5, 138.3, 137.5, 135.2, 134.3, 131.3, 130.7, 130.6, 129.7, 128.8, 128.1, 127.8, 126.4, 126.7, 125.0, 123.3, 121.6 ppm. ESI-MS: m/z calcd. for $[Ir(bzq)_2(dap)]^+$ ($C_{44}H_{26}N_4Ir$): 803.1787, found 803.1750 and m/z calcd. for $[Ir(bzq)_2]^+$ ($C_{26}H_{16}N_2Ir$): 549.0943, found 549.0943. Elemental analysis (%) calcd. for $C_{44}H_{26}F_6IrN_4P$ (947.9): C 55.75 H 2.76 N 5.91, found: C 55.68 H 2.79 N 5.88. IR (KBr pellet): v~ = 837 (s, P-F), 552 (m, P-F) cm^{-1}.



[Ir(piq)$_2$(dap)]PF$_6$. As describe in method B from [Ir(piq)$_2$Cl]$_2$ (0.254 g, 0.2 mmol) and dap (0.102 g, 0.4 mmol). Yield: 0.387 g (97%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD$_3$CN): δ = 9.02 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.8 Hz, 2H, 20-H), 8.72 (dd, $^3J_{H,H}$ = 5.9, $^4J_{H,H}$ = 2.5 Hz, 2H, 4-H), 8.41 (d, $^3J_{H,H}$ = 7.9 Hz 2H, 26-H), 8.02-8.00 (m, 4H, 5-H, 6-H), 7.92-7.77 (m,10H, 2-H, 3-H, 17-H, 18-H, 19-H), 7.49 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, 16-H), 7.30 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, 15-H), 7.20 (dt, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.2 Hz, 2H, 24-H), 6.94 (dt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.1 Hz, 2H, 25-H), 6.38 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.1 Hz, 2H, 23-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ□ = 169.6, 154.8, 154.7, 146.6, 143.9, 142.4, 138.0, 137.5, 134.4, 132.9, 132.8, 131.8, 131.5, 131.4, 129.9, 128.9, 128.5, 127.9, 127.7, 127.1, 126.7, 126.5, 123.5, 122.8 ppm. ESI-MS: m/z calcd. for [Ir(piq)$_2$(dap)]$^+$ ($C_{48}H_{30}N_4Ir$): 855.2100, found 855.2109 and m/z calcd. for [Ir(piq)$_2$]$^+$ ($C_{30}H_{20}N_2Ir$): 601.1256, found 601.1268. Elemental analysis (%) calcd. for $C_{44}H_{26}F_6IrN_4P$ (947.9): C 57.65 H 3.02 N 5.60, found: C 57.71 H 3.10 N 5.74. IR (KBr pellet): v~ = 844 (s, P-F), 554 (m, P-F) cm^{-1}.



[Ir(ppy)$_2$(dipdap)]PF$_6$. As describe in method B from [Ir(ppy)$_2$Cl]$_2$ (0.214 g, 0.2 mmol) and dipdap (0.135 g, 0.4 mmol). Yield: 0.205 g (52%). M.p.: >360°C. ^{1}H-NMR (300 MHz, CD$_3$CN): δ = 8.70-8.63 (m, 2H, 4-H), 8.06 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, 21-H), 8.01-7.97 (m, 6H, 3-H, 5-H, 6-H), 7.82 (dt, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.4 Hz, 2H, 22-H), 7.73 (dd, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.2 Hz, 2H, 30-H), 7.68 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, 24-H), 6.99-6.79 (m, 4H, 23-H, 28-H), 6.80 (dt, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.4 Hz, 2H, 29-H), 6.10 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.0 Hz, 2H, 27-H), 3.47 (sep, $^3J_{H,H}$ = 6.9 Hz, 2H, 13-H), 0.96 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, 15-H), 0.36 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, 14-H) ppm. ^{13}C-NMR (75 MHz, CD$_3$CN): δ□ = 168.5, 167.6, 156.4, 151.6, 148.0, 144.5, 139.4, 138.8, 134.2, 132.1, 131.0, 130.9, 128.3, 125.8, 125.6, 125.0, 123.9, 123.2, 123.0, 120.9, 36.7, 23.8, 23.1 ppm. ESI-MS: m/z calcd. for [Ir(ppy)$_2$(dipdap)]$^+$ ($C_{46}H_{38}N_4Ir$): 839.2726, found 839.2703 and m/z calcd. for [Ir(ppy)$_2$]$^+$ ($C_{22}H_{16}N_2Ir$): 501.0943, found 501.0959. Elemental analysis (%) calcd. for $C_{46}H_{38}F_6IrN_4P$ (984.02): C 56.15 H 3.89 N 5.69, found: C 56.22 H 3.95 N 5.73. IR (KBr pellet): v~ = 839 (s, P-F), 554 (m, P-F) cm^{-1}.

3 Crystal structure determinations and parameters of π–π stacking, X-H···π and Y-X···π interactions for $[Ir(ppy)_2(dap)]PF_6$, $[Ir(piq)_2(dap)]PF_6$, $[Ir(bzq)_2(dap)]PF_6$, $[Ir(ppy)_2(dmedap)]PF_6$ and $[Ir(ppy)_2(dipdap)]PF_6$, $[Ir(ppz)_2(dap)]PF_6$

Suitable crystals were directly taken from the mother liquor and mounted on a thin glass fiber using inert oil (perfluoropolyalkylether, viscosity 1600 cSt). X-ray intensity data were collected at 210(2) K on a STOE IPDS-2 diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Spherical absorption corrections were performed. The structure of the complex $[Ir(ppy)_2(dmedap)]PF_6$ was solved by the Patterson method, and all the other structures were solved by direct methods (SHELXS-97)[8]. All structures were refined by full-matrix least-squares methods on F^2 (SHELXL-97)[9] with anisotropic displacement parameters for the non-hydrogen atoms. With exception of $[Ir(ppy)_2(dipdap)]PF_6$, the unit cells contain high-disordered solvent molecules. The electronic density in this area could not be resolved satisfactorily. Therefore the program PLATON/SQUEEZE [10] was used to remove the contributions of the disordered solvent species from the structure factor calculations (for details - see cifs). Therefore, note that the dcalc, F(000), and M.W. refer to known unit cell contents only. Hydrogen atoms in $[Ir(ppy)_2(dap)]PF_6$ and $[Ir(ppy)_2(dipdap)]PF_6$ could be located in a difference Fourier map, the U_{iso}(H) values were set to $1.2U_{eq}$(C). Hydrogen atoms in $[Ir(bzq)_2(dap)]PF_6$, $[Ir(piq)_2(dap)]PF_6$, $[Ir(ppz)_2(dap)]PF_6$ and $[Ir(ppy)_2(dmedap)]PF_6$ were placed at ideal positions and refined with fixed isotropic displacement parameters by using a riding model.

CCDC 827351 $[Ir(ppy)_2(dap)]PF_6$, CCDC 827352 $[Ir(bzq)_2(dap)]PF_6$, CCDC 827353 $[Ir(piq)_2(dap)]PF_6$, CCDC 827354 $[Ir(ppy)_2(dipdap)]PF_6$, CCDC 827355 $[Ir(ppz)_2(dap)]PF_6$ and CCDC 827356 $[Ir(ppy)_2(dmedap)]PF_6$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

---

[8] G. M. Sheldrick, *SHELXS-97*. *Program for Crystal Structure Solution*, Göttingen **1997**.
[9] G. M. Sheldrick, *SHELXS-97*. *Program for Crystal Structure Solution*, Göttingen **1997**.
[10] A. L. Spek, *PLATON*. *A Multipurpose Crystallographic Tool*, Utrecht **2008**.

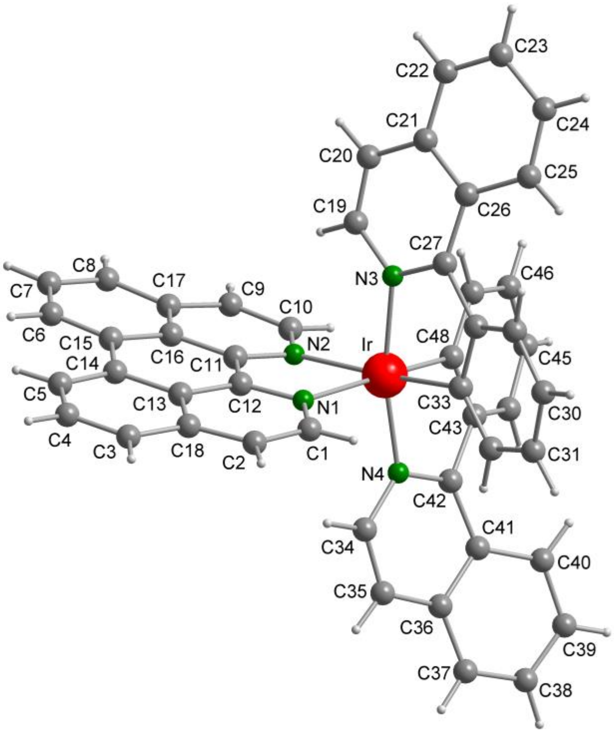


Fig. S1 Structure of $[Ir(piq)_2(dap)]^+$.

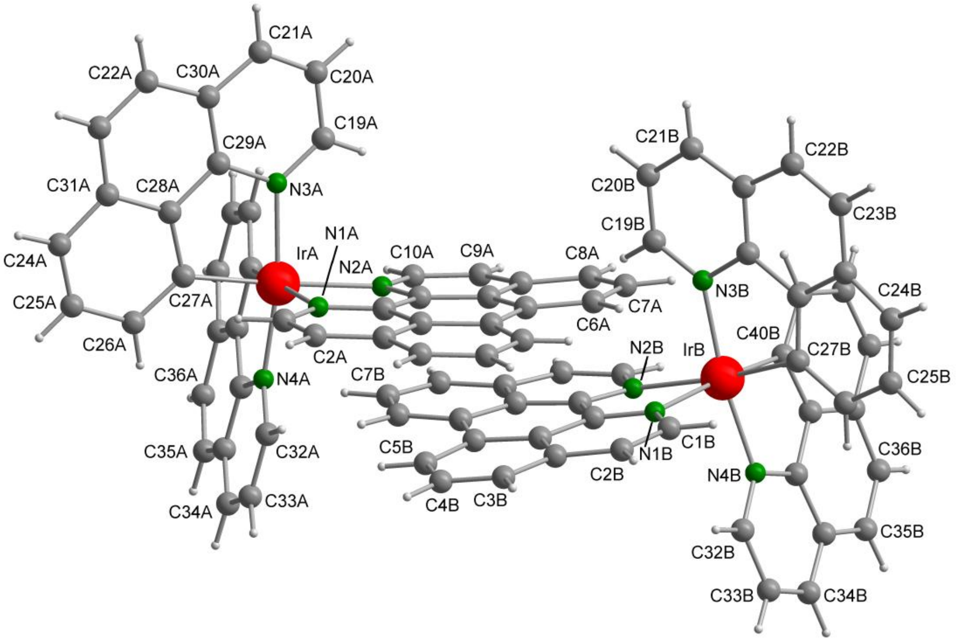


Fig. S2 Structure of $[Ir(bzq)_2(dap)]^+$. The asymmetric unit contains two cationic species.

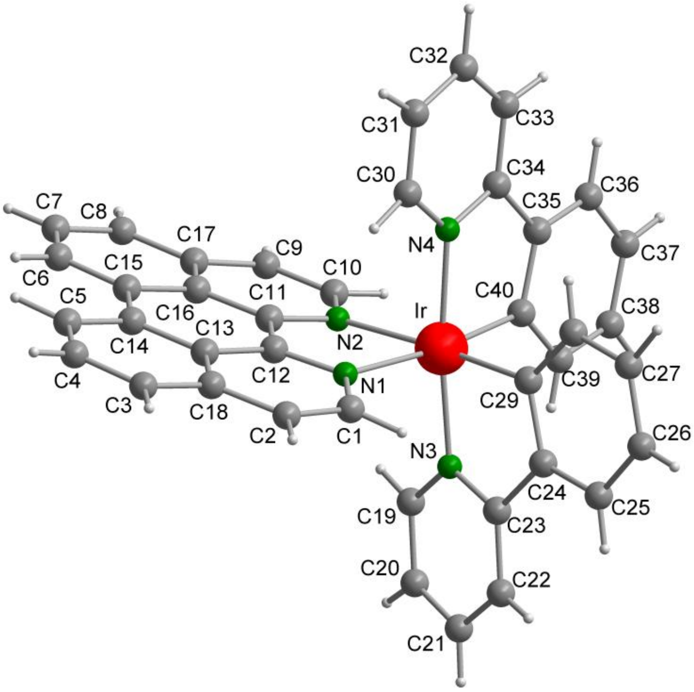


Fig. S3 Structure of $[Ir(ppy)_2(dap)]^+$.

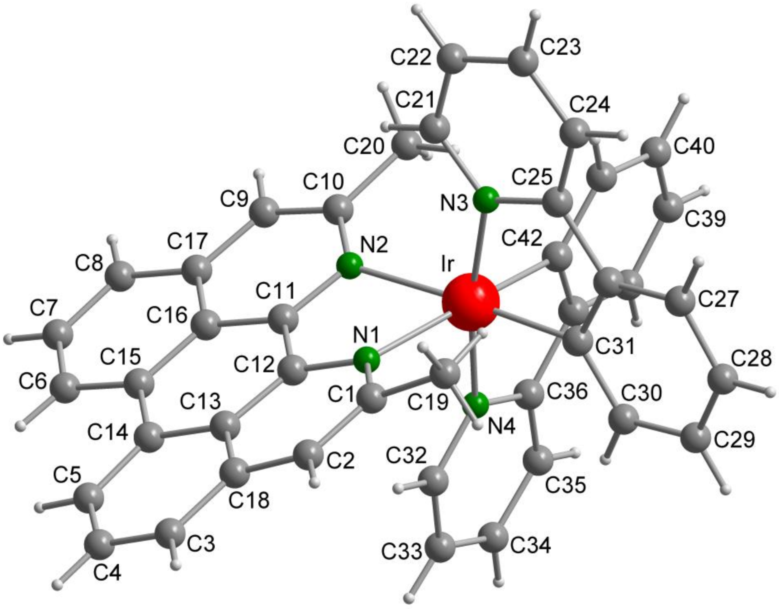


Fig. S4 Structure of $[Ir(ppy)_2(dimedap)]^+$.

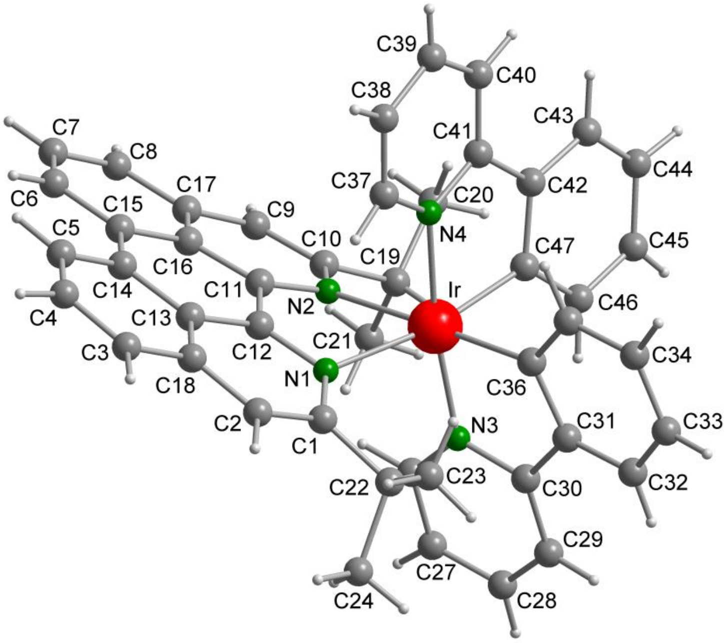


Fig. S5 Structure of $[Ir(ppy)_2(dipdap)]^+$.

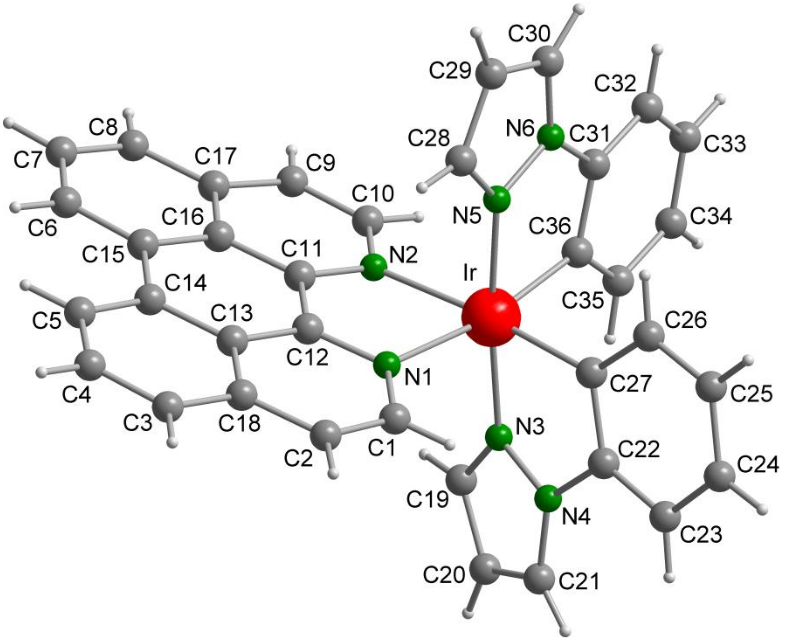


Fig. S6 Structure of $[Ir(ppz)_2(dap)]^+$.

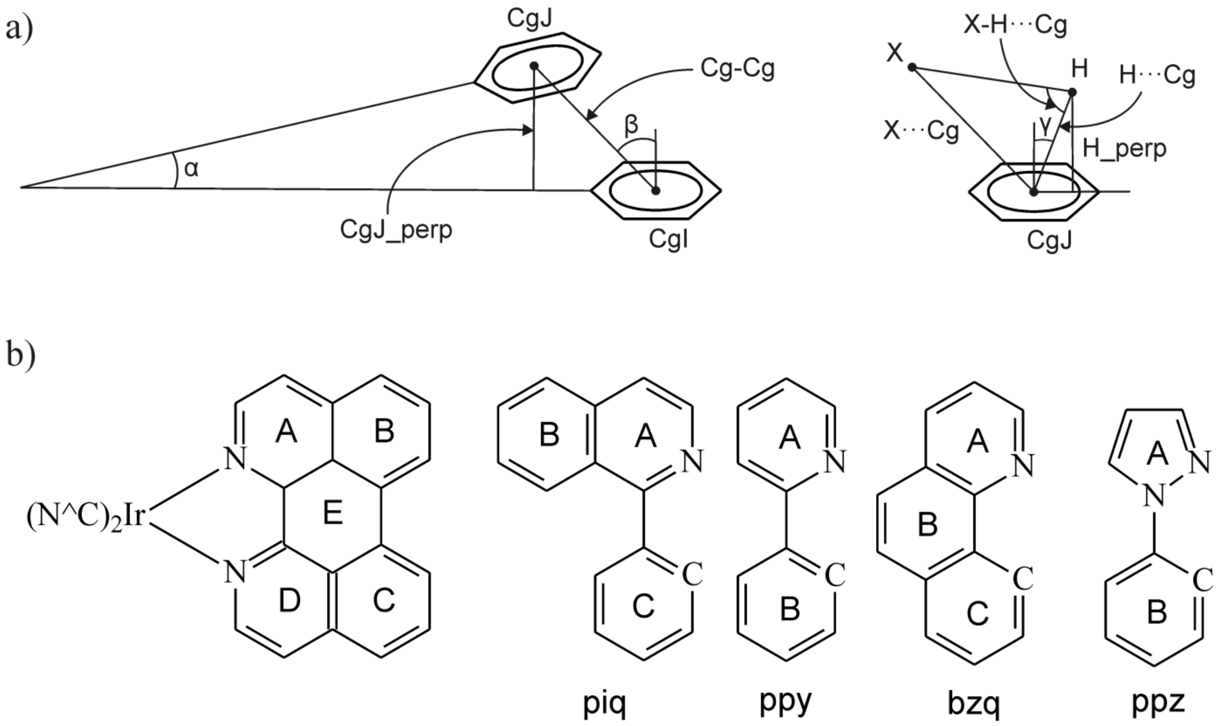


Fig. S7 a) Characterization of π-π and X-H···π ring interactions. b) Labelling of the 1,12-diazaperylene arene rings (C^N = cyclometalating ligand). If there are two complexes in the asymmetric unit, the dap labelling is being continued, so that the arene rings of the second residue (2)are indicated with A(2) = F, B(2) = G etc. The subscript arabic numeral stands for the (C^N) ligand 1 or 2.

Table S1 π-π stacking parameters observed in the crystalline iridium(III) complexes.

Complexes	Interacting arene rings	Cg-Cg/Å	α/°	β/°	CgJ_perp/Å
$[Ir(piq)_2(dap)]^+$	A-C^{V}	4.041(5)	2.2(4)	29.64	-3.513(4)
	A- E^{V}	4.144(5)	3.2(4)	32.68	-3.488(3)
	D-B^{V}	3.764(5)	2.6(4)	23.59	-3.449(4)
	B-C^{V}	3.638(6)	1.7(5)	18.01	-3.460(4)
	B-E^{V}	3.826(5)	2.6(4)	23.86	-3.499(3)
	C-A^{VI}	4.042(5)	2.2(3)	31.49	3.447(3)
	C-E^{VI}	3.757(5)	4.2(4)	19.66	3.538(3)
	B_{piq2}-$B_{piq2,XV}$	4.276(6)	15	22.92	-3.939(5)
$[Ir(bzq)_2(dap)]^+$	A···G	3.673(3)	11.0(3)	12.03	-3.593(2)
	B···F	3.781(4)	7.2(3)	28.42	-3.326(2)
	C···I^{I}	3.646(3)	6.0(3)	8.30	3.608(2)
	D···H^{I}	3.645(4)	4.2(3)	20.44	3.391(2)
	C···H^{I}	3.935(4)	4.2(3)	30.34	3.396(2)
	C···J^{I}	4.047(4)	8.0(3)	29.30	3.530(2)
	B···G	4.098(4)	7.5(3)	29.21	-3.577(2)
	A_{bzq1}···$F_{bzq1,II}$	3.733(4)	16.7(3)	13.92	-3.624(3)
$[Ir(ppy)_2(dap)]^+$	A···C^{IX}	3.845(2)	4.3(2)	26.41	3.443(1)
	D···B^{IX}	3.815(2)	3.4(2)	23.76	3.491(1)

	B···V^{IX}	3.668(2)	2.2(2)	18.76	3.495(1)
	B···E^{IX}	3.894(2)	1.7(1)	24.28	3.550(1)
	E···E^{IX}	3.833(2)	0	23.04	3.528(1)
[Ir(ppy)$_2$(dmedap)]$^+$	A···C^{XI}	3.815(5)	7.2(4)	23.93	-3.628(3)
	A···E^{XI}	4.230(4)	4.7(3)	27.92	-3.624(3)
	D···B^{XI}	3.863(4)	6.4(4)	16.15	-3.677(3)
	B···C^{XI}	4.168(5)	4.4(4)	31.79	-3.682(3)
	B···E^{XI}	3.904(3)	3.3(4)	18.64	-3.713(3)
	E···E^{XI}	3.906(4)	0	18.61	-3.702(3)
[Ir(ppy)$_2$(dipdap)]$^+$	B···C ^{XIII}	3.984(2)	7.4(1)	25.26	3.604(1)
	C···E ^{XIII}	3.786(2)	4.4(1)	11.12	3.715(1)
	E···E ^{XIII}	4.144(2)	0	25.20	3.750(1)
[Ir(ppz)$_2$(dap)]$^+$	A···C ^{IX}	3.770(5)	3.6(4)	26.47	3.375(3)
	D···B ^{IX}	3.731(5)	3.2(4)	23.99	3.409(3)
	B···C ^{IX}	3.619(5)	1.9(4)	20.11	3.398(3)
	B···E ^{IX}	3.777(5)	1.4(4)	23.61	3.460(3)
	E···E ^{IX}	3.757(5)	0	23.45	3.447(3)

symmetry codes: ^{I} 1+x,y,z ; ^{II} -x,y-0.5,0.5-z; ^{III} x-1,y,z; ^{IV} -x,0.5+y,0.5-z; ^{V} x,-y,z-0.5; ^{VI} x,-y,0.5+z; ^{VII} x,y,z-1; ^{VIII} 0.5-x,0.5-y,0.5+z; ^{IX} 0.5-x,2.5-y,-z; ^{X} 0.5-x,0.5+y,0.5-z; ^{XI} 0.5-x,0.5-y,1-z; ^{XII} 0.5-x,y-0.5,0.5-z; ^{XIII} -x,1-y,2-z; ^{XIV} -x,0.5+y,1.5-z; ^{XV} -x,y,1.5-z

Table S2 X-H···π ring interactions.

Complexes	X-H···Cg(J)	H···Cg/Å	H_perp/Å	γ/°	X-H···Cg/°	X···Cg/ Å
[Ir(piq)$_2$(dap)]$^+$	C6-H6···A$_{piq2,VI}$	2.93	-2.76	19.63	154	3.789(11)
	C19-H19···D	2.86	2.53	27.85	149	3.690(9)
	C30-H30···A$_{piq2,VII}$	2.97	2.60	28.77	154	3.823(8)
	C30-H30···B$_{piq2,VII}$	2.97	2.67	25.98	158	3.850(9)
	C32-H32-A$_{piq2}$	2.81	-2.62	21.37	142	3.593(8)
	C45-H45···C$_{piq1,VIII}$	2.77	2.70	12.74	127	3.409(11)
	C47-H47···A$_{piq1}$	2.80	2.56	23.88	142	3.581(9)
[Ir(bzq)$_2$(dap)]$^+$	C5A-H5A··· D$_{bzq2,I}$	2.87	-2.81	10.82	150	3.703(6)
	C5B-H5B··· A$_{bzq2}$	2.96	2.96	2.34	139	3.716(7)
	C8A-H8A··· D$_{bzq1}$	2.72	2.68	9.36	162	3.611(7)
	C8B-H8B··· A$_{bzq1,III}$	2.64	2.60	10.05	157	3.514(8)
	C19B-H19B···F	3.00	2.67	26.93	141	3.767(6)
	C23A-H23A···E$_{bzq2,II}$	2.66	2.65	4.24	160	3.549(8)
	C24A-H24A··· F$_{bzq2,II}$	2.94	2.89	9.63	155	3.800(8)
	C24B-H24B··· C$_{bzq2}$	2.73	-2.70	8.22	150	3.562(8)
[Ir(ppy)$_2$(dap)]$^+$	C1-H1···ir2	2.72(4)	2.63	15.33	110(3)	3.177(4)
	C20-H20···B$_{dap1,X}$	2.83(4)	-2.79	10.45	133(4)	3.506(4)
	C28-H28···ir3	2.94(4)	-2.70	23.02	104(3)	3.256(5)
	C30-H30···ir4	2.76(4)	-2.49	25.33	101(3)	3.089(4)
[Ir(ppy)$_2$(dmedap)]$^+$	C19-H19···ir5	2.16	-2.13	9.55	158	3.067(8)
	C22-H22···B$_{ppy2,XII}$	2.97	2.94	7.94	114	3.448(9)
	C22-H22···B$_{ppy1,XII}$	2.93	2.74	20.90	126	3.558(9)

	C30-H30···ir6	2.89	2.65	23.63	94	3.102(6)
	C32-H32···A	2.84	2.54	26.43	149	3.666(9)
	C41-H41···ir5	2.79	2.61	21.03	97	3.043(9)
	C41-H41···A_{ppy1}	3.00	2.63	28.72	141	3.761(9)
$[Ir(ppy)_2(dipdap)]^+$	C20-H20B···B_{ppy2}	2.81	2.76	10.50	117	3.346
	C22-H22···ir7	2.41	2.38	8.60	157	3.195
	C35-H35···ir8	2.83	-2.61	23.04	95	3.091
	C37-H37···A	2.63	-2.47	20.04	148	3.461
	C38-H38···$B_{ppy1,XIV}$	2.93	-2.86	12.29	137	3.639
	C46-H46···ir7	2.73	-2.61	17.14	97	3.021
$[Ir(ppz)_2(dap)]^+$	C20-H20···$B_{ppz2,X}$	2.89	-2.75	17.97	145	3.694(10)
	C26-H26···ir9	2.95	-2.78	19.92	100	2.251(10)

ir1=Ir/N1/N2/C11/C12; ir2=Ir/N3/C23/C24/C29; ir3=Ir/N4/C34/C35/C40; ir4=Ir/N1/C11/C12/N2; ir5=Ir/N3/C25/C26/C31; ir6=Ir/N4/C36/C37/C42; ir7=Ir/N3/C30/C31/C36; ir8=Ir/N4/C41/C42/C47; ir9=N5/N6/C31/C36

Table S3 Y-X··π ring interactions in $[Ir(bzq)_2(dap)]^+$.

Complex	Y-X···Cg(J)	X···Cg/Å	X_perp/Å	γ/°	Y-X···Cg/°	Y···Cg/ Å
$[Ir(bzq)_2(dap)]^+$	P1A-F1A···A	2.857(4)	2.818	9.40	141.9(3)	4.230(2)
	P1A-F5A···B	3.601(5)	3.370	20.65	108.5(2)	4.379(3)

4 Experimental details for ESI-MS CID measurements.

ESI-Mass spectra were obtained in positive ion mode using an ESI-Q-TOF_{micro} quadrupole time-of-flight mass spectrometer (Waters Inc. Manchester, UK). Solutions of the complexes in CH_3CN (HPLC-grade) were injected using an integrated syringe pump at a flow rate varying from 5 - 10 µL/min. The capillary voltage was set to 3.7 kV.

The elemental compositions of the complexes and the fragment ions were determined by accurate mass measurements with standard deviations less than 5 ppm. Leucine enkephaline was used as reference compound. Argon was used as collision gas for the tandem mass spectrometric (MSMS) measurements. The cone voltage was optimized for the MSMS experiments for maximum precursor ion abundance within the range of 30 - 35 V. The complex ion was selected and activated in collision induced decomposition (CID) mode. The collision energy was varied (5 - 60 eV) to identify the threshold for dissociations. The threshold activation voltage is defined in this study as the voltage sufficient to produce fragments that constitute 10% of the total ion intensity. The MS/MS product ion spectra were averaged over 100 accumulations for each collision energy step with high reproducibility.