Supporting Information

A Divergent Synthesis of Very Large Polyphenylene Dendrimers with Iridium(III) Cores: Molecular Size Effect on the Performance of Phosphorescent Organic Light-Emitting Diodes

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Experiment Part

Instrumentation and characterization: ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX250 and DRX500 spectrometers, respectively, and referenced to residual signals of the deuterated solvent. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet expected but not resolved; Field desorption mass spectra (FDMS) were performed with a VG Instruments ZAB 2-SE-FDP using 8 kV accelerating voltage. MALDI-TOF mass spectra were measured using a Bruker Reflex II, calibrated against poly(ethylene glycol) (3.000 g/mol). Samples for MALDI-TOF MS were prepared by mixing the analyte with the matrix (dithranol or silver ion) in dichloromethane in a ratio of 1/250.

Materials: *fac*-Tris(2-phenylpyridyl)Ir(III) ($Ir(ppy)_3$) was synthesized according to literature procedures.[1] All other chemicals and solvents were purchased from commercial sources and used without further purification. Solvents for synthesis were purified according to standard procedures. Reactions were all carried out under an argon atmosphere.

Synthesis:

***fac*-Tris[2-(3-iodophenyl)pyridyl]Ir(III) (1).** 5.08g (20 mmol) iodine and 3.22 g (10 mmol) iodobenzene diacetate were added to a solution of 1.32 g (2 mmol) $Ir(ppy)_3$ in 500 mL dichloromethane. The mixture was stirred at room temperature under argon for 36 h. The solvent was concentrated to 50 mL and mixed with 500 mL ethanol. The yellow precipitate was collected by filtration and washed with water and ethanol. After it was dried, 2.05 g product was recrystallized in hexane as yellow crystal in a quantitively yield.

^{1}H NMR (250 MHz, DMSO-d6) δ 8.22 (d, J = 8.4 Hz, 3H), 8.06 (d, J = 2.0 Hz, 3H), 7.83 (m, 3H), 7.45 (d, J = 5.4 Hz, 3H), 7.40 (m, 3H), 7.02 (dd, J = 2.0, 8.0 Hz, 3H), 6.41 (d, J = 8.0 Hz, 3H); FDMS (*m/z*): Calcd. For $C_{33}H_{21}I_3IrN_3$: 1032.5, found: 1032.7.

***fac*-Tris[2-(3-((trimethylsilyl)ethynyl)phenyl)pyridyl]Ir(III) (2).** A mixture of 2.00 g (1.93 mmol) complex **1** and 4.50 g (11.60 mmol) (tributylstannyl)trimethylsilane were dissolved in 150 mL anhydrate THF in the presence of 120 mg (0.17 mmol) $Pd(PPh_3)_2Cl_2$ and refluxed for 24 h at 85 °C. After cooling to room temperature, the reaction mixture was extracted with toluene followed by washing with aqueous solution of potassium fluoride to remove extra stannane. The organic phase was dried over $MgSO_4$, and then purified by column chromatography using toluene as the eluent, affording 1.09 g pure compound as a yellow powder in 60% yield.

^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.94 (d, *J* = 8.2 Hz, 3H), 7.76 (d, *J* = 1.6 Hz, 3H), 7.73 – 7.64 (m, 3H), 7.52 (d, *J* = 4.7 Hz, 3H), 6.97 (t, *J* = 5.9 Hz, 3H), 6.83 (dd, *J* = 1.7, 7.8 Hz, 3H), 6.70 (d, *J* = 7.8 Hz, 3H), 0.22 (s, 27H); MALDI-TOF (*m/z*): Calcd. For $C_{48}H_{48}IrN_3Si_3$: 943.4, found: 943.3.

***fac*-Tris[2-(3-ethynyl)phenyl)pyridyl]Ir(III) (3).** To a solution of 1.00 g (1.06 mmol) complex **2** in THF (25 mL) was added dropwise a solution of TBAF (1.25 g, 4.77 mmol) in THF (15 mL). The reaction was stirred at RT for 1 h and precipitate in 100 mL MeOH. The solid was dissolved in CH_2Cl_2 and purified by column chromatography using CH_2Cl_2 as eluent, affording 700 mg pure product as yellow powder in 90% yield.

^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.93 (d, *J* = 8.2 Hz, 3H), 7.74 (d, *J* = 1.6 Hz, 3H), 7.72 – 7.63 (m, 3H), 7.52 (d, *J* = 4.8 Hz, 3H), 6.96 (t, *J* = 5.8 Hz, 3H), 6.82 (dd, *J* = 1.8, 7.8 Hz, 3H), 6.70 (d, *J* = 7.6 Hz, 3H), 3.00 (d, *J* = 11.0 Hz, 3H); FDMS (*m/z*): Calcd. For $C_{39}H_{24}IrN_3$: 727.2, found: 727.0.

Dendrimer G1. 100 mg (0.137 mmol) complex **3** and 237 mg (0.617 mmol) tetraphenylcyclopentadienone **4** were dissolved in *o*-xylene (5 mL) in a microwave tube. The argon bubbled mixture was stirred at 170 °C in microwave reactor for 4 h. After cooling to RT, the reaction mixture was precipitated in MeOH, further purified by a GPC column using toluene as the eluent, affording 225 mg pure product as yellow powder in 92% yield.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.59 (s, 3H), 7.56 (s, 3H), 7.55 (d, *J* = 1.5 Hz, 3H), 7.48 (d, *J* = 5.4 Hz, 3H), 7.34 (d, *J* = 1.8 Hz, 3H), 7.18 – 7.11 (m, 15H), 6.95 – 6.85 (m, 48H), 6.67 (dd, *J* = 1.8, 7.8 Hz, 3H), 6.36 (d, *J* = 7.8 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 166.74, 159.24, 147.40, 143.74, 142.41, 142.37, 141.95, 141.22, 141.02, 140.90, 140.83, 139.72, 138.87, 136.48, 136.20, 133.44, 132.12, 132.01, 131.93, 131.59, 131.36, 130.39, 127.87, 127.19, 127.02, 126.92, 126.88, 126.48, 126.35, 125.84, 125.60, 122.38, 119.13; MALDI-TOF (*m/z*): Calcd. For $C_{123}H_{84}IrN_3$: 1795.6, found: 1795.4.

Synthesis of high generation dendrimers (G2, G3 and G4).

General Procedure. High generation Ir(III) dendrimers from **G2** to **G4** were synthesized by a divergent strategy according to a previous paper.[2]

All high generation polyphenylene dendrimers were synthesized from 200 mg (0.274 mmol) Ir(III) complexes core **3** with 918 mg (1.223 mmol) AB_2-type building block **5** by *Diels–Alder* [4+2] cycloaddition (Scheme 4). The triisopropylsilyl (TiPS) groups in dendrimers were deprotected with TBAF and the resulting ethynyl groups were further treated with either AB_2-type building block **5** to continue the divergent synthesis or tetraphenylcyclopentadienone **4** as the end-cap to obtain **G2**, **G3** and **G4**. The yield of the product ranges from 81% to 89% for each step and illustrated in Scheme 4.

[4+2] *Diels–Alder* cycloaddition:

Multi-ethynyl functionalized Ir(III) dendrimers (ca. 0.1 mmol) and tetraphenylcyclopentadienone **4** or AB_2-type building block **5** (1.2 eq. per ethynyl) were dissolved in 5 mL of *o*-xylene. The solution was stirred at 170 °C under argon for 4-12 h in microwave reactor. After cooling to RT, the reaction mixture was precipitated in MeOH, and further purified by a GPC column using toluene as the eluent.

TiPS group deprotection:

Multi-(triisopropylsilyl)ethynyl Ir(III) dendrimers (ca. 0.1 mmol) were dissolved in 5 mL of THF, and added dropwise to a solution of TBAF (1.2 eq. per TiPS) in THF (5 mL).

The reaction was stirred at RT for 1 h and precipitated in MeOH. The solid was dissolved in CH_2Cl_2 and purified by column chromatography using CH_2Cl_2 as the eluent.

The NMR and MALDI-TOF mass spectra data of the dendrimers are as follows.

Dendrimer 6: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.64 (s, 3H), 7.61 (d, *J* = 8.1, 3H), 7.54 (t, *J* = 7.7 Hz, 3H), 7.46 (d, *J* = 4.9 Hz, 3H), 7.37 (s, 3H), 7.21 (dd, *J* = 6.3, 18.1 Hz, 18H), 7.12 (d, *J* = 8.1 Hz, 6H), 7.07 (d, *J* = 8.1 Hz, 6H), 6.91 (s, 15H), 6.88 – 6.78 (m, 15H), 6.64 (d, *J* = 7.3, 3H), 6.49 (s, 3H), 1.19, (s, 18H), 1.18 (s, 108H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 166.88, 158.96, 146.66, 143.01, 142.25, 141.78, 140.90, 140.53, 140.48, 140.09, 139.25, 137.45, 136.12, 135.29, 132.47, 131.51, 131.30, 131.16, 130.85, 130.42, 130.17, 129.83, 127.36, 126.87, 126.56, 126.00, 125.54, 125.28, 121.11, 120.65, 120.42, 118.43, 107.82, 107.73, 89.98, 89.80, 18.44, 11.66, 11.44; MALDI-TOF (*m/z*): Calcd. For $C_{189}H_{207}IrN_3Si_6$: 2881.5, found: 2880.8.

Dendrimer 7: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.65 (s, 3H), 7.59 (d, *J* = 7.9 Hz, 3H), 7.54 (t, *J* = 7.2 Hz, 3H), 7.45 (s, 3H), 7.36 (s, 3H), 7.21 (d, *J* = 3.4 Hz, 18H), 7.13 (d, *J* = 8.1 Hz, 6H), 7.08 (d, *J* = 8.2 Hz, 6H), 6.94 – 6.85 (m, 21H), 6.83 (d, *J* = 7.7 Hz, 9H), 6.64 (s, 3H), 6.50 (s, 3H), 3.01 (d, *J* = 11.8 Hz, 6H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ ^{13}C NMR (125 MHz, $C_2Cl_4D_2$) δ 166.83, 159.04, 146.67, 143.05, 142.31, 141.60, 141.48, 141.05, 140.51, 140.33, 139.98, 139.21, 137.24, 136.13, 135.32, 132.34, 131.47, 131.41, 131.11, 130.85, 130.62, 130.36, 129.79, 127.39, 126.59, 126.08, 125.56, 125.35, 121.14, 119.13, 118.87, 118.43, 76.66, 76.49; MALDI-TOF (*m/z*): Calcd. For $C_{135}H_{87}IrN_3$: 1940.3, found: 1940.5

Dendrimer G2: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.55 (s, 3H), 7.54 (s, 6H), 7.47 (d, *J* = 5.5 Hz, 3H), 7.43 (s, 3H), 7.39 (s, 3H), 7.29 (s, 3H), 7.17 – 7.15 (m, 39H), 7.09 – 7.06 (m,

6H), 6.96 - 6.70 (m, 114H), 6.68 (d, *J* = 8.0 Hz, 6H), 6.60 (dd, *J* = 1.0, 7.7 Hz, 3H), 6.56 (d, *J* = 6.2 Hz, 6H), 6.52 (d, *J* = 6.1 Hz, 6H), 6.34 (d, *J* = 7.9 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 142.29, 142.07, 141.07, 140.84, 140.65, 140.45, 139.53, 139.46, 131.92, 131.49, 130.31, 127.88, 127.20, 127.14, 126.85, 126.56, 125.92, 125.62; MALDI-TOF (*m/z*): Calcd. For $C_{303}H_{204}IrN_3$: 4079.1, found: 4079.2.

Dendrimer 8: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.56 (s, 3H), 7.53 (s, 3H), 7.48 (s, 3H), 7.43 (d, *J* = 3.3 Hz, 9H), 7.33 (s, 6H), 7.18 (d, *J* = 13.6 Hz, 42H), 7.10 (d, *J* = 7.7 Hz, 15H), 7.05 (d, *J* = 7.2 Hz, 15H), 6.94 (s, 21H), 6.89 – 6.68 (m, 63H), 6.64 (d, *J* = 7.4 Hz, 9H), 6.59 (s, 6H), 1.17 (s, 252H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 141.52, 140.82, 140.55, 140.08, 139.57, 139.03, 138.21, 131.33, 131.15, 130.97, 130.44, 130.16, 129.70, 128.31, 128.13, 127.43, 126.73, 126.16, 125.49, 120.81, 120.53, 107.59, 89.97, 18.43, 11.42; MALDI-TOF (*m/z*): Calcd. For $C_{435}H_{447}IrN_3Si_{12}$: 6243.4, found: 6243.1.

Dendrimer 9: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ δ 7.58 (s, 6H), 7.53 (d, *J* = 7.6 Hz, 3H), 7.49 (s, 3H), 7.44 (s, 6H), 7.33 (s, 6H), 7.19 – 7.11 (m, 60H), 7.09 – 7.02 (m, 15H), 6.94 (d, *J* = 2.0 Hz, 21H), 6.89 – 6.69 (m, 63H), 6.65 (d, *J* = 7.7 Hz, 6H), 6.61 (d, *J* = 7.4 Hz, 6H), 3.01 (d, *J* = 10.3 Hz, 12H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 141.35, 141.13, 140.91, 140.61, 140.40, 139.42, 139.09, 138.05, 131.26, 130.98, 130.64, 130.36, 129.93, 129.67, 128.30, 128.02, 127.45, 127.16, 126.76, 126.37, 126.23, 125.61, 119.30, 119.00, 84.17, 76.61; MALDI-TOF (*m/z*): Calcd. For $C_{327}H_{207}IrN_3$: 4367.4, found 4367.4:

Dendrimer G3: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.53 (s, 9H), 7.47 (d, 3H, *J* = 4.6 Hz), 7.41 (d, *J* = 2.2 Hz, 6H), 7.37 (s, 9H), 7.33 (s, 3H), 7.27 (s, 6H), 7.21 – 6.99 (m, 108H), 6.97 – 6.57 (m, 264H), 6,56 – 6.41 (m, 33H), 6.33 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 142.27, 142.08, 141.08, 141.01, 140.62, 140.42, 139.55, 139.44, 131.90, 131.41, 130.30, 128.93, 128.65, 127.89, 127.15, 126.86, 126.58, 125.93, 125.62; MALDI-TOF (*m/z*): Calcd. For $C_{663}H_{444}IrN_3$: 8642.5, found: 8642.9.

Dendrimer 10: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.46 (s, 6H), 7.42 (s, 6H), 7.36 (s, 6H), 7.31 – 6.40 (m, 405H), 1.17 (s, 504H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 145.39, 141.49, 140.83, 140.51, 140.08, 139.54, 139.06, 138.39, 131.30, 131.15, 130.82, 130.44, 130.16, 129.68, 127.73, 127.44, 126.73, 126.17, 125.40, 125.26, 120.82, 120.55, 107.66, 90.01, 18.43, 11.42. MALDI-TOF (*m/z*): Calcd. For $C_{927}H_{927}IrN_3Si_{24}$: 12961.6, found: 12964.4 ($-K^+$).

Dendrimer 11: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.48 (s, 6H), 7.43 (s, 6H), 7.38 (s, 6H), 7.31 – 6.40 (m, 405H), 3.00 (d, J = 10.3 Hz, 24H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 141.39, 141.17, 140.43, 140.11, 140.03, 139.47, 139.21, 138.99, 131.47, 131.25, 130.93, 130.64, 130.26, 130.01, 129.55, 127.53, 127.34, 126.62, 126.04, 125.31, 125.16, 120.73, 120.57, 107.66, 84.01, 76.23; MALDI-TOF (*m/z*): Calcd. For $C_{711}H_{447}IrN_3$: 9214.4, found: 9214.7.

Dendrimer G4: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.53 (s, 6H), 7.41 (s, 9H), 7.37 (s, 6H), 7.36 (s, 6H), 7.31 (s, 6H), 7.27 (s, 6H), 7.27 – 6.20 (m, 891H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 131.50, 129.90, 128.05, 127.49, 126.76, 125.67; MALDI-TOF (*m/z*): Calcd. For $C_{663}H_{444}IrN_3$: 17776.4, found: 17787.0 ($-Ag^+$).

Measurements of Photophysical Properties: UV-Vis absorption and photoluminescence spectra were measured by Perkin-Elmer Lambda 35 Uv/Vis spectrometer and Perkin-Elmer LS 50B spectrofluorometer, respectively. Solution PL quantum efficiency was measured by a relative method using *fac*-Ir(ppy)$_3$ (Φ_p = 0.40 in toluene) as the standard. The film PL quantum efficiency was measured with an integrating sphere under an excitation wavelength of 409 nm.

Measurements of Electrochemical Properties: The CV measurements were conducted at a scan rate of 50 mVs^{-1} at room temperature under argon protection in deoxygenated 0.1 mmol/L DCM solutions with 0.1 mol/L tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) as the supporting electrolyte. A platinum electrode was used as the working electrode and an Ag/Ag^+ electrode as the reference electrode.

Device fabrication and testing: To fabricate OLEDs, a 50-nm-thick poly(ethylenedioxythiophene): poly(styrene sulfonic acid) (PEDOT : PSS, purchased from H. C. Starck) film was first deposited on the pre-cleaned ITO-glass substrates (20 Ω/square) and then cured at 120 °C in air for 30 min.. Then the film of dendrimers was spin-coated with chlorobenzene as the solvent, and annealed at 90 ^oC for 30 min. Successively, TPBI, LiF and Al were evaporated at a base pressure less than 10^{-6} Torr (1 Torr = 133.32 Pa) through a shadow mask with an array of 14 mm^2 openings. The electroluminescence (EL) spectra and Commission Internationale de L'Eclairage (CIE) coordinates were measured using a PR650 spectra colorimeter. The current-voltage and brightness-voltage curves of devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.

Reference

(1) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E.; *Inorg. Chem.* **2001**, *40,* 1704.

(2) Wiesler, U.; Müllen, K. *Chem. Commun*. **1999**, 2293