Blue-to-green electrophosphorescence of iridium-based cyclometallated materials

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General experimental procedure, syntheses and characterisation of **1**–**2**, OLED fabrication, quantum yield measurement and crystal data for **1a** and **1d**.

General Experimental Procedure

All reagents were purchased from Aldrich, Strem and Lancaster and used as received. All reactions were preformed under a nitrogen atmosphere unless specified otherwise. HPLC grade MeCN (Fluka) was used and DCM and hexane were distilled from calcium hydride and degassed prior to use. Column chromatography was performed using Merck 9385 silica gel 60 (0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400 (400 MHz and 100 MHz respectively) and Bruker DRX-500 (100 MHz and 125 MHz respectively) instruments. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. Elemental analyses were performed with an Exeter Analytical CE-440 analyser by the microanalysis section of University Chemical Laboratory at University of Cambridge. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea. UV-visible spectra were measured on a Hewlett-Packard 8453 diode array spectrophotometer. For photoluminescence measurements under inert atmosphere, the samples were held under vacuum in a continuous-flow helium cryostat. The samples were excited with the MLUV lines (351 and 364 nm) of an Argon ion continuous wave (cw) laser or the 325 nm line of a cw HeCd laser. The emitted light was collected with an optical fiber and recorded by an Oriel spectrograph coupled to a cooled CCD array (Oriel Instaspec IV). Photoluminescence quantum yields were measured under nitrogen atmosphere using the integrating sphere technique.[1] Excitation in this case was provided by a 405nm cw diode laser and spectra were taken with the Oriel spectrograph described above. Photoluminescence spectra under ambient conditions were recorded on an Aminco-Bowman Series 2 luminescence spectrometer.

The phenylpyridyl ligands (**L**) and dichloro-bridged diiridium complexes $[(\mathbf{L})_2\mathrm{Ir}(\mu\text{-}\mathrm{Cl})]_2$ were prepared by the general method described by Li *et al.*[2]

Synthesis and Characterisation of the Complexes

*Synthetic procedure for complex **1a–f***

A solution of the appropriate dichloro-bridged diiridium complex $[(\mathbf{L})_2\mathrm{Ir}(\mu\text{-}\mathrm{Cl})]_2$ (0.16 mmol) and 2-[3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl]pyridine (0.39 mmol) were dissolved in $CHCl_3$ (20 mL) to form a clear yellow solution and heated to reflux. NaOMe (0.09 mL, 28 % w/w in MeOH) was added dropwise. The resulting yellow solution was heated at reflux under N_2 overnight. The cloudy yellow mixture was cooled down to room temperature. $CHCl_3$ (20 mL) and distilled water (20 mL) were added. The organic phase was separated and dried over $MgSO_4$. Removal of solvent gave a yellow solid, which was then purified by silica column chromatography with DCM as eluent. The solvent was removed under vacuum to afford a yellow solid.

Bis[2-(2-pyridyl-κ*N*)-3,5-difluorophenyl-κC^1]{(5-pyridyl-κ*N*)-[3-(trifluoromethyl)-1*H*-1,2,4-triazolyl-κN^1]}iridium (**1a**): For $[(\mathbf{L})_2\mathrm{Ir}(\mu\text{-}\mathrm{Cl})]_2$ **L** = 2-(2-pyridyl-κ*N*)-3,5-difluorophenyl-κC^1. The product, **1a**, was obtained as a yellow powder. (Found: C, 43.55; H, 2.1; N, 9.8; $C_{30}H_{16}N_6F_7Ir\cdot0.5CH_2Cl_2$ requires C, 43.5; H, 1.95; N, 10.15%. HRMS *m/z* (ES^+) 787.1028 $[M+H]^+$. $C_{30}H_{17}N_6F_7Ir\cdot0.5CH_2Cl_2$ requires 787.1027). ν_{max}/cm^{-1} 3087 (w), 1604 (s), 1474 (s), 1405 (s), 1168 (s), 1128 (vs), 1102 (s), 1031 (m), 983 (vs), 841 (s), 827 (s), 764 (s), 752 (s), 712 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 5.56 (dd, 1H, ArH, J = 2.4, 8.8), 5.64 (dd, 1H, ArH, J = 2.3, 8.4 Hz), 6.80- 6.89 (m, 1H, ArH), 7.20-7.24 (m, 1H, ArH), 7.49-7.52 (m, 1H, ArH), 7.65 (d, 1H, ArH, J = 5 Hz), 7.72 (d, 1H, ArH, J = 5 Hz), 7.98 (t, 2H, ArH x 2, J = 7.7 Hz), 8.13-8.15 (m, 1H, ArH), 8.21-8.24 (m, 3H, ArH x 3), 8.47 (s, 2H, ArH x 2).

Bis[2-(4-methyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κ*C*^{1}]{(5-pyridyl-κ*N*)-[3-(trifluoromethyl)-1*H*-1,2,4-triazolyl-κ*N*^{1}]}iridium (**1b**): For [(**L**)$_2$Ir(μ-Cl)]$_2$ **L** = 2-(4-methyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κ*C*^{1}. The product, **1b**, was obtained as yellow powder. (Found: C, 44.2; H, 2.7; N, 8.9. $C_{32}H_{20}N_6F_7Ir\cdot CH_2Cl_2$ requires C, 44.1; H, 2.5; N, 9.35%). ν_{max}/cm^{-1} 1596 (s), 1469 (s), 1401 (m), 1197 (s), 1166 (s), 1120 (s), 1030 (m), 991 (s), 824 (vs), 756 (m), 738 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.52 (s, 3H, CH_3), 5.71 (dd, 1H, ArH, *J* = 2.4, 8.8 Hz), 5.82 (dd, 1H, ArH, *J* = 2.4, 8.4 Hz), 6.42-6.47 (m, 1H, ArH), 6.49-6.54 (m, 1H, ArH), 6.73 (dd, 1H, ArH, *J* = 1.5, 6.3 Hz), 6.83 (dd, 1H, ArH, *J* = 1.8, 6.1 Hz), 7.22-7.25 (m, 2H, ArH x 2), 7.58 (d, 1H, ArH, *J* = 6.0 Hz), 7.76 (dt, 1H, ArH, *J* = 1.5, 7.8 Hz), 8.11 (bs, 1H, ArH), 8.18 (bs, 1H, ArH), 8.30 (dd, 1H, ArH, *J* = 1.0, 7.9 Hz).

Bis[2-(4-octyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κ*C*^{1}]{(5-pyridyl-κ*N*)-[3-(trifluoromethyl)-1*H*-1,2,4-triazolyl-κ*N*^{1}]}iridium (**1c**): For [(**L**)$_2$Ir(μ-Cl)]$_2$ **L** = 2-(4-octyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κ*C*^{1}. The product, **1c**, was obtained as a yellow solid. (Found: C, 54.7; H, 4.9; N, 8.1. $C_{46}H_{48}N_6F_7Ir$ requires C, 54.7; H, 4.8; N, 8.3%. HRMS (ES$^+$) *m/z* 1011.3530 [M+H]$^+$. $C_{46}H_{49}N_6F_7Ir$ requires 1011.3531). ν_{max}/cm^{-1} 2927 (m), 1598 (s), 1468 (s), 1401 (s), 1196 (m), 1161 (vs), 1128 (s), 1106 (s), 1030 (m), 990 (s), 895 (w), 853 (m), 817 (s), 756 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88-0.91 (m, 6H, CH_3 x 2), 1.23-1.35 (m, 20H, CH_2 x 10), 1.64-1.71 (m, 4H, CH_2 x 2), 2.72-2.75 (m, 4H, CH_2 x 2), 5.59 (dd, 1H, ArH, *J* = 2.4, 8.7 Hz), 5.79 (dd, 1H, ArH, *J* = 2.4, 8.4 Hz), 6.42-6.47 (m, 1H, ArH), 6.49-6.54 (m, 1H, ArH), 6.73 (dd, 1H, ArH, *J* = 1.6, 6.1 Hz), 6.84 (dd, 1H, ArH, *J* = 1.6, 5.9 Hz), 7.22-7.27 (m, 2H, ArH x 2), 7.57 (d, 1H, ArH, *J* = 6.0 Hz), 7.77-7.78 (m, 1H, ArH), 7.91 (dt, 1H, ArH, *J* = 1.5, 7.8 Hz), 8.05 (bs, 1H, ArH), 8.10 (bs, 1H, ArH), 8.30-8.32 (m, 1H, ArH). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.0, 22.6, 28.8, 29.1, 29.2, 29.3, 31.8, 35.5, 98.0 (t, $J_{C\text{-}F}$

= 26.7 Hz), 98.3 (t, J_{C-F} = 26.7 Hz), 114.1 (t, J_{C-F} = 17.3 Hz), 119.2, 121.3, 121.9, 122.5, 123.1 (d, J_{C-F} = 19.1 Hz), 123.3, 123.4 (d, J_{C-F} = 18.4 Hz), 125.2, 127.7, 128.3, 138.7, 147.4, 149.4, 149.5, 151.0, 151.8 (d, J_{C-F} = 7.1 Hz), 154.3, 154.7, 156.3, 156.6, 157.3, 160.9 (dd, J_{C-F} = 12.8, 247.5 Hz), 161.1 (dd, J_{C-F} = 12.5, 258.7 Hz), 162.5 (d, J_{C-F} = 12.1 Hz), 163.5, 163.9 (d, J_{C-F} = 6.8 Hz), 164.7 (d, J_{C-F} = 7.1 Hz).

Bis[2-(5-bromo-2-pyridyl-κ*N*)-3,5-difluorophenyl-κC^1]{(5-pyridyl-κ*N*)-[3-(trifluoromethyl)-1*H*-1,2,4-triazolyl-κN^1]}iridium (**1d**): For [(**L**)$_2$Ir(μ-Cl)]$_2$ **L** = 2-(5-bromo-2-pyridyl-κ*N*)-3,5-difluorophenyl-κC^1. (Found: C, 36.5; H, 1.3; N, 8.4. $C_{30}H_{14}N_6Br_2F_7Ir{\cdot}CH_2Cl_2$ requires C, 36.2; H, 1.6; N, 8.2%. HRMS *m/z* 942.9246 $[M+H]^+$. $C_{30}H_{15}N_6Br_2F_7Ir{\cdot}CH_2Cl_2$ requires 942.9237). ν_{max}/cm^{-1} 3095 (w), 1603 (s), 1473 (s), 1137 (s), 992 (s), 843 (s), 756 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 (dd, 1H, ArH, *J* = 2.3, 8.5), 5.77 (dd, 1H, ArH, *J* = 2.3, 8.2), 6.44-6.50 (m, 1H, ArH), 6.52-6.58 (m, 1H, ArH), 7.28-7.31 (m, 1H, ArH), 7.80 (d, 1H, ArH, *J* = 2.1 Hz), 7.72-7.73 (m, 2H, ArH x 2), 7.83-7.88 (m, 2H, ArH x 2), 7.98 (dt, 1H, ArH, *J* = 1.5, 7.8 Hz), 8.12 (dd, 1H, ArH, *J* = 2.9, 16.8 Hz), 8.17 (dd, 1H, ArH, *J* = 3.0, 16.3 Hz), 8.36 (dd, 1H, ArH, *J* = 1.0, 7.8 Hz).

Bis[2-(5-bromo-4-octyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κC^1]{(5-pyridyl-κ*N*)-[3-(trifluoromethyl)-1*H*-1,2,4-triazolyl-κN^1]}iridium (**1e**): For [(**L**)$_2$Ir(μ-Cl)]$_2$ **L** = 2-(5-bromo-4-octyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κC^1. The product, **1e**, was obtained as a light yellow solid. (Found: C, 46.8; H, 3.9; N, 7.0. $C_{46}H_{46}N_6Br_2F_7Ir$ requires C, 47.3; H, 4.0; N, 7.2%. *m/z* (MALDI, DCTB matrix) 1664.6 $[M]^+$. $C_{46}H_{46}N_6Br_2F_7Ir$ requires 1664.6). ν_{max}/cm^{-1} 2926 (m), 1600 (s), 1572 (s), 1470 (s), 1378 (m), 1197 (s), 1161 (vs), 1108 (s), 991 (s), 826 (s), 753 (m), 723 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6H, CH_3 x 2), 1.26-1.41 (m, 20H, CH_2 x 10), 1.64-1.67 (m, 4H, CH_2 x 2), 2.78-2.82 (m, 4H, CH_2 x 2), 5.68 (dd, 1H, ArH, *J* = 2.3, 8.6), 5.77 (dd, 1H, ArH, *J* = 2.3, 8.3), 6.42-6.48 (m, 1H, ArH), 6.50-6.56 (m, 1H, ArH), 7.27-7.29 (m, 2H, ArH x 2), 7.30 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.74 (d, 1H, ArH, *J* = 5.0 Hz), 7.95 (dt, 1H, ArH, *J* = 1.5, 7.8 Hz), 8.06 (d, 1H, ArH, *J* = 2.8 Hz), 8.10 (d, 1H, ArH, *J* = 3.2 Hz), 8.34 (d, 1H, ArH, *J* = 7.9 Hz).

Bis{2-[5-(9-octyl-9*H*-carbazol-3-yl)-2-pyridyl-κ*N*]-3,5-difluorophenyl-κ*C*^{1}}{(5-pyridyl-κ*N*)-[3-(trifluoromethyl)-1*H*-1,2,4-triazolyl-κ*N*^{1}]}iridium (**1f**): For [(**L**)$_2$Ir(μ-Cl)]$_2$ **L** = 2-[5-(9-octyl-9*H*-carbazol-3-yl)-2-pyridyl-κ*N*]-3,5-difluorophenyl-κ*C*^{1}. (Found: C, 62.6; H, 4.6; N, 8.25. $C_{70}H_{62}N_8IrF_7$ requires C, 62.7; H, 4.7; N, 8.4%. *m/z* (MALDI, DCTB matrix) 1340.5 [M]$^+$. $C_{70}H_{62}N_8IrF_7$ requires 1340.5). ν_{max}/cm^{-1} 2925 (m), 1597 (s), 1468 (s), 1126 (s), 1030 (m), 988 (s), 843 (s), 802 (s), 744 (s), 729 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.85-0.88 (m, 6H, CH$_3$ x 2), 1.25-1.34 (m, 20H, CH$_2$ x 10), 1.86 (m, 4H, CH$_2$ x 2), 4.26-4.31 (m, 4H, N-CH$_2$ x 2), 5.90-5.95 (m, 2H, ArH x 2), 6.43-6.49 (m, 1H, ArH), 6.51-6.57 (m, 1H, ArH), 7.25-7.36 (m, 6H, ArH x 6), 7.41-7.43 (m, 2H, ArH x 2), 7.47-7.52 (m, 2H, ArH x 2), 7.79 (d, 1H, ArH, *J* = 1.8 Hz), 7.84 (bs, 1H, ArH), 7.93-8.03 (m, 4H, ArH x 4), 8.07-8.11 (m, 3H, ArH x 3), 8.15 (d, 1H, ArH, *J* = 7.8 Hz), 8.28-8.31 (m, 2H, ArH x 2), 8.43 (d, 1H, ArH, *J* = 7.9 Hz). ^{13}C-NMR (125 MHz, CDCl$_3$): δ 14.1, 22.6, 27.2, 28.9, 29.1, 29.3, 31.8, 43.2, 98.1 (t, J_{C-F} = 26.3 Hz), 98.5 (d, J_{C-F} = 26.0 Hz), 108.9, 109.1, 109.4, 109.6, 114.2 (t, J_{C-F} = 14.1 Hz), 118.0, 118.2, 119.29, 119.33, 120.2, 120.7, 121.4, 122.1, 122.5, 122.6, 122.9 (d, J_{C-F} = 23.8 Hz), 123.1 (d, J_{C-F} = 24.3 Hz), 123.5, 123.7, 124.0 (d, J_{C-F} = 22.5 Hz), 125.3, 125.5, 126.0, 126.2, 126.3, 127.5 (q, J_{C-F} = 22.1 Hz), 128.3, 135.5, 135.7, 136.1, 136.9, 139.0, 140.4, 140.8, 140.9 (d, J_{C-F} = 2.3 Hz), 145.9, 147.4, 149.9, 151.2, 151.5 (d, J_{C-F} = 6.9 Hz),156.6 (d, J_{C-F} = 6.3 Hz), 156.8, 157.1, 157.4, 159.9 (t, J_{C-F} = 12.2 Hz), 161.7 (d, J_{C-F} = 6.9 Hz), 161.9 (t, J_{C-F} = 12.8 Hz), 162.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 163.0 (dd, $J_{C\text{-}F}$ = 12.4, 254.0 Hz), 163.4 (dd, $J_{C\text{-}F}$ = 12.0, 255.5 Hz), 163.9.

*Synthetic procedures for complexes **2a** and **2b***

A solution of the appropriate dichloro-bridged diiridium complex $[(\mathbf{L})_2Ir(\mu\text{-}Cl)]_2$ (0.25 mmol) in DCM (10 mL) was treated with silver trifluoromethylsulfonate (AgOTf) (0.53 mmol) in MeOH (10 mL). The yellow slurry was stirred at room temperature for two hours. The solution was then centrifuged and the clear yellow solution was decanted. Removal of solvent gave a yellow oil which then dissolved in MeCN (50 mL). Potassium tetrakis(1-pyrazolyl)borate (0.76 mmol) was then added. The yellow suspension was heated to reflux under N_2 overnight. The yellow mixture was cooled down to room temperature and the solvent was removed under vacuum. The residue was partitioned between DCM and water. The organic layer was separated and dried over $MgSO_4$. Removal of solvent gave an orange solid which was then purified by silica column chromatography with DCM as eluent to afford the product.

Bis[2-(5-bromo-4-octyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κ*C*^{1}] [tetrakis(1-pyrazolyl)borato]iridium (**2a**): For $[(\mathbf{L})_2Ir(\mu\text{-}Cl)]_2$ **L** = 2-(5-bromo-4-octyl-2-pyridyl-κ*N*)-3,5-difluorophenyl-κ*C*^{1}. (Found: C, 48.3; H, 4.3; N, 11.05. $C_{50}H_{54}BN_{10}Br_2F_4Ir$ requires C, 48.7; H, 4.4; N, 11.35%. *m/z* (MALDI, DCTB matrix) 1232.3 $[M]^+$. $C_{50}H_{54}BN_{10}Br_2F_4Ir$ requires 1232.2). ν_{max}/cm^{-1} 2926 (m), 1599 (s), 1380 (s), 1294 (s), 1225 (s), 1108 (s), 1070 (s), 989 (s), 817 (vs), 754 (vs). ^1H NMR (400 MHz, $CDCl_3$): δ 0.86-0.91 (m, 6H, CH_3 x 2), 1.26-1.44 (m, 20H, CH_2 x 10), 1.61-1.69 (m, 4H, CH_2 x 2), 2.75-2.81 (m, 4H, CH_2 x 2), 5.55 (dd, 2H, ArH x 2, *J* = 2.3, 8.5), 5.99-6.00 (m, 2H, ArH x 2), 6.18 (d, 2H, ArH x 2, *J* = 2.2 Hz), 6.28-6.29 (m, 2H, ArH x 2), 6.45-6.51 (m, 2H, ArH x 2), 6.94 (d, 2H, ArH x 2, *J* = 1.4 Hz), 7.08 (s, 2H, ArH x 2), 7.21 (d, 2H, ArH x 2, *J* = 2.4 Hz), 7.73 (d, 2H, ArH x 2, *J* = 1.0 Hz), 7.99 (d, 2H, ArH x 2, *J* = 2.9 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.1, 22.6, 28.8, 29.0, 29.26, 29.3, 29.4, 31.8, 35.8, 98.5 (t, $J_{C\text{-}F}$ = 26.7 Hz), 105.3, 107.4, 113.9 (d, $J_{C\text{-}F}$ = 17.0 Hz), 119.6, 123.0 (d, $J_{C\text{-}F}$ = 20.1 Hz), 127.9, 133.3, 139.2, 142.8, 144.1, 150.6, 153.4, 153.7 (d, $J_{C\text{-}F}$ = 6.3 Hz), 160.8 (dd, $J_{C\text{-}F}$ = 12.6, 258.6 Hz), 162.7 (d, $J_{C\text{-}F}$ = 7.1 Hz), 163.4 (dd, $J_{C\text{-}F}$ = 12.4, 255.4 Hz).

Bis{2-[5-(9-octyl-9*H*-carbazol-3-yl)-2-pyridyl-κ*N*]-3,5-difluorophenyl-κ*C*^{1}}[tetrakis(1-pyrazolyl)borato]iridium (2b): For $[(\mathbf{L})_2Ir(\mu\text{-}Cl)]_2$ **L** = 2-[5-(9-octyl-9*H*-carbazol-3-yl)-2-pyridyl-κ*N*]-3,5-difluorophenyl-κ*C*^{1}. (Found: C, 63.2; H, 4.95; N, 11.9. $C_{74}H_{70}N_{12}BF_4Ir$ requires C, 63.2; H, 5.0; N, 11.95%. *m/z* (MALDI, DCTB matrix) 1406.6 $[M]^+$. $C_{74}H_{70}N_{12}BF_4Ir$ requires 1406.6). ν_{max}/cm^{-1} 2924 (w), 1598 (s), 1467 (m), 1386 (m), 1294 (s), 1226 (s), 1104 (s), 1070 (m), 988 (m), 817 (s), 746 (vs). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6H, CH_3 x 2), 1.26-1.43 (m, 20H, CH_2 x 2), 1.86-1.94 (m, 4H, CH_2 x 2), 4.32 (t, 4H, CH_2 x 2, *J* = 7.2), 5.79 (dd, 2H, ArH x 2, *J* = 2.2, 8.5), 5.84-5.85 (m, 2H, ArH x 2), 6.26 (d, 2H, ArH x 2), 6.28-6.29 (m, 2H, ArH x 2), 6.49-6.55 (m, 2H, ArH x 2), 7.11 (d, 2H, ArH x 2, *J* = 1.2), 7.16 (d, 2H, ArH x 2, *J* = 1.2), 7.24-7.28 (m, 2H, ArH x 2), 7.36 (d, 2H, ArH x 2, *J* = 2.1 Hz), 7.43-7.46 (m, 4H, ArH x 4), 7.49-7.55 (m, 4H, ArH x 4), 7.63 (d, 2H, ArH x 2, *J* = 1.9 Hz), 8.10-8.05 (m, 2H, ArH x 2), 8.16-8.19 (m, 4H, ArH x 4), 8.25-8.27 (m, 2H, ArH x 2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 27.3, 29.0, 29.2, 29.4, 31.8, 43.2, 98.3 (t, $J_{C\text{-}F}$ = 26.7 Hz), 105.1, 107.3, 108.9, 109.2, 114.1 (d, $J_{C\text{-}F}$ = 14.9 Hz), 118.8, 119.1, 120.8, 122.5 (d, $J_{C\text{-}F}$ = 30.2 Hz), 123.0, 123.6, 124.7, 126.0, 126.3, 128.7, 133.3, 135.0, 136.5, 139.1, 140.6, 140.9, 142.5, 144.4, 147.6, 153.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 160.7 (dd, $J_{C\text{-}F}$ = 12.5, 258.0 Hz), 161.4 (d, $J_{C\text{-}F}$ = 7.0 Hz), 163.0 (dd, $J_{C\text{-}F}$ = 12.2, 254.5 Hz).

OLED Fabrication Procedure

Light-emitting diodes were fabricated on indium-tin oxide (ITO) patterned glass substrates which were cleaned in an ultrasonic bath with acetone followed by propan-2-ol prior to oxygen plasma etching for ten minutes at 150W. A conventional photo-resist spin-coater was used to deposit first a 20 nm layer of filtered PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid)]. The PEDOT:PSS layer was dried under nitrogen at 110 ºC for 1 h to remove any residual water prior to spinning on the emissive layer inside a glovebox. A solution consisting of 19 wt. % of PBD and 5 wt. % of Ir complex were blended with PVK and dissolved in HPLC grade $CHCl_3$. The polymer solution was filtered and a 90 nm thick film was spin-cast on top of the PEDOT:PSS layer. A 20 nm calcium cathode was evaporated onto the device through a shadow mask and capped with aluminium (120 nm). Current-voltage characteristics were measured using a Keithley 230 voltage source and a Keithley 195 digital multimeter and luminance was detected using a silicon photodiode and a Keithley 2000 digital multimeter. Electroluminescence spectra were taken with an optical fibre coupled to the Oriel Instaspec IV spectrometer described above. All electrical measurements were carried out under vacuum.

Crystal structure determination

Crystallographic data for **1a** were collected at 150 K using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer. Crystallographic data for **1d** were collected at 180 K on a Nonius KappaCCD with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The images were processed with the DENZO and SCALEPACK programs.[3] The structures were solved by direct methods using the program programs SIR92[4] The refinement (on F) and graphical calculations were performed using the CRYSTALS[5] program suite.

Table 1. Crystallographic Data of **1a** and **1d**

Compound	**1a**	**1d**
Empirical formula	$C_{30}H_{16}F_7IrN_6·0.5CH_2Cl_2$	$C_{30}H_{14}Br_2F_7IrN_6·2CHCl_3$
Formula weight	785.70	1182.25
Temperature, K	150	180
Crystal system	monoclinic	monoclinic
Space group	*C*1 2/*c* 1	*P*1 21/*c* 1 (no. 14)
Unit cell dimensions		
a (Å)	31.9711(13)	10.2543(1)
b (Å)	10.4764(4)	21.6017(3)
c (Å)	15.9719(7)	17.3654(3)
α (deg)	90	90
β (deg)	91.6650(10)	101.4341(6)
γ (deg)	90	90
Volume ($Å^3$)	5347.4(4)	3770.27(9)
Z	8	4
Density, calcd (g/cm^3)	1.952	2.083
Absorption coefficient (mm^{-1})	5.077	6.156
F(000)	3024	2248
θ range for data collection (deg)	1 – 25	1 – 27
Reflections collected	29052	31368
Independent reflections	8135	8289
Goodness-of-fit on F^2	1.09	1.09
Final *R* indices [$I > 2\sigma(I)$]	0.0223	0.0497
R indices (all data)	0.029	0.086

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