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Oligo(fluorenyl)pyridine ligands and their tris-cyclometalated iridium(III) complexes: synthesis, photophysical properties and electrophosphorescent devices

Mustafa Tavasli,^a Sylvia Bettington,^a Martin R. Bryce,^{*a} Hameed A. Al Attar,^b Fernando B. Dias,^b Simon King^b and Andrew P. Monkman^b

^a Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, UK. E mail: m.r.bryce@durham.ac.uk

^b Department of Physics, University of Durham, South Road, Durham, DH1 3LE, UK.

Experimental Section

General Details. All reactions were performed under an argon atmosphere, which was dried by passage through a column of phosphorus pentoxide. All reagents were of standard reagent grade and purchased from Aldrich, Lancaster and Fluorochem and used as supplied unless otherwise stated. THF was dried and distilled, prior to use, over potassium or sodium metal. All other solvents were used without prior purification. Column chromatography was carried out on silica-gel (40-60 μm). ¹H-NMR spectra were recorded on a Varian Unity 300 at 300 MHz or a Varian VXR 400s at 400 MHz or a Varian Inova 500 spectrometer at 500 MHz using deuteriated solvent as the lock and tetramethylsilane as the internal reference. ¹³C-NMR spectra were recorded using broad-band decoupling on the above spectrometers at 75, 100 and 125 MHz, respectively. Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionisation mode as indicated. Electrospray high resolution mass spectra were obtained on a Micromass LCT (TOF). Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser. Melting points were recorded on a Stuart Scientific SMP3 apparatus and are uncorrected. MALDI-TOF spectra were obtained on a Applied Biosystems Voyager-DE STR operating in reflector mode.

Photophysical Measurements.

Steady-state photophysical measurements were carried out on solutions of complexes **4-6** (0.01 mg) in toluene (5 cm³) using Jobin Yvon Fluoromax-3 and Perkin Elmer Lambda 19 UV/Vis/NR spectrophotometers. All solutions were freshly prepared and degassed prior to measurements. Aerated solutions showed strong phosphorescence quenching by oxygen. Furthermore, storage of solutions for several weeks caused increased susceptibility to fluorenone formation (on the ligands

1-3) and also other solvent-induced effects that reduced the overall phosphorescence efficiencies.

Lifetimes. The luminescence decays of the ligands **1-3** and their complexes **4-6** were measured using picosecond time correlated single photon counting (TCSPC). The excitation source consists of a picosecond diode laser from Picoquant ($\lambda=390$ nm), repetition rate 20 MHz, FWHM=75 ps. Signal acquisition was performed using a TCSPC module from Becker and Hickl (Model SPC 430). The luminescence decays were deconvoluted using an updated Linux version of George Striker's program.¹ Time-resolved emission spectroscopy (TRES) measurements were carried out using a pulsed Nd-yttrium aluminum garnet (Nd:YAG) laser ($\lambda=355$ nm), repetition rate 1-10 Hz, FWHM=120 ps and maximum pulse energy of 7 mJ. The light emitted by the samples was dispersed through a spectrograph (TRIAX 180, Jobin Yvon-Spex) and the separated spectra were subsequently detected by a gated intensified charge coupled device (CCD) camera (4 pico, Stanford Computer Optics). The gated setting for the phosphorescence emission decay-kinetics measurements was stepped in 200 ns delay time increments with a fixed gate time of 100 ns. This method provides a true time-dependent intensity since the gate time is smaller than the delay time. Furthermore, the initial time delay of 200 ns prevents detection of any intense fluorescence signals.

Thin Films. Thin films, used to study low temperature (30K) phosphorescence emission of the ligands **1-3** and their complexes **4-6**, were spin-coated on quartz from 1×10^{-5} M chlorobenzene solutions in poly(methyl methacrylate) (PMMA).

OLEDs. All devices were fabricated on indium tin oxide (ITO)-coated glass substrates of thickness 125 nm and possessing a sheet resistance of 13 Ω/\square . Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS), obtained commercially from Bayer A.G. Germany, was spin coated at 2500 rpm to produce a ~ 30 nm thick hole-transporting layer (HTL). These HTL-coated substrates were then dried at 50 °C for 16 h under high vacuum (0.1 mm-Hg) to remove any residual

water. The 10 mg / 1 cm³ of poly(9,9'-spirobifluorene) (PSF) and 1.4x10⁻³ M dopant (complexes 4-6) solutions were prepared in chlorobenzene. The dependence on molar concentration, rather than on weight percent, was to ensure an equal number of active iridium sites in all of the dopants 4-6 and hence to study the electrophosphorescence characteristics of the devices as a function of ligand length. Dopant solutions (50 μL) were thoroughly mixed with PSF (200 μL) at 40 °C for 3 h. This concentration ratio ensured that at low current densities all the emission emanated from complexes 4-6. The polymer:dopant solution mixtures were then spin-coated onto the HTL-coated substrates at 2500 rpm to produce 80 nm thick active layers. In order to account for the dopant effect on the device performance, pure PSF samples were also prepared. Each PSF sample was shadow masked to produce eight identical devices; the samples were then introduced into a nitrogen glove box, where 50 nm calcium cathodes were evaporated onto the device at a rate of ~ 1 Å/s under vacuum at a pressure of ca. 1x10⁻⁵ mm Hg. This was

followed by the deposition of a 100 nm capping layer of aluminum under the same evaporation conditions.

The electrical and luminance characteristics of the devices were tested under vacuum at a pressure of 2x10⁻² mm Hg. The current-voltage (I-V) characteristics and the emission intensities were measured using a home-written NI LabView program which controlled Keithley 2000 and Keithley 2400 voltmeters, and a current source meter, respectively. The electroluminescence (EL) and electrophosphorescence (EP) spectra were measured using an Ocean Optics USB2000 spectrometer.

Materials: Poly(9,9'-spirobifluorene) (PSF) was supplied by Covion.² The compounds depicted in Chart 1 were synthesised according to the literature procedures: 2-bromo-9,9-dihexylfluorene (Fl₁Br) **21**,^{3,4} 9,9-dihexylfluorene-2-ylboronic acid (Fl₁B(OH)₂) **7**,⁵ 2-(9,9-dihexylfluorene-2'-yl)pyridine (Fl₁Py) **1**,⁴ 2,7-dibromo-9,9-dihexylfluorene (BrFl₁Br) **12**,⁶ 2-bromo-9,9,9',9'-tetrahexylbifluorene (Fl₂Br) **22**,⁶ 9,9,9',9'-tetrahexylbifluorene-2-ylboronic acid (Fl₂B(OH)₂) **11**,⁵ tris[2-(9,9-dihexylfluorene-2'-yl)pyridine]iridium (Ir[Fl₁Py]₃) **4**.⁴

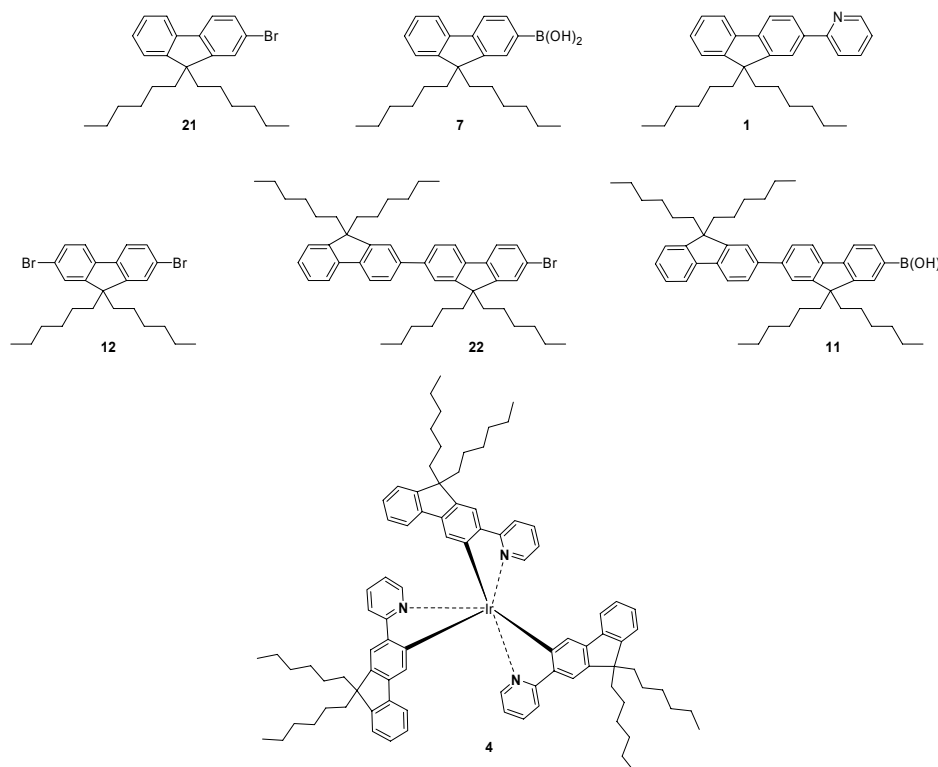
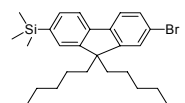


Chart 1 Structures of known literature compounds (**21**, **7**, **1**, **12**, **22**, **11** and **4**) used in this work.

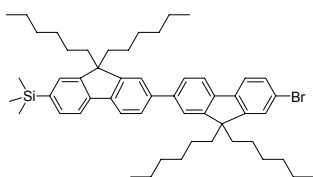
Synthesis of TMS-Fl_nBr Derivatives (n = 1,2).

TMS-Fl₁Br 13: A solution of n-BuLi in hexanes (2.5 M, 28.6 cm³, 71.6 mmol, 1.0 eq.) was added slowly to a solution of Br-Fl₁Br **12** (35.3 g, 71.6 mmol) in dry THF (300 cm³) at -78 °C. The mixture was stirred for 1 h at this temperature, and then chlorotrimethylsilane (11.7 g, 107.4 mmol, 1.5 eq.) was added. The whole mixture was stirred for 30 min at 20 °C, and then poured into distilled water (700 cm³). After the organic products were extracted into petroleum-



ether (5 x 100 cm³), the combined extracts were dried over MgSO₄, filtered and concentrated in vacuo. Purification on a silica column (eluent: petroleum-ether) yielded **13** (31.1 g, 90%) as a clear oil. R_f: 0.47 (petroleum-ether); ¹H NMR (500 MHz, CDCl₃) δ: 0.33 (s, 9H), 0.56-0.72 (m, 4H), 0.79 (t, J = 7.2 Hz, 6H), 1.02-1.18 (m, 12H), 1.88-2.03 (m, 4H), 7.44-7.53 (m, 4H), 7.57 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.6, 14.3, 22.8, 23.9, 29.9, 31.7, 40.4, 55.6, 119.3, 121.4, 121.4, 126.5, 127.9, 130.2, 132.3, 140.0, 140.4, 141.0, 149.8, 153.5; MS (EI) m/z 487 (M⁺, 38%), 486 (M⁺, 80%),

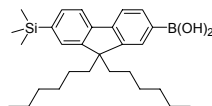
485 (M^+ , 38%), 484 (M^+ , 76%), 73 (100%); HRMS calculated for $C_{28}H_{41}BrSi$ (M^+): 484.21609; found 484.21632 (-0.5 ppm).



TMS-Fl₂Br 15: A mixture of TMS-Fl₁B(OH)₂ **14** (8.8 g, 19.6 mmol), Br-Fl₁-Br **12** (31.4 g, 63.7 mmol, 3.2 eq.) and Pd(PPh₃)₄ (752 mg, 0.6 mmol, 3% eq.) was partitioned between toluene (125 cm³) and aqueous Na₂CO₃ (2 M, 35 cm³, 70 mmol). The mixture was degassed several times and then heated at 90 °C for 3 days under argon. The reaction mixture was allowed to cool to 20 °C, and then diluted with petroleum-ether (300 cm³). The organic layer was washed with distilled water (3 x 100 cm³), dried over MgSO₄, filtered and concentrated in vacuo to give a pale orange liquid. Purification on a silica column by gradient elution with a mixture of petroleum-ether and dichloromethane gave **15** (11.1 g, 69%) as a clear gummy oil. R_f: 0.23 (petroleum-ether : CH₂Cl₂ 98:2 v/v); ¹H NMR (500 MHz, CDCl₃) δ: 0.36 (s, 9H), 0.67-0.85 (m, 20H), 1.04-1.22 (m, 24H), 1.95-2.12 (m, 8H), 7.47-7.56 (m, 4H), 7.59-7.70 (m, 5H), 7.74 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.5, 14.3, 22.8, 22.9, 24.1, 29.9, 30.0, 31.7, 31.8, 40.4, 40.6, 55.4, 55.9, 119.4, 120.3, 120.4, 121.3, 121.4, 121.8, 121.8, 126.4, 126.6, 126.6, 128.0, 130.3, 132.2, 139.4, 139.5, 140.2, 140.8, 141.4, 141.7, 150.5, 151.4, 152.1, 153.6; MS (EI) m/z 819 (M^+ , 73%), 818 (M^+ , 100%), 817 (M^+ , 72%), 816 (M^+ , 93%); HRMS calculated for C₅₃H₇₃BrSi (M^+): 816.4665; found 816.4651 (1.7 ppm); MS (MALDI-TOF) m/z calculated for C₅₃H₇₃BrSi (M^+): 816.47, Found: 816.31.

Synthesis of TMS-Fl₁B(OH)₂ 14 and TMS-Fl₂B(OR)₂ 16 Derivatives: General Procedure: A solution of n-BuLi in hexanes (1.6 M / 2.5 M, 1.1 eq.) was added slowly to a solution of TMS-Fl_nBr (1.0 eq.) in dry THF (150-300 cm³) at -78 °C. The mixture was stirred for 1 h at this temperature, and then (iPrO)₃B (2.0-3.0 eq.) / 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 eq.) was added. The mixture was stirred for 21 h whilst gradually warming to 20 °C. The mixture was then poured into a large amount of distilled water (in the case of the pinacol ester, into brine). Organic products were extracted into diethyl ether (5 x 50-100 cm³). Combined extracts were dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product. This was purified on a silica gel column by gradient elution with a mixture of either petroleum-ether and ethyl acetate or petroleum-ether and dichloromethane.

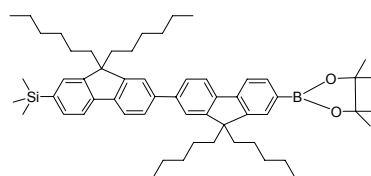
TMS-Fl₁B(OH)₂ 14: TMS-Fl₁Br **13** (31.1 g, 64.1 mmol), n-BuLi (2.5 M, 28.2 cm³, 70.5 mmol) and (iPrO)₃B (24.1 g, 128.2 mmol) gave **14** (22.6 g, 78%) as a white foamy solid. R_f: 0.27 (petroleum-ether : AcOEt, 7:3 v/v); ¹H NMR (500 MHz, CDCl₃) δ: 0.38 (s, 9H), 0.59-0.85 (m, 4H), 0.80 (t, J = 7.0 Hz, 6H), 1.02-1.22



(m, 12H), 2.04-2.22 (m, 4H), 7.58 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 8.27 (s, 1H), 8.35 (d, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.5, 14.4, 22.8, 24.1, 30.0, 31.8, 40.5, 55.3, 119.7, 120.0, 128.1, 129.4, 130.1, 134.9, 140.6, 141.7, 145.9, 150.7, 151.1; MS (EI) m/z 423 (M^+ -2xCH₃, 20%), 422 (M^+ -2xCH₃, 55%), 406 (M^+ -B(OH)₂, 27%), 407 (M^+ -B(OH)₂, 16%).

(m, 12H), 2.04-2.22 (m, 4H), 7.58 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 8.27 (s, 1H), 8.35 (d, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.5, 14.4, 22.8, 24.1, 30.0, 31.8, 40.5, 55.3, 119.7, 120.0, 128.1, 129.4, 130.1, 134.9, 140.6, 141.7, 145.9, 150.7, 151.1; MS (EI) m/z 423 (M^+ -2xCH₃, 20%), 422 (M^+ -2xCH₃, 55%), 406 (M^+ -B(OH)₂, 27%), 407 (M^+ -B(OH)₂, 16%).

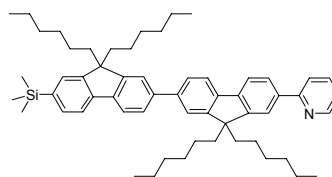
TMS-Fl₂B(OR)₂ 16: TMS-Fl₁Br **13** (8.2 g, 10.0 mmol), n-BuLi (2.5 M, 4.5 cm³, 11.0 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.8 g, 14.9 mmol) gave **16** (5.4 g, 62%) as a white foamy solid. R_f: 0.19 (petroleum-ether : CH₂Cl₂ 9:1 v/v); ¹H NMR (400 MHz, CDCl₃) δ: 0.35 (s, 9H), 0.65-0.88 (m, 20H), 1.01-1.22 (m, 24H), 1.43 (s, 12H), 2.00-2.15



(m, 8H), 7.53 (s, 1H), 7.54 (dd, J = 7.5 and 0.7 Hz, 1H), 7.63-7.69 (m, 4H), 7.72-7.85 (m, 5H), 7.87 (dd, J = 7.5 and 0.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.5, 14.3, 14.4, 22.8, 22.9, 24.0, 25.3, 29.9, 30.0, 31.7, 31.8, 40.4, 40.6, 55.4, 55.6, 84.0, 119.3, 119.4, 120.3, 120.6, 121.8, 121.8, 126.4, 127.9, 129.2, 132.2, 134.1, 139.3, 140.4, 140.6, 140.9, 141.4, 141.7, 144.2, 150.5, 150.5, 152.0, 152.4; Anal. Calcd. for C₅₉H₈₅BO₂Si: C, 81.90%; H, 9.90%; Found: C, 81.65%; H, 9.92%; MS (EI) m/z 866 (M^+ , 44%), 865 (M^+ , 79%), 864 (M^+ , 100%), 863 (M^+ , 39%); MS (MALDI-TOF) m/z calculated for C₅₉H₈₅BO₂Si (M^+): 864.64, Found: 864.57.

Synthesis of TMS-Fl_nPy Derivatives: General Procedure. A mixture of TMS-Fl₁B(OH)₂ **14** (1.1-1.2 eq.), Br-Fl_nPy (1.0 eq.) and Pd(PPh₃)₄ (5-7% eq.) was partitioned between toluene (30-40 cm³) and aqueous Na₂CO₃ (2 M, 10 eq.). The mixture was degassed several times and then heated at 90 °C for ca. 2.5 days under argon. The reaction mixture was cooled to 20 °C and diluted with distilled water. After the organic layer was separated, the organic products were further extracted into dichloromethane (4x 40 cm³). Combined extracts were dried over MgSO₄, filtered and concentrated under reduced pressure to give a dark brown liquid or solid which was purified on a silica gel column by gradient elution with a mixture of petroleum-ether and dichloromethane.

TMS-Fl₂Py 17: TMS-Fl₁B(OH)₂ **14** (3.6 g, 8.0 mmol), Br-Fl₁Py **10** (3.6 g, 7.3 mmol), Pd(PPh₃)₄ (421 mg, 0.4 mmol), toluene (40



cm³) and Na₂CO₃ (2 M, 36.4 cm³, 72.8 mmol) were heated at 90 °C for 72 h. Compound **17** (4.79 g, 81%) was obtained as a pale orange solid. R_f: 0.19 (petroleum-ether :

CH₂Cl₂ 1:1 v/v); mp 134-135 °C; ¹H NMR (500 MHz, CDCl₃) δ: 0.34 (s, 9H), 0.68-0.82 (m, 20H), 1.01-1.18 (m, 24H), 2.04 (m, 4H), 2.11 (m, 4H), 7.27 (m, 1H), 7.51 (s, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.62-7.70 (m, 4H), 7.73 (d, J = 7.5 Hz, 1H), 7.78-7.87 (m, 5H), 8.03 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H), 8.76 (d, J = 4.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.5, 14.4, 22.8, 22.9, 24.0, 24.2, 29.9, 30.0, 31.7, 31.8, 40.4, 40.8, 55.4, 55.8, 119.4, 120.4, 120.6, 121.1, 121.6, 121.8, 121.9, 122.3, 126.4, 126.4, 126.5, 128.0, 132.2, 137.4, 139.3, 140.1, 140.7, 140.9, 141.3, 141.7, 142.3, 149.7, 150.5, 152.0, 152.4, 158.0; Anal. Calcd. for C₅₈H₇₇NSi: C, 85.34%; H, 9.51%; N, 1.72%; Found: C, 85.62%; H, 9.55%; N, 1.85%; MS (EI) m/z 816 (M⁺, 68%), 815 (M⁺, 100%); MS (MALDI-TOF) m/z calculated for C₅₈H₇₇NSi (M⁺): 815.58, Found: 815.56.

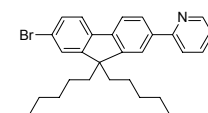
TMS-Fl₃Py 19: TMS-Fl₁B(OH)₂ **14** (3.0 g, 6.8 mmol), Br-Fl₂Py **18**, Pd(PPh₃)₄ (439 mg, 0.4 mmol), toluene (30 cm³) and Na₂CO₃ (2 M, 27.2 cm³, 54.3 mmol) were heated at 90 °C for 66 h. Compound **19** (5.08 g, 81%) was obtained as a light brown solid. R_f: 0.38 (petroleum-ether : CH₂Cl₂ 4:6 v/v) mp 58-63 °C; ¹H

NMR (300 MHz, CDCl₃) δ: 0.33 (s, 9H), 0.64-0.91 (m, 30H), 0.99-1.24 (m, 36H), 1.96-2.20 (m, 12H), 7.28 (m, 1H), 7.50 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.58-7.77 (m, 9H), 7.77-7.90 (m, 7H), 8.04 (d, J = 7.8 Hz, 1H), 8.06 (s, 1H), 8.77 (d, J = 4.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: -0.5, 14.4, 22.8, 22.9, 22.9, 24.1, 24.2, 29.9, 30.0, 30.0, 31.7, 31.8, 31.8, 40.5, 40.7, 40.8, 55.4, 55.7, 55.8, 119.3, 120.3, 120.4, 120.6, 121.1, 121.6, 121.8, 122.2, 126.3, 126.4, 126.5, 128.0, 132.2, 137.2, 138.3, 139.3, 140.1, 140.2, 140.3, 140.4, 140.6, 140.8, 140.9, 140.9, 141.2, 141.7, 142.2, 149.8, 150.5, 152.0, 152.1, 152.1, 152.4, 158.1; Anal. Calcd. for C₈₃H₁₀₉NSi: C, 86.77%; H, 9.56%; N, 1.22%; Found: C, 86.09%; H, 10.07%; N, 1.23%; MS (MALDI-TOF) m/z calculated for C₈₃H₁₀₉NSi (M⁺): 1148.84, Found: 1148.85.

Synthesis of BrFl_nPy Derivatives (n = 1,2,3): general procedure. Method A: Bromine (2.5 eq.) was added to a mixture of Fl₁Py **1** (1.0 eq.) and FeCl₃ (10% eq.) in CH₂Cl₂ at -20 °C and the mixture was stirred in the dark for 67 h at 20 °C. The mixture was diluted with CH₂Cl₂, and washed with 7% aqueous Na₂S₂O₃ (4 x 30 cm³), 2 M aqueous Na₂CO₃ (2 x 40 cm³) and distilled water (40 cm³). The organic phase was separated, dried over MgSO₄ and concentrated in vacuo to give a brown liquid, which was purified on a silica gel column by gradient elution with a mixture of petroleum-ether and dichloromethane. **Method B:** Bromine (4.0 eq.) was added to a mixture of TMS-Fl_nPy (1.0 eq.) and sodium acetate (2.0 eq.) in THF at 0 °C, and then the mixture was stirred for 1-1.5 h in the dark. Triethylamine (8.0 eq.) was added, and excess Br₂ was immediately quenched with saturated aqueous Na₂SO₃ solution. After the organic layer was separated, the organic products were further extracted into CH₂Cl₂ (4 x 30 cm³). The combined extracts were dried over MgSO₄, filtered and concentrated under

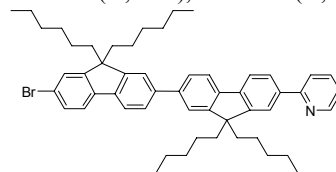
reduced pressure to give a dark-brown solid, which was purified as in Method A.

Br-Fl₁Py 10: Following Method A, Fl₁Py **1** (2.2 g, 5.4 mmol), FeCl₃ (88 mg, 0.5 mmol) and Br₂ (2.2 g, 13.4 mmol) in CH₂Cl₂ (10 cm³) gave **10** (1.9 g, 73%) as a viscous oil. R_f: 0.30



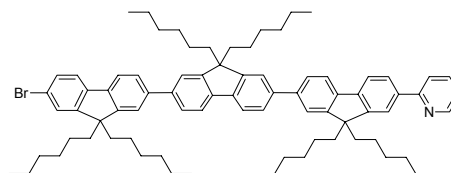
(petroleum-ether : CH₂Cl₂ 3:7 v/v); ¹H NMR (400 MHz, CDCl₃) δ: 0.52-0.71 (m, 4H), 0.75 (t, J = 6.9 Hz, 6H), 0.95-1.17 (m, 12H), 1.91-2.10 (m, 4H), 7.25 (ddd, J = 6.6, 4.8 and 1.7 Hz, 1H), 7.47 (dd, J = 7.2 and 1.7 Hz), 7.48 (s, 1H), 7.59 (dd, J = 7.3 and 1.6 Hz), 7.73-7.83 (m, 3H), 7.97-8.01 (m, 2H), 8.73 (d, J = 4.8 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ: 14.2, 22.8, 24.0, 30.0, 31.7, 40.6, 55.9, 120.2, 120.8, 121.4, 121.6, 121.6, 122.2, 126.3, 126.5, 130.3, 136.9, 138.9, 139.9, 141.2, 149.9, 151.2, 153.8, 157.8; MS (EI) m/z 492 (M⁺, 33%), 491 (M⁺, 89%), 490 (M⁺, 35%), 489 (M⁺, 89%), 407 (35%), 406 (100%), 405 (38%), 404 (100%); HRMS (EI) calculated for C₃₀H₃₆BrN: 489.20311; found 489.20396 (-1.7 ppm).

Br-Fl₂Py 18: Following Method B, TMS-Fl₂Py **17** (4.8 g, 5.9 mmol), CH₃CO₂Na (963 mg, 11.7 mmol), Br₂ (3.75 g, 23.5 mmol) and Et₃N (4.8 g, 47.0 mmol) in THF (50 cm³) gave **18** (4.5 g, 92%) as a yellow solid. R_f: 0.46 (petroleum-ether : CH₂Cl₂ 2:8 v/v); mp 45-48 °C; ¹H NMR (500 MHz, CDCl₃) δ: 0.66-0.82 (m, 20H), 1.00-1.19 (m, 24H), 1.91-2.17 (m, 8H), 7.27



(m, 1H), 7.48 (dd, J = 7.9 and 1.8 Hz, 1H), 7.50 (s, 1H), 7.57-7.69 (m, 5H), 7.76 (d, J = 7.9 Hz, 1H), 7.77-7.88 (m, 4H), 8.03 (dd, J = 8.0 and 1.4 Hz, 1H), 8.05 (s, 1H), 8.76 (d, J = 4.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 14.2, 14.3, 22.8, 24.0, 24.1, 30.0, 31.7, 40.5, 40.6, 55.7, 55.8, 120.3, 120.3, 120.5, 121.0, 121.2, 121.3, 121.6, 121.7, 121.7, 122.2, 126.3, 126.4, 126.4, 126.6, 130.2, 137.3, 139.5, 140.1, 140.2, 140.9, 141.2, 142.1, 149.7, 151.4, 152.0, 152.4, 153.5, 157.9; MS (EI) m/z 824 (M⁺, 55%), 823 (M⁺, 100%), 822 (M⁺, 54%), 821 (M⁺, 88%); HRMS (EI) calculated for C₅₅H₆₈BrN: 821.4535; found 821.4523 (1.5 ppm); MS (MALDI-TOF) m/z calculated for C₅₅H₆₈BrN (M⁺): 821.45, Found: 821.43.

Br-Fl₃Py 20: Following Method B, TMS-Fl₃Py **19** (5.08 g, 4.42 mmol), CH₃CO₂Na (725 mg, 8.84 mmol) and Br₂ (2.83 g, 17.68 mmol) in THF (40 cm³) gave **20** (4.43 g, 87%) as a light red/brown foamy solid. R_f: 0.31 (petroleum-ether : CH₂Cl₂ 4:6

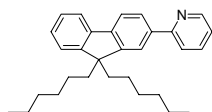


v/v); mp 67-72 °C. ¹H NMR (500 MHz, CDCl₃) δ: 0.69-0.90 (m, 50H), 1.03-1.22 (m, 36H), 1.96-2.20 (m, 12H), 7.27 (m, 1H), 7.50 (dd, J = 7.9 and 1.6 Hz, 1H), 7.52 (s, 1H), 7.59-7.74 (m, 9H), 7.76-7.82 (m, 2H), 7.83-7.89 (m, 5H), 8.05 (dd, J = 7.9 and 1.3 Hz, 1H), 8.08 (s, 1H), 8.77 (d, J = 4.5 Hz, 1H); ¹³C NMR

(125 MHz, CDCl₃) δ : 14.3, 22.8, 22.8, 22.9, 24.0, 24.1, 29.9, 29.9, 30.0, 31.7, 31.7, 31.8, 40.6, 40.6, 40.7, 55.6, 55.7, 55.8, 120.3, 120.5, 121.0, 121.3, 121.4, 121.5, 121.7, 121.8, 121.8, 122.2, 126.2, 126.4, 126.5, 126.6, 130.3, 137.1, 138.3, 139.5, 140.1, 140.1, 140.3, 140.4, 140.6, 140.8, 141.1, 141.3, 142.1, 149.9, 151.4, 152.0, 152.1, 153.4, 153.5, 158.0; MS (MALDI-TOF) m/z calculated for C₈₀H₁₀₀BrN (M⁺): 1156.71, Found: 1156.60.

Synthesis of Fl_nPy Ligands (n = 1,3,5): General Procedure. A mixture of Fl_nB(OH)₂ (1.0-1.2 eq.), BrFl_nPy (1.0-1.3 eq.) and Pd(PPh₃)₄ (3-10% eq.) was partitioned between toluene (20–40 cm³) and aqueous Na₂CO₃ (2 M; 3-10 eq.). The mixture was degassed several times and then heated at 90 °C for ca. 2.5 days under argon. The reaction mixture was allowed to cool to 20 °C and then diluted with distilled water. After the organic layer was separated, organic products were further extracted into dichloromethane (4 x 40 cm³). The combined extracts were then dried over MgSO₄, filtered and concentrated in vacuo to give a dark brown liquid or solid which was purified on a silica gel column, eluting with a mixture of petroleum-ether and ethyl acetate or a mixture of petroleum-ether and dichloromethane.

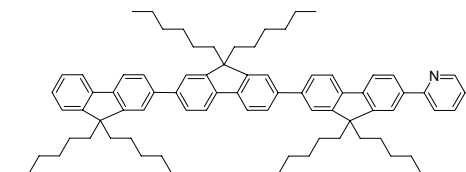
Fl₁Py 1⁴: Fl₁B(OH)₂ **7** (3.4 g, 9.0 mmol), 2-bromopyridine **8** (1.8 g, 11.7 mmol), Pd(PPh₃)₄ (312 mg, 0.3 mmol), toluene (20 cm³) and Na₂CO₃ (2 M, 13.5 cm³, 27.0 mmol) were reacted at 90 °C for 64 h. Upon purification and removal of excess 2-



bromopyridine by distillation (ca. 1 mm Hg, 100 °C), compound **1** (2.8 g, 77 %) was obtained as clear oil which solidified on standing overnight, mp 56.8-58.8 °C. R_f: 0.22 (petroleum-

ether : AcOEt 95:5 v/v). ¹H NMR (400 MHz, CDCl₃) δ : 0.54-0.71 (m, 4H), 0.74 (t, J = 7.0 Hz, 6H), 0.94-1.15 (m, 12H), 1.95-2.11 (m, 4H), 7.23 (dd, J = 5.0 and 1.5 Hz, 1H), 7.29-7.38 (m, 3H), 7.71-7.84 (m, 4H), 7.98 (dd, J = 7.7 and 1.5 Hz, 1H), 8.00 (s, 1H), 8.73 (d, J = 4.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ : 14.2, 22.8, 24.0, 30.0, 31.8, 40.7, 55.5, 120.1, 120.2, 120.8, 121.4, 122.1, 123.1, 126.1, 127.1, 127.6, 136.9, 138.4, 140.9, 142.4, 149.8, 151.5, 151.6, 158.0; MS (EI) m/z 412 (36%), 411 (M⁺, 81%), 327 (44%), 326 (100%), 134 (96%).

Fl₃Py 2: Fl₂B(OH)₂ **11** (3.4 g, 4.8 mmol), BrFl₂Py **18** (1.92 g, 3.91 mmol), Pd(PPh₃)₄ (135 mg, 0.1 mmol), toluene (20 cm³) and Na₂CO₃ (2 M, 6.0 cm³, 12.0 mmol) were reacted at 90 °C for 69 h. Upon purification, compound **2** (2.2 g, 52%) was obtained as a pale orange solid. R_f: 0.42 (petroleum-ether : CH₂Cl₂ 3:7 v/v);

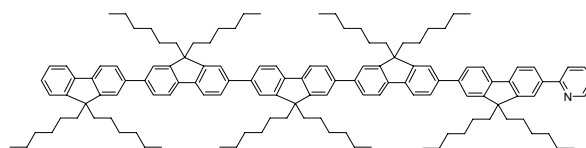


mp 60-64 °C; ¹H NMR (400 MHz,

CDCl₃) δ : 0.64-0.92 (m, 30H), 1.01-1.22 (m, 36H), 1.98-2.22 (m, 12H), 7.26 (dd, J = 4.9 and 1.1 Hz), 7.31-7.41 (m, 3H), 7.63-7.73 (m, 8H), 7.74-7.88 (m, 8H), 8.04 (dd, J = 7.9 and 1.5 Hz, 1H), 8.06 (s, 1H), 8.76 (d, J = 4.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ : 14.3, 22.8, 22.8, 22.8, 24.0, 24.1, 29.9, 30.0, 31.7, 31.7, 31.8, 40.6, 40.6, 40.7, 55.4, 55.6, 55.7, 120.0, 120.1, 120.2, 120.5, 121.0, 121.5, 121.7, 121.8, 122.2, 123.2, 126.2, 126.3, 126.4, 127.0, 127.2, 137.1, 138.3, 140.1, 140.2, 140.3, 140.6, 140.7, 140.7, 140.8, 141.0, 141.1, 142.1, 149.9, 151.2, 151.7, 151.9, 152.0, 152.0, 152.3, 158.0; Anal. Calcd. for C₈₀H₁₀₁N: C, 89.24%; H, 9.46%; N, 1.30%; Found: C, 88.97%; H, 9.47%; N, 1.10%; MS (MALDI-TOF) m/z calculated for C₈₀H₁₀₁N (M⁺): 1075.79, Found: 1075.64.

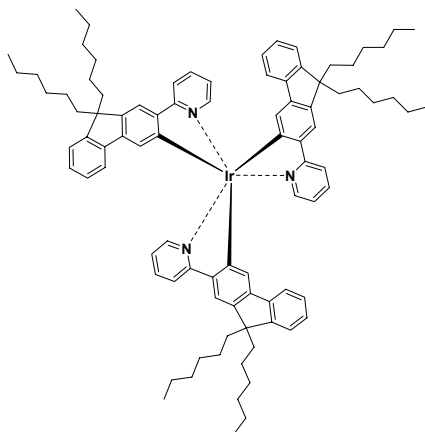
Fl₅Py 3: Fl₂B(OH)₂ **11** (1.70 g, 2.39 mmol), BrFl₃Py **20** (2.30 g, 1.99 mmol), Pd(PPh₃)₄ (230 mg, 0.20 mmol), toluene (40 cm³) and Na₂CO₃ (2 M, 10.0 cm³, 20.0 mmol) were reacted at 90 °C for 64 h. Upon purification, compound **3** (1.99 g, 87 %) was obtained as a pale orange solid. R_f: 0.192 (petroleum-ether : CH₂Cl₂ 1:1 v/v); mp 66-73 °C; ¹H NMR (500 MHz, CDCl₃) δ : 0.58-0.85 (m, 50H), 0.94-1.14 (m, 60H), 1.90-2.11 (m, 20H), 7.16-7.32 (m, 4H), 7.55-7.65 (m, 16H), 7.65-7.80 (m, 12H), 7.96 (d, J = 7.9 Hz, 1H), 7.98 (s, 1H), 8.68 (d, J = 4.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ : 14.3, 22.8, 22.8, 24.0, 24.1, 29.9, 30.0, 31.7, 31.7, 31.8, 40.6, 55.4, 55.6, 55.7, 120.0, 120.2, 120.2, 120.5, 121.1, 121.6, 121.7, 121.8, 122.2, 123.2, 126.3, 126.4, 127.0, 127.2, 140.0, 140.2, 140.2, 140.3, 140.3, 140.6, 140.7, 140.7, 140.8, 141.0, 141.1, 142.2, 149.6, 151.2, 151.7, 152.0, 152.1, 152.4, 157.9, 160.4; Anal. Calcd. for C₁₃₀H₁₆₅N: C, 89.65%; H, 9.55%; N, 0.80%; Found: C, 89.40%; H, 9.84%; N, 0.82%; MS (MALDI-TOF) m/z calculated for C₁₃₀H₁₆₅N (M⁺): 1741.30, Found: 1741.19.

Synthesis of Iridium Complexes of Fl_nPy Ligands: General Procedure. The ligand **1-3** (1.7 eq.) and Ir(acac)₃ (1.0 eq.) were dissolved in glycerol, and the mixture was degassed several times at varying temperatures (50 – 135 °C) under vacuum, then heated at 220 °C for 16-60 h in the dark under argon. The mixture was cooled to 20 °C and diluted with distilled water. The organic

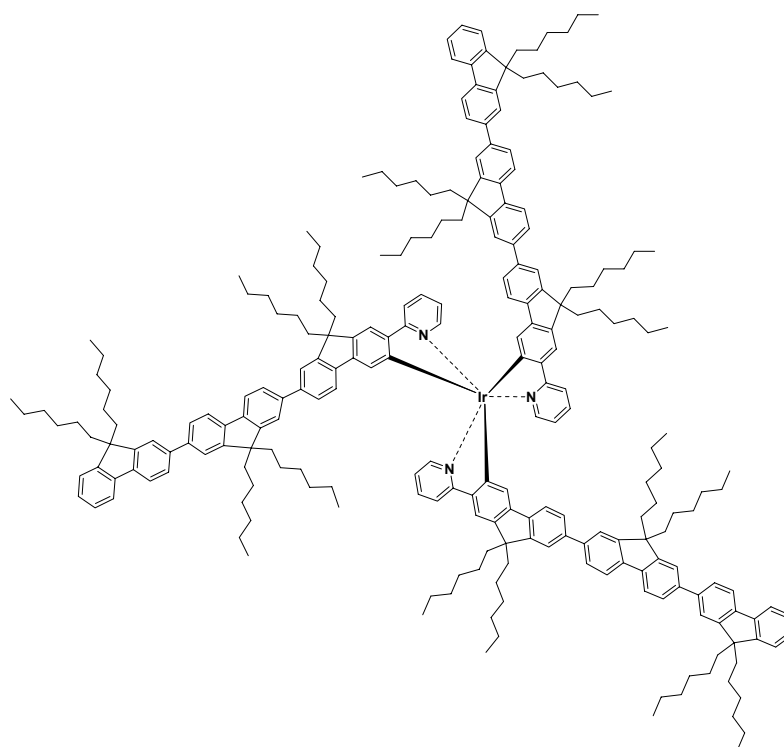


compounds were extracted into dichloromethane (4x40 cm³), the combined extracts were dried over MgSO₄, filtered and concentrated under reduced pressure to give the crude product, usually as dark brown liquid. This was purified on a silica gel column, by gradient elution either with a mixture of petroleum ether and chloroform or a mixture of petroleum ether and dichloromethane.

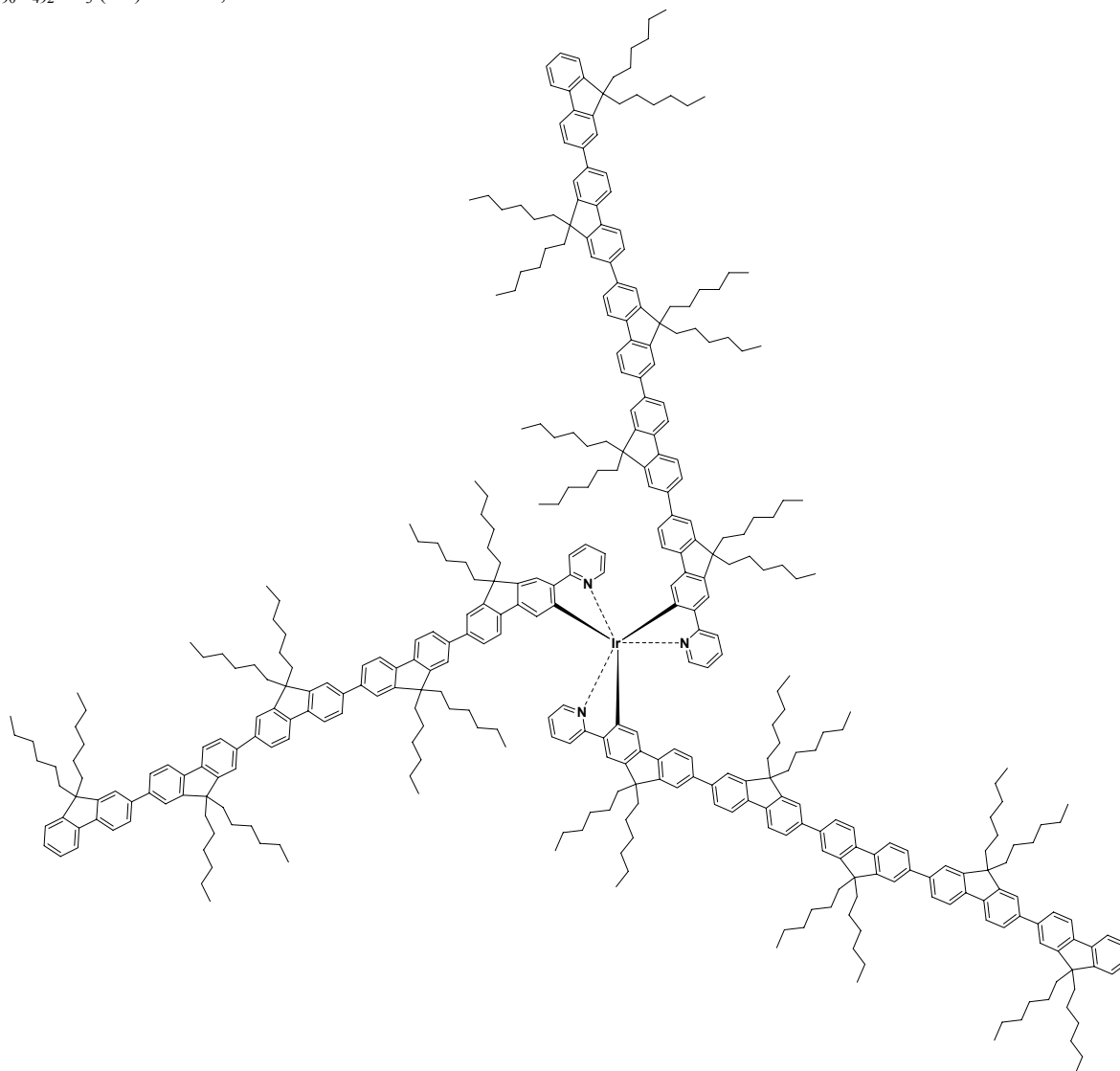
Ir(Fl₁Py)₃ 4⁴: Fl₁Py **1** (684 mg, 1.7 mmol) and Ir(acac)₃ (157 mg, 0.3 mmol) in glycerol (15 cm³) were reacted for 16 h to yield complex **4** (100 mg, 22%) as a brown solid. *R_f*: 0.50 (petroleum-ether : CHCl₃ 9:1 v/v); ¹H NMR (400 MHz, CDCl₃) δ: 0.20-1.20 (m, 66H), 1.90 (m, 12H), 6.60 (t, *J* = 6.3 Hz, 3H), 6.91 (t, *J* = 7.5 Hz, 3H), 6.98-7.16 (m, 12H), 7.33 (t, *J* = 7.3 Hz, 3H), 7.43 (d, *J* = 5.5 Hz, 3H), 7.52 (s, 3H), 7.75 (d, *J* = 8.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 14.3, 14.4, 22.9, 23.2, 24.0, 24.1, 30.1, 30.2, 31.7, 31.7, 41.3, 41.6, 54.2, 117.9, 119.2, 120.6, 121.4, 122.4, 126.4, 126.5, 128.7, 135.7, 142.1, 142.7, 143.2, 143.8, 147.22, 151.7, 160.0, 167.0. MS (MALDI-TOF) *m/z* calculated for C₉₀H₁₀₈IrN₃ (M⁺): 1423.82; Found: 1423.50.



Ir(Fl₃Py)₃ 5: Fl₃Py **2** (1.1 g, 1.0 mmol) and Ir(acac)₃ (100 mg, 0.2 mmol) in glycerol (15 cm³) were reacted for 17 h to yield complex **5** (69 mg, 10%) as a brown solid. *R_f*: 0.19 (petroleum-ether : CH₂Cl₂ 8:2 v/v); ¹H NMR (500 MHz, CDCl₃) δ: 0.52-0.85 (m, 30H), 0.91-1.10 (m, 30H), 1.12-1.30 (m, 6H), 1.86-2.05 (m, 10H), 2.06-2.28 (broad m, 2H), 6.50 (broad s, 1H), 7.19-7.34 (m, 6H), 7.43-7.60 (m, 8H), 7.63-7.74 (m, 5H), 7.84 (broad s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 13.0, 13.1, 13.2, 21.4, 21.5, 21.6, 22.0, 22.7, 23.0, 23.0, 28.5, 28.6, 28.7, 28.8, 29.0, 30.3, 30.4, 30.4, 30.5, 30.6, 39.2, 39.3, 54.1, 54.2, 118.6, 118.7, 118.8, 119.5, 120.3, 120.4, 120.4, 121.9, 124.3, 125.0, 125.7, 125.9, 124.3, 125.0, 125.7, 125.9, 134.4, 138.6, 138.7, 139.0, 139.2, 139.3, 139.3, 139.7, 139.8, 140.4, 146.4, 150.0, 150.4, 150.6, 150.7, 151.3; MS (MALDI-TOF) *m/z* calculated for C₂₄₀H₃₀₀IrN₃ (M⁺): 3419.33; Found: 3419.25.



Ir(Fl₅Py)₃ 6: Fl₅Py **3** (1.8 g, 1.0 mmol) and Ir(acac)₃ (100 mg, 0.2 mmol) in glycerol (15 cm³) were reacted for 60 h to yield complex **6** (42 mg, 4%) as a brown solid. R_f: 0.19 (petroleum-ether : CH₂Cl₂ 8:2 v/v); ¹H NMR (500 MHz, CDCl₃) δ: 0.56-0.85 (m, 50H), 0.92-1.12 (m, 48H) 1.13-1.32 (m, 12H), 1.88-2.17 (m, 20H), 6.73 (broad s, 1H), 7.20-7.36 (m, 6H), 7.46-7.63 (m, 17H), 7.64-7.78 (m, 9H), 7.95 (d, J = 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 13.0, 13.1, 13.2, 21.5, 22.0, 22.7, 22.8, 28.6, 28.6, 28.7, 28.8, 29.0, 30.4, 30.4, 30.6, 39.3, 54.1, 54.2, 54.3, 118.7, 118.8, 118.9, 119.8, 120.2, 120.4, 120.5, 121.9, 124.4, 124.9, 125, 125.1, 125.8, 126.0, 134.5, 138.6, 138.9, 138.9, 139.0, 139.1, 139.2, 139.3, 139.4, 139.5, 139.8, 140.2, 146.2, 150.0, 150.4, 150.6, 150.7, 151.2; MS (MALDI-TOF) m/z calculated for C₃₉₀H₄₉₂IrN₃ (M⁺) 5413.83, Found: 5413.90.



References

- 1 G. Striker, V. Subramaniam, C. A. M. Seidel and A. Volkmer, *J. Phys. Chem. B*, 1999, **103**, 8612-8617.
- 2 World Patent PCT WO 03/020790 A2; H. Becker, S. Heun, K. Treacher, A. Büsing and A. Falcau, *SID, Digest of Technical Papers*, 2002, **33**, 780.
- 3 P. K. Tzolakis and J. K. Kallitsis, *Chem. Eur. J.*, 2003, **9**, 936-943.
- 4 J. C. Ostrowski, M. R. Robinson, A. J. Heeger and G. C. Bazan, *Chem. Commun.*, 2002, 784-785.
- 5 L. Kanibolotsky, R. Berridge, P. J. Skabara, I. Perepichka, D. C. C. Bradley and M. Koeberg, *J. Am. Chem. Soc.*, 2004, **126**, 13695-13702.
- 6 G. Hughes, C. Wang, A. S. Batsanov, M. Fearn, S. Frank, M. R. Bryce, I. F. Perepichka, A. P. Monkman and B. P. Lyons, *Org. Biomol. Chem.*, 2003, **2**, 3069-3077.

Figures and Tables:

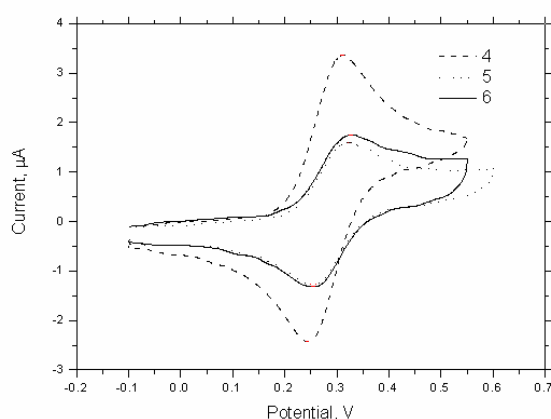


Fig. SI-1 The room temperature cyclic voltammograms of iridium(III) complexes (**4-6**) in CH_2Cl_2 solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($\text{n-Bu}_4\text{NPF}_6$), scan rate 100 mV/s. Electrodes: Working, Pt disk = 1.8 mm; Counter, Pt wire; Reference, $\text{Ag}/\text{AgNO}_3 - \text{CH}_3\text{CN}$.

Table SI-1 Oxidation potentials versus Ag/AgNO_3 obtained from cyclic voltammograms for a Pt electrode in contact with a 0.1 M $\text{n-Bu}_4\text{NPF}_6 / \text{CH}_2\text{Cl}_2$ solution of the iridium (III) complex (**4-6**) and ferrocene (Fc); scan rate 100 mV/s.

Complex	$E_{1\text{ox}}^{1/2}$ (V)	$E_{1\text{ox}}^{\text{Anodic}}$	$E_{1\text{ox}}^{\text{Cathodic}}$	ΔE (mV)
4	+0.28	+0.31	+0.24	70
5	+0.29	+0.32	+0.26	60
6	+0.30	+0.33	+0.25	80
Fc	+0.19	+0.22	+0.15	70

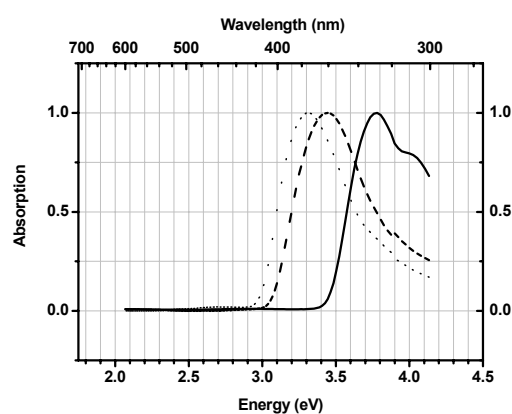


Fig. SI-2 The normalised solution-state absorption spectra of ligands **1-3** in toluene at 293 K, (—) $\text{Fl}_1\text{Py 1}$; (---) $\text{Fl}_3\text{Py 2}$; (···) $\text{Fl}_3\text{Py 3}$.

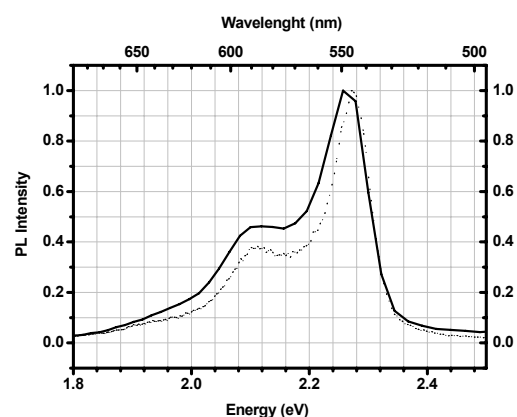


Fig. SI-3* Normalised photoluminescence (PL) (...) and electro-luminescence (EL) (—) spectra of complex **6**. *The PL spectrum is narrower than the EL spectrum. This is most likely due to a condensed phase effect. The films are too thin for optical interference to be a viable explanation. Moreover, interference would give narrower EL than PL spectra, which is not the case.

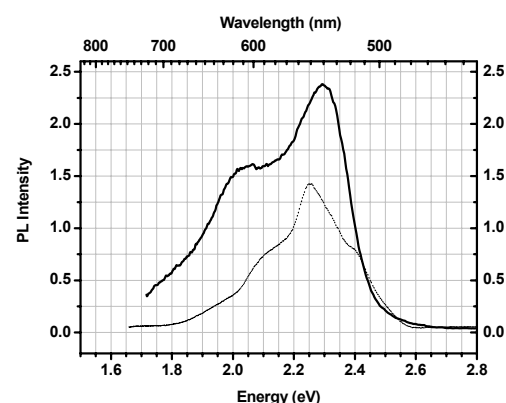


Fig. SI-4 Thin-film photoluminescence (PL) spectra of free ligand $\text{Fl}_1\text{Py 1}$ (...) and its complex **4**, $\text{Ir}[\text{Fl}_1\text{Py}]_3$ (—) at 30 K, after a delay of 1 μs .

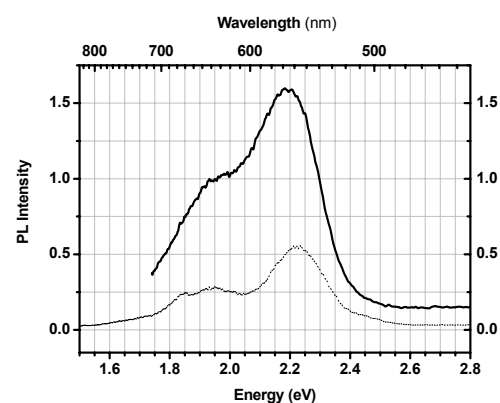


Fig. SI-5 Thin-film photoluminescence (PL) spectra of free ligand $\text{Fl}_3\text{Py 2}$ (...) and its complex **5**, $\text{Ir}[\text{Fl}_3\text{Py}]_3$ (—) at 30 K, after a delay of 1 μs .