Supporting Information for

Solution-Processible Conjugated Electrophosphorescent Polymers

Albertus J. Sandee[a], Charlotte K. Williams[a], Nicholas R. Evans[a], John E. Davies[a], Clare E. Boothby[b], Anna Köhler[b], Richard H. Friend[b] and Andrew B. Holmes[a]*

[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

[b] Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

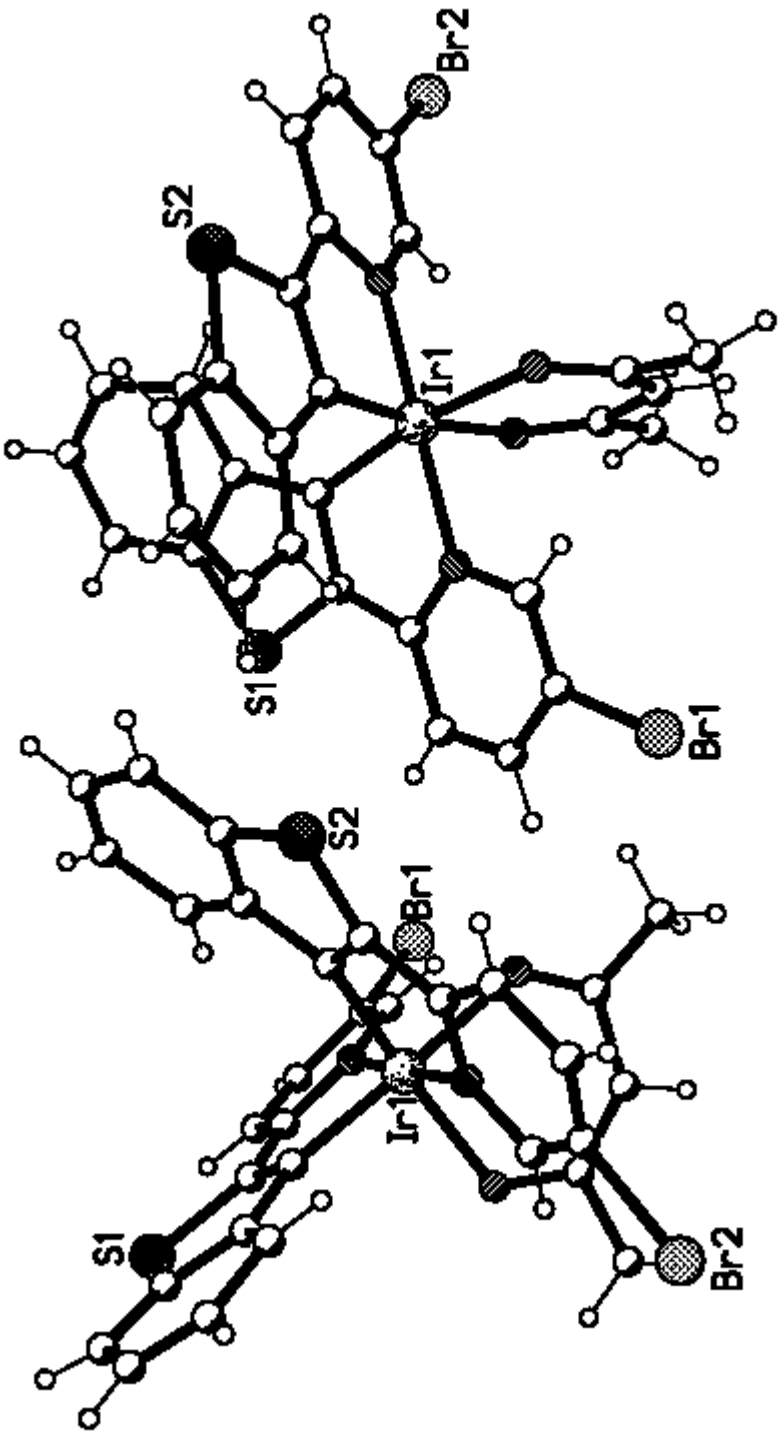

Figure S1: Representation of the X-ray crystal structure of complex **17**

Experimental

General Procedures. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen filled glove box. All solvents were distilled and degassed prior to use; CH_2Cl_2 was distilled from CaH_2 and THF, toluene, diethyl ether and hexanes were distilled over Na. Where water was used it was distilled water and de-gassed by bubbling nitrogen through it prior to use. 2,7-dibromo-9,9-dioctylfluorene and 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9,9-dioctylfluorene were prepared according to the literature[1] and all other reagents were commercial grade and used as received. Column Chromatography was performed using silica gel [Merck 9385 Kieselgel 60(230-400 ASTM)]. TLC was performed on 0.25 mm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel. ^{1}H NMR spectra were recorded on Bruker DPX-400 (400 MHz) and Bruker-500 (500 MHz) instruments using $CDCl_3$ as an internal deuterium lock. $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker DPX-400 (100 MHz) and a Bruker DPX-500 (125 MHz) instruments using an internal deuterium lock and proton decoupling. The Mass Spectrometry Services at the University of Swansea recorded Mass spectra. Electron Ionization (EI) low-resolution spectra were carried out on a VG model 12-253 under ACE conditions. High-resolution measurements were recorded on a +VG ZAB-E instrument. GPC were recorded in $CHCl_3$ on a PL gel Mixed B column and with a differential refractometer, at a flow rate of 1 $mLmin^{-1}$.

Optical Measurements. All compounds were dissolved at a concentration of 10 $mgmL^{-1}$ in CH_2Cl_2. For optical measurements, films were spun onto quartz substrates using a conventional photo-resist spin-coater. Absorption spectra were measured using a Hewlett-Packard UV-VIS spectrometer. For photoluminescence measurements, the samples were held under vacuum in a continuous-flow helium cryostat. The temperature was controlled with an Oxford-Intelligent Temperature Controller (ITC 502). The samples were excited with the UV lines (355 and 365 nm) of an Argon ion continuous-wave 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 a nitrogen atmosphere using the integrating sphere technique.[2]

Light-emitting diodes were fabricated on indium-tin oxide (ITO) patterned glass substrates which were cleaned in an ultrasonic bath of acetone followed by isopropanol prior to oxygen plasma etching for ten minutes.[3] A conventional photo-resist spin-coater was used to deposit first a 50 nm layer of filtered PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)) followed by a 70 nm layer of oligomer or polymer. The PEDOT:PSS layer was dried under nitrogen at 120 ºC for 1 h to remove any residual water prior to spinning on the emitting layer. A 100nm calcium cathode was evaporated onto the device through a shadow mask and capped with aluminium. Current-voltage characteristics were measured using a Keithly 230 voltrage source and a 195 DMM and luminance using a silicon photodiode and Keithley 2000 multimeter. Electroluminescence spectra were taken with an optical fibre coupled to the Instaspec IV decribed above. All electrical measurements were carried out under vacuum.

2-(4'-Bromophenyl)pyridine[4] (**1**)

An aqueous solution of $NaNO_2$ (30 mL of an 8M solution in water, 0.24 mmol, 2 eq.) was slowly added to a suspension of *p*-bromoaniline (20.00 g, 0.12 mmol, 1 eq.) in concentrated HCl (40 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and was carefully poured into pyridine (500 mL). The resulting brown solution was stirred at 40 °C for 4 h and then Na_2CO_3 (200 g) was added and the slurry was stirred at the same temperature for a further 18 h. On cooling the organic product was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic fractions were dried ($MgSO_4$) and evaporated to dryness. Column chromatography (silica gel, Toluene:MeOH 95:5) yielded the pure product (8.40 g, 0.04 mmol, 33%).

Anal. Calcd. For $C_{11}H_8BrN$: C 56.44 %, H 3.44 %, N 5.98 %; Found C 56.24 %, H 3.35 %, N 5.90 %; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 8.68 (d, ^3J = 4.3 Hz, 1H, C_5H_4N), 7.88 (d, ^3J = 8.4 Hz, 2H,

C_5H_4Br), 7.75 (d, ^3J = 7.5 Hz, 1H, C_5H_4N), 7.70 (d, ^3J = 7.8 Hz, 1H, C_5H_4N), 7.60 (d, ^3J = 8.4 Hz, 2H, C_5H_4Br), 7.24 (br s, 1H, C_5H_4N); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ:156.2, 149.8, 138.3, 136.8, 131.9, 128.5, 123.4, 122.4, 120.2; Exact Mass (EI) *m/z*: 233.9920 [M+H] (Calcd. 233.9918 (^{79}Br)).

2-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-trimethylsilyl-9,9-dioctylfluorene (3)

t-BuLi (7.30 mL of a 1.7 M solution in hexanes, 12.50 mmol, 2.5 eq.) was slowly added to a solution of 2-bromo-7-trimethylsilyl-9,9-dioctylfluorene (2.70 g, 4.99 mmol, 1 eq.) in THF (50 mL) at -78 °C and the solution stirred for 1 h resulting in evolution of a green suspension. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 g, 6.48 mmol, 1.2 eq.) was added and the reaction mixture warmed to room temperature and stirred for a further 18 h. Water (15 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic fractions were dried ($MgSO_4$) and evaporated to dryness. Column chromatography (silica gel, CH_2Cl_2:Hexane, 1:4) enabled isolation of the pure product as a white powder (1.35 g, 2.64 mmol, 53 %).

Anal. Calcd. for $C_{38}H_{71}BO_2Si$: C 77.52 %, H 10.44 %; Found C 77.35 %, H 10.33 %; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ:7.80 (d, ^3J = 7.5 Hz, 1H, Ar*H*), 7.75 (s, 1H, Ar*H*), 7.70 (d, ^3J = 7.5 Hz, 2H, Ar*H*), 7.48 (d, ^3J = 7.5 Hz, 1H, Ar*H*), 7.46 (s, 1H, Ar*H*), 1.97 (t, 4H, ^3J = 8.3 Hz, $OC(CH_3)_2(CH_2)_2C(CH_3)_2O$), 1.39 (s, 12H, $OC(CH_3)_2(CH_2)_2C(CH_3)_2O$), 1.15-1.05 (m, 20H, CH_2), 0.81 (t, ^3J = 7.1 Hz, 6H, CH_3CH_2), 0.61 (m, 4H, CH_2), 0.31 (s, 9H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3, ppm) δ: 150.4, 150.1, 144.1, 141.5, 139.6, 133.6, 131.7, 128.9, 127.6, 119.3, 119.0, 83.7, 55.0, 40.0, 31.7, 30.0, 29.1, 29.0, 24.9, 23.6, 22.6, 14.0, 0.9; Exact Mass (EI) *m/z*: 588.4534 (Calcd. 588.4534), 475.4 $(M-C_8H_{17})^+$, 363.3 $(M-(C_8H_{17})_2)^+$, 333.3 $(M-(C_8H_{17}+CH_3+C_6H_{12}BO_2))^+$.

2-(4'-(9'',9''-Dihexylfluoren-2''-yl)phenyl)pyridine (4)

2-(4',4',5',5',-Tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9,9-dihexylfluorene (0.50 g, 1.12 mmol, 1 eq.), 2-(4'-bromophenyl)pyridine (0.26 g, 1.12 mmol, 1 eq.) and $Pd(PPh_3)_4$ (0.50 mg, 0.01 mmol) were

suspended in toluene (4 mL) and Et_4NOH (2 mL of a 20 % aqueous solution) and the reaction was stirred at 90 °C for 18 h. The orange solution was extracted with CH_2Cl_2 (40 mL), washed with water (2 x 50 mL), dried ($MgSO_4$) and evaporated to dryness. Column chromatography (silica gel, CH_2Cl_2) yielded pure product (0.26 g, 0.53 mmol, 47%).

Anal. Calcd. For $C_{36}H_{41}N$: C 88.65 %, H 8.47 %, N 2.87 %; Found: C 88.37 %, H 8.40 %, N 3.11 %; ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 8.73 (d, ^3J = 4.9 Hz, 1H, C_5H_4N), 8.12 (d, ^3J = 8.2 Hz, 2H, Ar*H*), 7.80-7.78 (m, 4H, Ar*H*), 7.73 (d, ^3J = 7.8 Hz, 1H, C_5H_4N), 7.64 (d, ^3J = 7.9 Hz, 1H, C_5H_4N), 7.62 (m, 1H, C_5H_4N), 7.36-7.33 (m, ^3J = 1.0 Hz and 7.5 Hz, 3H, Ar*H*), 7.25 (m, 2H, Ar*H*), 2.04-2.00 (dd, ^3J = 5.0 Hz and 5.2 Hz, 4H, CH_2), 1.15-1.05 (m, 12H, CH_2), 0.78 (t, ^3J = 6.7 Hz, 6H, CH_3), 0.68 (m, 4H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, CDCl3, ppm) δ: 156.8, 151.2, 150.8, 149.5, 142.0, 140.5, 139.1, 137.8, 136.5, 127.2, 127.0, 126.8, 126.5, 126.0, 122.7, 121.8, 121.1, 120.2, 119.7, 119.5, 54.9, 40.2, 31.2, 29.5, 23.5, 22.3, 13.7; Exact Mass (EI) *m/z*: 488.3317 [M+H] (Calcd. 488.3317), 402.3 [M-(C_6H_{13})]$^+$, 332.2 [M-(C_6H_{13})-(C_5H_{11})]$^+$ 318.2 [M-(C_6H_{13})$_2$]$^+$.

2-(4'-(7''-trimethylsilyl-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (5)

2-(4'-Bromophenyl)pyridine (0.24 g, 1.02 mmol, 1 eq.), 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-trimethylsilyl-9,9-dioctylfluorene (0.60 g, 1.02 mmol, 1 eq.) and $Pd(PPh_3)_4$ (4.00 mg, 0.004 mmol) were suspended in toluene (10 mL) and Et_4NOH (2.50 mL of a 20 % solution in water). The two-phase solution was stirred for 48 h at 110 °C, after which it was extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were dried ($MgSO_4$) and the solvents were removed under reduced pressure. Column chromatography (silica gel, CH_2Cl_2, R*f*: 0.47) enabled isolation of the pure product as an off-white solid (0.55 g, 0.89 mmol, 88 %).

Anal. Calcd. For $C_{43}H_{57}NSi$: C 83.84 %, H 9.33 %, N 2.27 %; Found: C 83.99 %, H 9.41 %, N 2.33 %; ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 8.73 (d, ^3J = 4.9 Hz, 1H, C_5H_4N), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar*H*), 7.80-7.78 (m, 4H, Ar*H*), 7.73 (d, ^3J = 4.5 Hz, 2H, C_5H_4N), 7.69 (d, ^3J = 4.6 Hz, 2H, C_5H_4N), 7.63

(d, ^3J = 8.0 Hz, 2H, C_5H_4N), 7.25 (s, 1H, Ar*H*), 2.01 (t, ^3J = 8.2 Hz, 4H, CH_2), 1.15-1.05 (m, 20H, CH_2), 0.78 (t, ^3J = 6.6 Hz, 6H, CH_3), 0.70 (m, 4H, CH_2), 0.32 (s, 9H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (125 MHz, CDCl3, ppm) δ: 156.8, 151.5, 149.9, 149.5, 142.0, 141.1, 140.4, 139.2, 138.9, 137.8, 136.5, 131.6, 127.4, 127.2, 127.0, 125.7, 121.8, 121.2, 120.1, 119.8, 118.8, 54.9, 39.9, 31.5, 28.9, 28.8, 29.7, 23.5, 22.3, 13.8, –1.1; Exact Mass (EI): [M+H]: 616.4340 (Calcd. 616.4338).

2-(4'-(7''-Iodo-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (6)

ICl (1.50 mL of a 1.0 M solution in MeOH) was slowly added to a solution of 2-(4'-(7''-trimethylsilyl-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (0.50 g, 0.81 mmol, 1 eq.) in CH_2Cl_2 (5 mL). The resulting dark red solution was stirred for 2 h at room temperature, then the reaction was quenched by addition of a large excess of aqueous $Na_2S_2O_3$ solution. The mixture was extracted with CH_2Cl_2 (2 x 20 mL), the combined organic fractions were dried ($MgSO_4$) and the solvents were removed under reduced pressure. Column chromatography (silica gel, CH_2Cl_2, R*f*: 0.36) enabled isolation of the product as a white solid (0.45 g, 0.69 mmol, 85%).

Anal. Calcd. For $C_{40}H_{48}IN$: C 71.74 %, H 7.22 %, N 2.09 %; Found: C 72.34 %, H 7.20 %, N 2.12 %; ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 8.73 (d, ^3J = 4.7 Hz, 1H, C_5H_4N), 8.12 (d, ^3J = 8.5 Hz, 2H, Ar*H*), 7.80-7.73 (m, 4H, Ar*H*), 7.68 (s, 2H, Ar*H*), 7.65 (d, ^3J = 5.0 Hz, 2H, C_5H_4N), 7.60 (s, 2H, Ar*H*), 7.48 (d, 1H, ^3J = 8.4 Hz, Ar*H*), 2.05-1.94 (m, 4H, CH_2), 1.25-1.05 (m, 20H, CH_2), 0.81 (t, ^3J = 6.6 Hz, 6H, CH_3), 0.70 (br m, 4H, CH_2); ^{13}C{^{1}H}NMR (125 MHz, CDCl3, ppm) δ: 157.0, 153.4, 150.9, 149.8, 142.0, 140.4, 140.0, 139.6, 138.2, 136.8, 135.9, 132.1, 127.5, 127.3, 126.1, 122.1, 121.5, 121.3, 120.4, 120.1, 92.6, 55.5, 40.2, 31.7, 29.9, 29.2, 29.1, 23.7, 22.6, 14.1; Exact Mass (EI) *m/z*: 669.2825 $[M]^+$ (Calcd. 669.2832), 543.6 $[M-I]^+$, 318.4 $[M-(C_8H_{17})-I]^+$.

2-(4'-(7''-(9''',9'''-Dihexylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (7)

To a solution of 2-(4'-(7''-iodo-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (0.40 g, 0.60 mmol, 1 eq.), 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9,9-dioctylfluorene (0.36 g, 0.60 mmol, 1 eq.) and

$Pd(PPh_3)_4$ (4.00 mg, 0.004 mmol) in toluene (10 mL) was added Et_4NOH (2.50 mL of a 20 % solution in water). The two-phase reaction mixture was stirred for 48 h at 110 °C and then it was extracted with CH_2Cl_2 (2x 20 mL). The organic layers were dried ($MgSO_4$) and the solvents were removed under reduced pressure. The crude product was purified using flash chromatography (silica gel) to yield the pure product as a white powder (0.45 g, 0.52 mmol, 86%).

Anal. Calcd. For $C_{65}H_{81}N$: C 89.09 %, H 9.32 %, N 1.60 %; Found: C 88.60 %, H 9.25 %, N 1.52 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.74 (d, ^3J = 4.9 Hz, 1H, C_5H_4N), 8.13 (d, ^3J = 4.6 Hz, 2H, Ar*H*), 7.84-7.77 (m, 6H, Ar*H*), 7.74 (d, ^3J = 6.0 Hz, 2H, C_5H_4N), 7.69-7.63 (m, 6H, Ar*H*), 7.39-7.30 (m, 3H, Ar*H*), 7.27-7.24 (m, 1H (obscured by $CHCl_3$ peak, Ar*H*), 2.11-2.02 (m, 8H, CH_2), 1.18-1.09 (m, 32H, CH_2), 0.81-0.74 (m, 20H, CH_2CH_3); ^{13}C{^{1}H}NMR (125 MHz, CDCl3, ppm) δ: 157.1, 151.8, 151.4, 151.0, 149.8, 142.2, 140.8, 140.6, 140.42, 140.39, 140.3, 139.9, 139.3, 138.1, 136.8, 127.5, 127.3, 126.9, 126.8, 126.1, 126.0, 122.1, 122.0, 121.44, 121.38, 120.4, 120.0, 119.8, 119.7, 55.3, 55.1, 40.4, 31.7, 31.5, 30.0, 29.7, 29.18, 29.16, 23.8, 23.7, 22.6, 22.5, 14.03, 13.99; Exact Mass(EI) *m/z*: 875.6367 $[M]^+$ (Calcd. 875.6369), 762.3 $[M-(C_8H_{17})]^+$, 650.4 $[M-(C_8H_{17})_2]^+$.

2-(4'-(7''-(7'''-Iodo-9''',9'''-dioctylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (8)

To a solution of 2-(4'-(7''-iodo-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (0.30 g, 0.45 mmol, 1eq.), 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-trimethylsilyl-9,9-dioctylfluorene (0.32 g, 0.54 mmol, 1.1 eq.) and $Pd(PPh_3)_4$ (4.00 mg, 0.004 mmol) in toluene (10 mL) was added Et_4NOH (2.50 mL of a 20 % solution in water). The two-phase reaction mixture was stirred for 24 h at 110 °C, after which it was extracted using CH_2Cl_2 (2x 20 mL). The organic layers were dried ($MgSO_4$) and the solvents were removed under reduced pressure. The crude product was purified using flash chromatography (silica gel, CH_2Cl_2, R*f*: 0.30) enabling isolation of 2-(4'-(7''-(7'''-trimethylsilyl-9''',9'''-dioctylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine as a white solid (0.39 g, 0.39 mmol, 88%). This was subsequently dissolved in CH_2Cl_2 (5 mL) and ICl (5 mL of a 1.0M solution in MeOH)

was added. The resulting dark red solution was stirred for 2 h at room temperature and then it was quenched by addition of a large excess of an aqueous $Na_2S_2O_3$ solution. The mixture was extracted with CH_2Cl_2 (2 x 20 mL), the combined organic layers were dried ($MgSO_4$) and the solvents were removed under reduced pressure. The crude product was purified using column chromatography (silica gel, CH_2Cl_2) to yield the product as a white solid (0.36 g, 0.33 mmol, 85%).

Anal. Calcd. For $C_{69}H_{88}IN$: C 78.30 %, H 8.38 %, N 1.32 %; Found: C 78.02 %, H 8.31 %, N 1.35 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.74 (d, ^3J = 4.6 Hz, 1H, C_5H_4N), 8.13 (d, ^3J = 8.4 Hz, 2H, Ar*H*), 7.82-7.78 (m, 5H, Ar*H*), 7.75 (d, ^3J = 7.9 Hz, 2H, C_5H_4N), 7.69-7.64 (m, 5H; Ar*H*), 7.60 (d, 2H, Ar*H*), 7.48 (d, 1H, C_5H_4N) 7.26-7.24 (m, 2H (obscured by $CHCl_3$ peak, Ar*H*), 2.17-1.94 (m, 8H, CH_2), 1.24-1.09 (m, 40H, CH_2), 0.90-0.71 (m, 20H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3, ppm) δ: 157.0, 153.4, 151.83, 151.77, 150.9, 149.8, 142.1, 141.1, 140.5, 140.4, 140.3, 140.1, 139.4, 139.3, 138.1, 136.8, 135.9, 132.1, 127.5, 127.3, 126.2, 126.2, 126.1, 122.1, 121.4, 121.3, 120.4, 120.1, 120.0, 92.5, 55.5, 55.3, 40.4, 40.2, 31.8, 30.0, 29.9, 29.2, 23.8, 23.7, 22.6, 14.1; *m/z* (EI): 1058.7 $[M]^+$, 944.4 $[M-(C_8H_{17})]^+$.

2-(4'-(7''-(7'''-(9'''',9''''-Dihexylfluoren-2''''-yl)-9''',9'''-dioctylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (9)

To a solution of 2-(4'-(7''-(7'''-iodo-9''',9'''-dioctylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine (0.30 g, 0.29 mmol, 1eq.), 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9,9-dioctylfluorene (0.23 g, 0.37 mmol, 1.3 eq.) and $Pd(PPh_3)_4$ (4.00 mg, 0.004 mmol) in toluene (5 mL) was added Et_4NOH (2.50 mL of a 20% solution in water). The two-phase solution was stirred for 24 h at 110 °C, after which it was extracted using CH_2Cl_2 (3 x 10 mL), the combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified using flash chromatography (silica gel, CH_2Cl_2:hexane 1:1, R*f* 0.24) enabling isolation of the product as a white solid (0.19 g, 0.15 mmol, 52%).

Anal. Calcd. For $C_{94}H_{121}N$: C 89.25 %, H 9.64 %, N 1.11 %; Found: C 89.25 %, H 9.71 %, N 1.21 %; ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 8.75 (d, ^{3}J = 4.6 Hz, 1H, C_5H_4N), 8.14 (d, ^{3}J = 8.4 Hz, 2H, Ar*H*), 7.86-7.73 (m, 10H, Ar*H*), 7.74-7.62 (m, 10H, Ar*H*), 7.40-7.31 (m, 3H, Ar*H*), 7.28-7.23 (m, 1H (obscured by $CHCl_3$), Ar*H*), 2.17-2.02 (m, 12H, CH_2), 1.25-1.01 (m, 52H, CH_2), 0.90-0.64 (m, 30H, CH_2CH_3); ^{13}C{^{1}H} NMR (125 MHz, CDCl3, ppm) δ: 157.1, 151.8, 151.4, 151.0, 149.7, 142.2, 140.8, 140.6, 140.5, 140.4, 140.3, 140.0, 139.9, 136.7, 127.4, 127.3, 126.8, 126.1, 126.0, 122.9, 121.4, 120.0, 119.9, 119.8, 119.7, 55.3, 55.1, 40.3, 31.7, 31.4, 30.0, 29.7, 29.2, 23.9, 23.8, 22.6, 22.5, 14.0; *m/z* (EI): 1265 $[M+H]^+$.

Diiridium(III) di-μ-chlorotetrakis(2-(4'-bromophenyl)pyridinato-*N*,*C*$^{2'}$)

A mixture of $IrCl_3.xH_2O$ (0.50 g, 1.42 mmol, 1 eq.) and 2-(4'-bromophenyl)pyridine (1.40 g, 6.37 mmol, 4.5 eq.) in 2-ethoxyethanol (50 mL) and water (15 mL) was heated to 110 °C for 18 h. After the mixture cooled to room temperature, the precipitate was filtered and washed with EtOH:H_2O (95:5, 50 mL). The precipitate was then dissolved in acetone (30 mL), dried ($MgSO_4$) and the solvent was removed under reduced pressure to yield the product as an orange solid (0.64 g, 0.92 mmol, 65%).

Anal. Calcd. For $C_{44}H_{32}Br_4Cl_2Ir_2N_4$: C 38.08 %, H 2.03 %, N 4.04 %; Found: C 37.73 %, H 2.10 %, N 4.04 %; ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 9.12 (d, ^{3}J = 5.7 Hz, 4H, C_5H_4N), 7.86 (d, ^{3}J = 4.5 Hz, 4H, Ar*H*), 7.80 (dd, ^{4}J = 1.5 Hz and ^{3}J = 7.2 Hz, 4H, Ar*H*), 7.38 (d, ^{3}J = 9.4 Hz, 4H, C_5H_4N), 7.02 (dd, ^{3}J = 1.9 Hz and 9.0 Hz, 4H, Ar*H*), 6.84 (dd, ^{4}J = 1.7 Hz and ^{3}J = 5.6 Hz, 4H, C_5H_4N), 5.94 (d, ^{4}J = 1.9 Hz, 4H, Ar*H*); *m/z* (FAB): 1387 $[M]^+$, 1352 $[M-Cl]^+$, 659 $[Ir(L)_2]^+$.

Iridium(III) bis(2-(4'-bromophenyl)pyridinato-*N*,*C*$^{2'}$)(acetylacetonate) (10)

Diiridium(III) di-μ-chlorotetrakis(2-(4'-bromophenyl)pyridinato-*N*,*C*$^{2'}$) (0.30 g, 0.22 mmol, 1 eq.) was dissolved in 2-ethoxyethanol (30 mL) in the presence of acetyl acetone (0.11 g, 1.08 mmol, 5 eq.) and Na_2CO_3 (0.22 g, 2.04 mmol). The resulting yellow suspension was stirred at 110 °C for 8 h. After

the mixture was cooled to room temperature water (10 mL) was added. The yellow precipitate was filtered, washed with H_2O (30 mL), hexane (30 mL) and cold Et_2O (20 mL) and dried *in vacuo* (0.19 g, 0.25 mmol, 57 %).

Anal. Calcd. For $C_{27}H_{21}Br_2IrN_2O_2.H_2O$: C 41.82 %, H 2.99 %, N 3.61 %; Found: C 42.02 %, H 2.60 %, N 3.54 %; ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 8.44 (d, ^3J = 5.5 Hz, 2H, C_5H_4N), 7.83 (d, ^3J = 8.5 Hz, 2H, Ar*H*), 7.78 (m, ^3J = 5.5 Hz and ^4J = 1.5 Hz, 2H, C_5H_4N), 7.41 (d, ^3J = 8.3 Hz, 2H, C_5H_4N), 7.19 (dt, ^3J = 6.4 Hz and ^4J = 1.5 Hz, 2H, Ar*H*), 7.00 (dd, ^3J = 6.3 Hz and ^4J = 2 Hz, 2H, Ar*H*), 6.28 (d, ^4J = 2Hz, 2H, Ar*H*), 5.23 (s, 1H, OC(CH_3)C*H*), 1.79 (s, 6H, OC(CH_3)CH); ^{13}C{^{1}H} NMR (125 MHz, CDCl3, ppm) δ: 184.8, 167.5, 148.2, 143.8, 137.3, 135.4, 125.1, 124.1, 121.9, 118.7, 100.5, 28.6; *m/z* (EI): 755.9593 (Calcd. 755.9599 for $[M]^+$ with (^{193}Ir)(^{79}Br)), 658.8 $[M\text{-acac}]^+$, 579.0 $[M\text{-acac-Br}]^+$, 499 $[M\text{-acac-}(Br)_2]^+$.

Iridium(III) bis(2-(4'-(9'',9''-dihexylfluoren-2''-yl)phenyl)pyridinato-*N*,*C*$^{2'}$)(acetylacetonate) (11)

Synthetic route is analogous to synthesis of iridium(III) bis(2-(4'-bromophenyl)pyridinato-*N*,*C*$^{2'}$)(acetylacetonate), with the chloride bridged dimeric compound being used without complete characterization, enabled isolation of compound as green powder (0.08 g, 0.06 mmol, 51%).

Anal. Calcd. For $C_{77}H_{87}IrN_2O_2.H_2O$: C 72.10 %, H 6.99 %, N 2.18 %; Found: C 72.40 %, H 6.87 %, N 2.27 %. ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ: 8.63 (d, ^3J = 5.7 Hz, 2H, C_5H_4N), 7.92 (d, ^3J = 7.9 Hz, 2H, Ar*H*), 7.76 (t, ^3J = 7.2 Hz and ^4J = 1.4 Hz, 2H, Ar*H*), 7.64 (d, ^3J = 6.0 Hz, 2H, Ar*H*), 7.58 (d, ^3J = 5.9 Hz, 2H, Ar*H*), 7.30-7.20 (m, ^3J = 8.0 Hz, 12H, Ar*H*), 7.20-7.10 (m, ^3J = 7.1 Hz, 4H, Ar*H*), 6.59 (s, 2H, Ar*H*), 2.00-1.80 (m, 8H, CH_2), 1.20-0.90 (m, 24H, CH_2), 0.77 (m, 12H, CH_3), 0.60-0.40 (m, 8H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, CDCl3, ppm) δ: 184.7, 168.5, 150.8, 150.6, 148.4, 144.0, 141.4, 140.9, 140.4, 139.9, 136.7, 126.7, 126.6, 125.8, 124.0, 122.7, 121.4, 121.3, 121.1, 120.0, 119.5, 119.3,

118.4, 100.4, 54.9, 40.53, 40.48, 31.5, 29.8, 28.8, 23.6, 22.6, 14.0, 13.9; *m/z* (EI): 1178.3 $[M-(C_6H_{13})]^+$, 1165.2 $[M-(acac)]^+$, 1009 $[M-(C_6H_{13})_3]^+$.

Iridium(III) bis(2-(4'-(7''-(9''',9'''-dihexylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate) (12)

Synthetic route is analogous to synthesis of iridium(III) bis(2-(4'-bromophenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate), without complete characterization of the chloride bridged dimeric species, enabled isolation of title compound (0.08 g, 0.04 mmol, 59 %).

Anal. Calcd. For $C_{135}H_{167}IrN_2O_2$: C 79.40 %, H 8.24 %, N 1.37 %; Found: C 79.12 %, H 8.13 %, N 1.17 %**;** ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.65 (d, ^3J = 5.1 Hz, 2H, C_5H_4N), 7.86 (d, ^3J = 7.8 Hz, 2H, Ar*H*), 7.75-7.58 (m, 24H, Ar*H*), 7.37-7.16 (m, 10H, Ar*H*), 6.61 (s, 2H, C_5H_4N), 5.27 (s, 1H, $OC(CH_3)CH$), 2.03-1.94 (m, 16H; CH_2), 1.85 (s, 6H, $OC(CH_3)CH$), 1.32-0.91 (m, 64H, CH_2), 0.88-0.70 (m, 40H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3, ppm) δ: 184.7, 168.5, 151.6, 151.4, 151.0, 148.4, 144.1, 141.5, 140.8, 140.5, 140.2, 139.6, 136.7, 126.9, 126.7, 126.0, 125.9, 124.0, 122.9, 121.5, 121.3, 119.8, 119.7, 119.4, 118.4, 100.8, 55.1, 55.0, 40.6, 40.5, 40.3, 31.8, 31.4, 30.2, 29.7, 29.3, 29.2, 28.8, 23.7, 22.6, 22.5, 14.1, 14.0; *m/z* (EI): 2041.4 $[M]^+$, 1942.4 $[M–(acac)]^+$.

Iridium(III) bis(2-(4'-(7''-(7'''-(9'''',9''''-dihexylfluoren-2''''-yl)-9''',9'''-dioctylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate) (13)

Synthetic route is analogous to synthesis of iridium(III) bis(2-(4'-bromophenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate), without complete characterization of the chloride bridged dimeric compound, enabled isolation of title compound (0.10 g, 0.04, 57%).

Anal. Calcd. For $C_{193}H_{247}IrN_2O_2$: C 82.22 %, H 8.83 %, N 0.88 %; Found: C 81.93 %, H 8.77 %, N 1.10 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.65 (d, ^3J = 5.4 Hz, 2H, C_5H_4N), 7.94 (d, ^3J = 8.3 Hz, 2H, Ar*H*), 7.82-7.78 (m, 8H, Ar*H*), 7.75-7.72 (t, ^3J = 8.2 Hz, 4H, Ar*H*), 7.67-7.63 (m, 22H; Ar*H*), 7.38-7.31 (m, 8H; Ar*H*), 7.21-7.17 (m, 4H, Ar*H*), 6.61 (s, 2H, C_5H_4N), 5.28 (s, 1H, $OC(CH_3)CH$), 2.11-2.02

(m, 24H, CH_2), 1.85 (s, 6H, OC(CH_3)CH), 1.20-1.07 (m, 104H, CH_2), 0.82-0.67 (m, 60H, CH_2CH_3); ^{13}C{^{1}H} NMR (125 MHz, CDCl3, ppm) δ: 184.7, 166.4, 151.7, 151.6, 151.4, 151.0, 143.3, 140.7, 140.4, 140.3, 139.9, 126.9, 126.7, 126.1, 126.0, 125.9, 122.8, 121.4, 119.9, 119.8, 119.7, 100.8, 55.3, 55.1, 40.5, 40.3, 31.7, 31.4, 30.1, 30.0, 29.6, 29.2, 29.1, 28.7, 23.9, 23.7, 22.5, 14.0, 13.9; *m/z* (EI): 2819 $[M]^+$, 2719 $[M–(acac)]^+$.

2-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-bromo-9,9-dioctylfluorene (16)

2,7-Dibromo-9,9-dioctylfluorene (4.00 g, 7.30 mmol, 1 eq.) was dissolved in diethyl ether (50 ml) at –78°C and *n*BuLi (4.80 mL of a 1.6 M solution in hexanes, 7.66 mmol, 1.1 eq.) was slowly added to it. The resulting white milky solution was allowed to warm to 0 °C until a clear-yellow solution was formed. The solution was cooled back to –78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.49 g, 8.03 mmol, 1.1 eq.) was added causing formation of a turbid white suspension after 1 h. The mixture was warmed to room temperature and stirred for 18 h. Water (10 mL) was added and the layers were separated, the organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo*. Column chromatography (silica gel, CH_2Cl_2, R*f*: 0.5) enabled isolation of the pure product as a white powder (2.20 g, 3.72 mmol, 51%).

Mp. 58-60 °C; Anal. Calcd. For $C_{35}H_{52}BBrO_2$: C 70.59 %, H 8.80 %; Found: C 70.25 %, H 8.47 %; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 7.80 (d, ^3J = 7.6 Hz, 1H, Ar*H*), 7.72 (s, 1H, Ar*H*), 7.66 (d, ^3J = 7.5 Hz, 1H, Ar*H*), 7.57 (d, ^3J = 7.5 Hz, 1H, Ar*H*), 7.47 (s, 1H, ArH), 7.45 (d, ^3J = 7.5 Hz, 1H, Ar*H*), 1.97 (m, 2H, OC(CH_3)$_2$(CH_2)$_2$C(CH_3)$_2$O), 1.91 (m, 2H, OC(CH_3)$_2$(CH_2)$_2$C(CH_3)$_2$O), 1.39 (s, 12H, OC(CH_3)$_2$(CH_2)$_2$C(CH_3)$_2$O), 1.18-1.02 (m, 20H, CH_2), 0.82 (t, ^3J = 7.1 Hz, 6H, CH_3CH_2), 0.56 (m, 4H, CH_2); ^{13}C{^{1}H} NMR (500 MHz, CDCl3, ppm) δ: 153.3, 149.2, 142.7, 139.7, 127.9, 133.6, 129.6, 128.6, 126.0, 121.2, 118.8, 83.5, 55.2, 39.9, 31.5, 29.6, 28.9, 24.6, 23.4, 22.3, 13.8.

Iridium(III) bis(2-(4'-(ω-bromo-oligo[9'',9''-dioctylfluoren-2'',7''-diyl])phenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate) (*n*=10) (14)

A solution of 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-bromo-9,9-dioctylfluorene (0.42 g, 0.70 mmol, 20 eq.), iridium(III) bis(2-(4'-bromophenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate) (26.40 mg, 0.0349 mmol, 1 eq.), $Pd(OAc)_2$ (2.00 mg, 0.008 mmol) and tricyclohexylphosphine (4.00 mg, 0.016 mmol) in toluene (25 mL) was heated to 90 °C and Et_4NOH (2.50 mL of a 20 % solution in water) was added. The solution was stirred at 110 °C for 20 h. The solution was poured into a large excess of MeOH, which resulted in the precipitation of a yellow polymer. This was filtered, washed with water (40 mL), MeOH (40 mL) and acetone (30 mL) and filtered through a short silica column using toluene as the eluent. The resulting solution was concentrated (to 20 mL) and Na_2CO_3 (0.10 g), acetyl acetone (1.00 mL) and 2-ethoxyethanol (8 mL) were added. The reaction mixture was stirred for 2 h at 110 °C and subsequently cooled down to room temperature. The solution was poured into an excess of MeOH and the yellow precipitate filtered, washed with H_2O (40 mL) and MeOH (40 mL) and dried *in vacuo*. The pure product was isolated as a yellow powder (0.15 g, 0.02 mmol, 55%).

Anal. Calcd. For $C_{607}H_{821}N_2O_2Br_2Ir$: C 85.53 %, H 9.71 %, N 0.33 %; Found: C 82.78 %, H 9.44 %, N 0.25 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.70 (d, *J* = 4.6 Hz, C_5H_4N), 7.90-7.50 (m, 6H, Ar*H*), 7.40-7.10 (m, Ar*H*), 6.60 (s, C_5H_4N), 5.30 (s, $OC(CH_3)CH$), 2.30-2.00 (m, 4H, CH_2), 1.90 (s, $OC(CH_3)CH$), 1.30-1.00 (m, 20H, CH_2), 0.90-0.70 (m, 10H, CH_3CH_2).

Iridium(III) bis(2-(4'-(ω-bromo-oligo[9'',9''-dioctylfluoren-2'',7''-diyl])phenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate) (*n*=30) (15)

It was synthesized in an analogous manner as before, using a solution of 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-bromo-9,9-dioctylfluorene (0.42 g, 0.70mmol, 40 eq.) and iridium(III)

bis(2-(4'-bromophenyl)pyridinato-*N*,$C^{2'}$)(acetylacetonate) (13.20 mg, 0.017 mmol), this enabled isolation of the title compound (0.23 mg, 0.010 mmol, 55%).

Anal. Calcd. For $C_{1767}H_{2421}N_2O_2Br_2Ir$: C 88.16 %, H 10.14 %, N 0.12 %; Found: C 87.10 %, H 10.02 %, N 0.20 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.70 (d, *J* = 5.0 Hz, C_5H_4N), 7.90-7.50 (m, 6H, Ar*H*), 7.40-7.10 (m, Ar*H*), 6.60 (s, C_5H_4N), 5.30 (s, $OC(CH_3)CH$), 2.30-2.00 (m, 4H, CH_2), 1.90 (s, $OC(CH_3)CH$), 1.30-1.00 (m, 20H, CH_2), 0.90-0.70 (m, 10H, CH_3CH_2).

2-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolane)benzo[*b*]thiophene

Benzo[*b*]thiophene (5.05 g, 37.70 mmol, 1 eq.) was dissolved in diethyl ether (100 mL) and cooled to -78 ºC. *n*-BuLi (24.00 mL of a 1.6M solution in Hexanes, 38.50 mmol, 1 eq.) was added dropwise over 10 min, causing evolution of a yellow precipitate. The suspension was stirred for 30 min and then warmed to room temperature and stirred for a further 30 min causing the precipitate to dissolve. The solution was again cooled to -78 ºC and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.00 mL, 54.00 mmol, 1.4 eq.) added causing immediate formation of a white precipitate. Additional diethyl ether (50 mL) was added and the suspension stirred for 1h at -78 ºC and 16 h at room temperature. Water (30 mL) was added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL), acidified to pH 1 by addition of HCl and then extracted again with CH_2Cl_2 (3 x 50 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated to give a crude yellow solid. Column Chromatography (silica gel, CH_2Cl_2:hexanes, 3:2, R*f* = 0.5) enabled isolation of the product as a white solid (8.00 g, 30.70 mmol, 81%).

Mp. 72-74 ºC; Anal. Calcd. For $C_{14}H_{17}BO_2S$: C 64.63 %, H 6.59 %; Found: C 64.63 %, H 6.57 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.94-7.86 (m, 3H, Ar*H*), 7.38 (m, 2H, Ar*H*), 1.40 (s, 12H, CH_3CO); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ: 143.8, 140.5, 134.5, 125.4, 124.4, 124.2, 122.6, 84.4, 24.8; *m/z* (EI) 278.1386 $[M]^+$, (Calcd. 278.1386); *m/z* (CI, NH_3) 280.2, 279.2, 278.2, 277.1, 261.2, 260.2, 259.2, 174.1.

2-(2'-Benzo[*b*]thienyl)-5-bromopyridine

2,5-Dibromopyridine (2.81 g, 11.50 mmol, 1 eq.) and $Pd(PPh_3)_4$ (0.66g, 0.60 mmol, 5 mol%) were dissolved in THF (30 mL). Na_2CO_3 (4.24 g, 30.00 mmol) was dissolved in distilled water (40 mL) and de-gassed for 1 h, it was then added to the THF solution and vigorously stirred. The solution was heated to 75 ºC. 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane)benzo[*b*]thiophene (3.00 g, 12.50 mmol, 1.1 eq.) was dissolved in THF (20 mL) and degassed for 30 min. The solution was taken into a syringe (20 mL) and added via a syringe pump over 6 h to the solution of 2,5-dibromopyridine. The solution was then stirred at room temperature for 16 h. The THF was removed *in vacuo* and the aqueous residue extracted with CH_2Cl_2 (3 x 50 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated to give a yellow solid. Unreacted 2,5-dibromopyridine was removed by sublimation (80 ºC, 0.1 mmHg) for 8 h. The crude material was purified by column chromatography (silica gel, CH_2Cl_2:hexanes, 1:1, R*f* = 0.35), which enabled isolation of the product as a white powder (2.00 g, 6.90 mmol, 60%).

Mp. 152-154 °C; Anal. Calcd. For $C_{13}H_8BrNS$: C 53.81 %, H 2.78 %, N 4.83 %; Found: C 53.69 %, H 2.74 %, N 4.70%; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 8.68 (d, $^4J_{H\text{-}H}$ 2.4 Hz, 1H, C_5H_3N), 7.87-7.80 (m, 4H, Ar*H*), 7.68 (d, $^3J_{H\text{-}H}$ 8.4 Hz, 1H, C_5H_3N,), 7.38-7.35 (m, 2H, C_5H_3N + C_4SH); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ: 151.1, 150.7, 143.5, 140.7, 140.3, 139.2, 125.3, 124.7, 124.2, 122.6, 121.7, 120.6, 119.3; Exact Mass (EI) *m/z*: 289.1933 $[MH]^+$ (Calcd. 289.1934), 212.2 $[M\text{-}Br]^+$; IR (CH_2Cl_2, cm^{-1}) ν: 2933, 2858, 2429, 2313, 1713, 1607, 1573, 1534, 1476, 1371, 1094, 1005, 961, 860, 828.

Diiridium(III) di-μ-chlorotetrakis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N*,*C*$^{3'}$)

2-(2'-Benzo[*b*]thienyl)-5-bromopyridine (0.048 g. 0.270 mmol, 2 eq.) and iridium(III) trichloride (0.049 g, 0.140 mmol, 1 eq.) were dissolved in a 2-ethoxyethanol (9 mL) and water (3 mL). The solution was heated to 111 ºC for 18 h. The suspension was filtered and the precipitate washed with ethanol (20 mL). The red-orange product (0.140 g, 0.090 mmol, 64%) was insoluble in most organic

solvents preventing NMR analysis and, showing sparing solubility in CH_2Cl_2, sufficient for EI mass spectrometry.

Exact Mass (MALDI, DCTB Matrix): 1611.6 $[M]^+$ (Calcd. 1611.7), 805 $[M/2]^+$.

Iridium(III) bis(2-(2'-benzo[b]thienyl)-5-bromopyridinato-*N, C*$^{3'}$)(acetylacetonate) (17)

Diiridium(III) di-μ-chlorotetrakis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N*,*C*$^{3'}$) (0.14 g, 0.09 mmol, 1 eq.), acetyl acetone (0.05 g, 0.49 mmol, 5 eq.), Na_2CO_3 (0.10 g, 0.92 mmol) and 2-ethoxyethanol (15 mL) were heated at 111 ºC for 18 h. Water (10 mL) was added causing precipitation of a red solid which was filtered and washed with Water (10 mL), Hexanes (20 mL) and ice-cold diethyl ether (20 mL). Recrystallisation from CH_2Cl_2 and Hexanes enabled isolation of the pure product as red crystals (0.06 g, 0.07 mmol, 77 %).

Anal. Calcd. For $C_{31}H_{21}Br_2IrN_2O_2S_2$: C 42.81 %, H 2.43 %, N 3.22 %; Found: C 42.74 %, H 2.36 %, N 3.08 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.47 (d, $^4J_{H\text{-}H}$ 2.0 Hz, 1H, C_5H_3N), 7.87 (dd, $^4J_{H\text{-}H}$ 1.8 Hz, $^3J_{H\text{-}H}$ 8.0 Hz, 1H, C_5H_3N), 7.64 (d, $^3J_{H\text{-}H}$ 8.0 Hz, 1H, C_5H_3N), 7.51 (d, $^3J_{H\text{-}H}$ 8.0 Hz, 1H, C_5H_3N), 7.10 (m, 1H, C_6H_4), 6.87 (m, 1H, C_6H_4), 6.24 (d, $^3J_{H\text{-}H}$ 8.0 Hz, 1H, C_6H_4), 5.33 (s, 0.5 H, $OC(CH_3)CH$), 1.84 (s, 3H, $OC(CH_3)$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ: 185.1, 164.9, 150.7, 149.7, 147.2, 146.5, 142.4, 140.8, 134.4, 125.5 (d, *C*Ir, $^1J_{Ir\text{-}C}$ 119 Hz), 124.9, 123.9, 122.8, 118.8, 112.1, 100.9, 29.7, 28.5; EI (LSIMS) 869 $[M]^+$, 771 [M-acac]$^+$; Exact Mass (EI) *m/z*: 867.9035 $[M]^+$ (Calcd. 867.9043); IR (CH_2Cl_2, cm^{-1}) ν: 2860, 2798, 2688, 2523, 2412, 1592, 1578, 1518, 1474, 1099, 1065, 1022, 825, 596.

Iridium(III)bis(2-(2'-benzo[b]thienyl)-5-(ω-bromo-oligo[9'',9''-dioctylfluoren-2'',7''-diyl])-pyridinato-*N, C*$^{3'}$) (acetylacetonate) (*n* = 5) (18)

Iridium(III) bis(2-(2'-benzo[*b*]thienyl)-5-bromopyridine-*N, C*$^{3'}$)(acetylacetonate) (0.045 g, 0.040 mmol, 1 eq.), 2-Bromo-7-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane)-9,9-dioctylfluorene (0.310 g, 0.500 mmol, 13 eq.), palladium acetate (0.002 g, 0.008 mmol) and tricyclohexylphosphine (0.004 g,

0.016 mmol) were dissolved in toluene (20 mL) and heated to 111 ºC for 10 min. Et_4NOH (2.500 mL, 3.100 mmol) was added and the solution vigorously stirred for 18 h. The layers were separated and the organic layer washed with water (20 mL). The organic layer was dropped into excess MeOH causing precipitation of an orange solid. The orange precipitate was filtered and washed with MeOH (50 mL), Water (30 mL) and acetone (30 mL). The precipitate was re-dissolved in toluene (50 mL) and passed through a short silica gel column. The toluene was reduced (to around 5 mL) and Na_2CO_3 (0.100 g, 0.920 mmol), acetyl acetone (1.000 mL, 0.500 mmol) and 2-ethoxyethanol (8 mL) were added. The solution was heated to 111 ºC for 2 h. The solution was cooled to room temperature and poured into excess MeOH, causing precipitation of the polymer. The orange polymer was filtered and washed with Water (20 mL), MeOH (20 mL) and acetone (20 mL). The precipitate was dissolved in toluene (50 mL), filtered through silica and the solvent removed *in vacuo*. Solvent residues were removed by freeze-drying a benzene (10 mL) solution and the crude product purified by Soxhlet extraction with acetone (2 x 100 mL) for 24 h, yielding pure product as an orange solid (0.100 g, 0.012 mmol, 58 %).

Anal. Calcd.: C 81.06 %, H 8.92 %, N 0.58 %; Found: C 80.70 %, H 9.20 %, N 0.29 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.87 (s, 1H, $C_{13}H_7NS$), 8.12 (m, 1H, $C_{13}H_7NS$), 7.86-7.63 (m, 27H, n=5, Ar*H*), 7.60-7.36 (m, 2H, $C_{13}H_7NS$), 6.86 (m, 1H, $C_{13}H_7NS$), 6.45 (m, 1H, $C_{13}H_7NS$), 5.43 (s, 0.5H, $OC(CH_3)CH$), 2.30-2.00 (m, 17H (n=4), CH_2), 1.91 (s, 3H, $OC(CH_3)$), 1.21-0.91 (m, 98H (n=5), CH_2), 0.83-0.78 (m, 47H (n=5), CH_2 + CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ: 151.8, 140.4, 139.9, 128.7, 126.1, 121.5, 119.9, 55.5, 40.3, 31.8, 30.8, 29.2, 23.8, 22.6, 14.0; M*w* Calcd. For $C_{321}H_{421}Br_2IrN_2O_2S_2$: 4800; GPC ($CHCl_3$, Polystyrene Standards): M*p* =17,000, M*n* = 5,000, M*w* = 18,000, PDI = 3.2; IR (CH_2Cl_2, cm^{-1}) ν: 2858, 2765, 2655, 2313, 2126, 2054,1607, 1468, 1001, 820.

Iridium(III)bis(2-(2'-benzo[*b*]thienyl)-5-(ω-bromo-oligo[9",9"-dioctylfluoren-2",7"-diyl])-pyridinato-*N, C*$^{3'}$) (acetylacetonate) (*n* = 10) (19)

The same protocol as above except using different quantities of iridium(III) bis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N, C*$^{3'}$)(acetylacetonate) (0.030 g, 0.030 mmol, 1 eq.) and 2-bromo-7-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane)-9,9-dioctylfluorene (0.420 g, 0.700 mmol, 23 eq.). The reaction yielded a deep red solid (0.250 g, 0.030 mmol, 98 %).

Anal. Calcd.: C 84.84%, H 9.58 %, N 0.32 %. Found: C 82.86 %, H 9.47 %, N 0.28 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.88 (s, 1H, $C_{13}H_7NS$), 8.11 (m, 1H, $C_{13}H_7NS$), 7.86-7.68 (m, 62H (n=6), Ar*H*), 7.36-7.32 (m, 3H, $C_{13}H_7NS$), 7.08-7.00 (m, 1H, $C_{13}H_7NS$), 6.87 (m, 1H, $C_{13}H_7NS$), 6.45 (m, 1H, $C_{13}H_7NS$), 5.44 (s, 0.5H, $C_5H_7O_2$), 2.30-2.00 (m, 43H (n=10), C_8H_{17}), 1.91 (s, 3H, OC(CH_3)), 1.26-0.96 and 0.84-0.80 (m, 330H (n=11), CH_2+ CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ:151.8, 140.5, 140.0, 126.1, 121.5, 119.9, 53.3, 40.4, 31.8, 30.8, 29.2, 23.8, 22.6, 14.1; M*w* Calcd. For $C_{611}H_{821}Br_2IrN_2O_2S_2$: 8642; GPC ($CHCl_3$, Polystyrene Standards): M*p* =14,000, M*n* = 9,000, M*w* = 21,000, PDI = 2.4 ; IR (CH_2Cl_2, cm^{-1}) ν: 2910, 2858, 2765, 2413, 2313, 1713, 1605, 1468, 1011, 820.

Iridium(III)bis(2-(2'-benzo[*b*]thienyl)-5-(ω-bromo-oligo[9",9"-dioctylfluoren-2",7"-diyl])-pyridinato-*N, C*$^{3'}$) (acetylacetonate) (*n* = 20) (20)

The same protocol with iridium(III) bis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N, C*$^{3'}$)(acetylacetonate) (0.015 g, 0.018 mmol, 1 eq.) and 2-bromo-7-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane)-9,9-dioctylfluorene (0.415 g, 0.697 mmol, 40 eq.). The reaction yielded a deep red solid (0.160 g, 0.010 mmol, 55 %).

Anal. Calcd.: C 87.15 %, H 9.95 %, N 0.15 %; Found: C 81.00 %, H 9.66 %, N 0.18 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.89 (s, 1H, $C_{13}H_7NS$), 8.13-7.80 (m, 124H (n=20), Ar*H*), 6.77 (m, 1H, $C_{13}H_7NS$), 6.48 (m, 1H, $C_{13}H_7NS$), 5.46 (s, 0.5H, $C_5H_7O_2$), 2.19-2.14 (m, 84H (n=21), CH_2), 1.93 (br s, 3H, OC(CH_3)), 0.96-0.92 and 0.86-0.81 (m, 748H (n=25), CH_2 + CH_3); ^{13}C{^{1}H} NMR (125 MHz,

$CDCl_3$, ppm) δ : 151.8, 140.4, 140.0, 128.7, 126.1, 121.5, 119.9, 55.3, 40.3, 31.7, 29.9, 29.2, 23.8, 22.5, 14.0; M*w* Calcd. For $C_{1191}H_{1621}Br_2IrN_2O_2S_2$: 16,000; GPC ($CHCl_3$, Polystyrene Standards): M*p* =22,000, M*n* = 14,000, M*w* = 47,000, PDI = 3.4; IR (CH_2Cl_2, cm^{-1}) ν: 2920, 2858, 2809, 2190, 2089, 1734, 1609, 1009, 858.

Iridium(III)bis(2-(2'-benzo[*b*]thienyl)-5-(ω-bromo-oligo[9",9"-dioctylfluoren-2",7"-diyl])-pyridinato-*N, C*$^{3'}$) (acetylacetonate) (*n* = 40) (21)

The same protocol with iridium(III) bis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N, C*$^{3'}$)(acetylacetonate) (0.0076 g, 0.0088 mmol, 1 eq.) and 2-bromo-7-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane)-9,9-dioctylfluorene (0.4150 g, 0.6970 mmol, 80 eq.). The reaction yielded a deep red solid (0.1300 g, 0.0050 mmol, 57 %).

Anal. Calcd.: C 88.07 %, H 10.44 %, N 0.09 %; Found: C 86.43 %, H 10.23 %, N 0.15 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.91 (s, 1H, $C_{13}H_7NS$), 8.16-7.62 (m, 232H (n=39), Ar*H*), 7.09 (m, 1H, $C_{13}H_7NS$), 6.89 (m, 1H, $C_{13}H_7NS$), 6.48 (m, 1H, $C_{13}H_7NS$), 5.46 (s, 0.5H, $C_5H_7O_2$), 2.49-2.15 (m, 129H (n=33), CH_2), 1.94 (s, 3H, OC(CH_3)), 1.25-1.12 and 0.98-0.83 (m, 1219H (n=40), CH_2 + CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ: 151.8, 140.4, 140.0, 128.7, 126.1, 121.5, 119.9, 55.3, 40.3, 31.7, 29.9, 29.2, 23.8, 22.5, 14.0 ; M*w* Calcd. For $C_{23511}H_{3321}Br_2IrN_2O_2S_2$: 32,000; GPC ($CHCl_3$, Polystyrene Standards): M*p* =100,000, M*n* = 62,000, M*w* = 200,000, PDI = 3.2; IR (CH_2Cl_2, cm^{-1}) ν: 2919, 2857, 2801, 1609, 1009, 858.

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