

**Facile Synthesis of Self-Host Function Iridium Dendrimers Up to Fourth Generation with *N*-phenylcarbazole-Based Polyether Dendrons for Nondoped Phosphorescent Organic Light-Emitting Diodes**

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## Experimental

**General Information:** All chemicals and reagents were used as received from commercial suppliers without further purification. Solvents for chemical synthesis were purified according to the standard procedures. G0 and DPSF were prepared in our lab according to the literatures. [1-2]

**Instrumentation and Characterization:** NMR spectra were recorded with Bruker Avance NMR spectrometers. MALDI-TOF mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT) using dithranol or 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as the matrix. Elemental analysis was performed using a Bio-Rad elemental analysis system. Molecular weight and PDI of the dendrimers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as a standard and THF as the eluent. Thermal properties of the dendrimers were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C/min. Recycling preparative GPC purifications were carried out on a Shimadzu HPLC system, which consisted of a model SPD-20A tunable absorbance detector, a model RID-10A differential refractometer, an in-line degasser, a model LC-6AD Pump, a model CBM-20A controller, and a Shodex KF-802 preparative GPC column. The Shimadzu model LC-6AD pump was fitted with a 1.0 mL loop and a three directional recycling manifold that allowed for the product to be cycled back onto the column.

**Measurements of Photophysical Properties:** UV–visible (UV–vis) absorption and photoluminescent spectra were measured with a Perkin-Elmer Lambda 35 UV–vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. Solution PL quantum efficiency was measured in argon atmosphere by a relative method using *fac*-Ir(ppy)<sub>3</sub> ( $\Phi_p = 0.40$  in toluene) as the standard. [3] The neat films of the dendrimers were prepared by drop-coating on quartz substrates. The lifetimes of phosphorescence from the samples were measured in argon atmosphere by exciting the samples with 355 nm light pulses with ca. 3 ns pulse width from a Quanta-Ray DCR-2 pulsed Nd:YAG laser. The lifetimes measured in solutions were obtained by a monoexponential fit of emission decay curves, while those measured in solid films were obtained by a biexponential fit of emission decay curves, and average lifetimes could be calculated according to the equation:  $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ .

**Measurements of Electrochemical Properties:** Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 mol/L tetrabutylammonium perchlorate in anhydrous DCM at a scan rate of 100 mV/s. A Pt electrode with a diameter of 2 mm, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. All potentials were calibrated against the ferrocene/ferrocenium couple (Fc/Fc<sup>+</sup>). The HOMO levels were calculated according to the equation  $HOMO = -e(E_{ox} + 4.8 \text{ V})$ , where  $E_{ox}$  was the first oxidation peak measured from DPV, and the LUMO levels were calculated according to the equation  $LUMO = HOMO + \Delta E_g$ , where  $\Delta E_g$  is the optical band gap estimated from

the onset of the absorption spectrum. [4]

***Device Fabrication and Measurements:***

*Hole-only devices:* The structure of hole-only device is ITO/PEDOT: PSS (45nm)/EML (80nm)/Au (75nm). For the device fabrication, firstly a 45 nm thick PEDOT:PSS (Clevios P AI4083) was spin-coated onto the pre-cleaned ITO substrates and then annealed at 120 °C for 40 min in air condition. The EML was spin-coated from its chlorobenzene solution and then annealed at 100 °C for 30 min to remove residual solvent in glove box. Finally a 75 nm Au electrode was thermally deposited in a vacuum chamber at a pressure less than  $4 \times 10^{-4}$  Pa through a shadow mask with an array of 14 mm<sup>2</sup> openings.

*Organic light-emitting diodes (OLEDs):* To fabricate OLEDs, a 25-nm-thick poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) film was first deposited on the pre-cleaned ITO-glass substrates (20Ω per square) and subsequently baked at 120 °C for 40 min. Then, solutions of the dendrimers in chlorobenzene were spin-coated onto PEDOT:PSS as the emissive layer (EML). The thickness of the EML was about 35 nm. Successively, a 65-nm-thick film of DPSF was thermally evaporated on top of the EML at a base pressure less than  $4 \times 10^{-4}$  Pa. Finally, 1 nm LiF and 100 nm Al were deposited as the cathode through a shadow mask with an array of 14 mm<sup>2</sup> openings. The EL spectra and 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 measurements were carried out at room temperature under

ambient conditions.

***Synthetic Procedures:***

***3,6-Di-tert-butyl-carbazole (1):*** To a solution of carbazole (28.4 g, 0.2 mol) in CH<sub>2</sub>Cl<sub>2</sub> (85 mL) and CH<sub>3</sub>NO<sub>2</sub> (42 mL) were added ZnCl<sub>2</sub> (69.5 g, 0.5 mol). Then 2-chloro-2-methylpropane (56.1 mL, 0.5 mol) was added dropwise. After stirring for 24 h at room temperature, the mixture was filtered, washed with 1 M HCl and then petroleum ether to give the product (33.5 g) in a yield of 70%.

***4-(3,6-Di-tert-butyl-carbazol-9-yl)benzaldehyde (2):*** **1** (13.4 g, 48 mmol), 4-bromobenzaldehyde (9.8 g, 52.8 mmol), potassium carbonate (16.7 g, 120 mmol), Pd(OAc)<sub>2</sub> (108 mg, 0.5 mmol), P(*t*-Bu)<sub>3</sub> (292 mg, 1.4 mmol) were added to 200 mL degassed toluene under argon atmosphere. The reaction mixture was heated to reflux for 24 h. Then the mixture was filtered, the solvent was removed by vacuum distillation, followed by adding 150 mL CH<sub>2</sub>Cl<sub>2</sub>. The crude product was washed with water, brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The pure product (16.0 g) was obtained by column chromatography using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 4:1 as eluent in a yield of 87%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 10.01 (s, 1H), 8.13 (d, *J* = 1.6 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H) 7.78 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 1.47 (s, 18H).

***(4-(3,6-Di-tert-butyl-carbazol-9-yl)phenyl)methanol (D1-OH):*** NaBH<sub>4</sub> (516 mg, 13.8 mmol) dissolved in aqueous NaOH solution (0.1 M, 22 mL) was added dropwise into

**2** (9.6 g, 25 mmol) in the mixture of ethanol (50 mL) and THF (50 mL). The mixture was reacted at room temperature for 3 h. The solution was poured into water and filtered to give pure product (9.5 g) in a yield of 98%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.08 (s, *J* = 1.6 Hz, 2H), 7.62-7.55 (m, 4H), 7.46 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 4.83 (s, 2H), 1.67 (s, 1H), 1.46 (s, 18H). MALDI-TOF MS: calcd for C<sub>27</sub>H<sub>31</sub>NO: 385.2 found: 385.2 [M<sup>+</sup>].

*3,6-Dibromocarbazole (3)*: Carbazole (20.0 g, 0.1 mol) was dissolved in 70 mL DMF under an ice bath, and was added slowly with NBS (42.7 g, 0.2 mol) which was dissolved in 70 mL DMF before. The mixture was reacted for 4 h and then poured into water to give a white solid. The pure product (31.0 g) was obtained by recrystallization from ethanol in a yield of 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.14 (d, *J* = 1.8 Hz, 2H), 8.10 (s, 1H), 7.52 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H).

*3,6-Dimethoxycarbazole (4)*: Dry methanol (20 mL) in a flask was cooled to 0 °C with ice bath before sodium (2.1 g, 92 mmol) was added. The ice water bath was removed and the mixture was stirred until the sodium disappeared. To this sodium methoxide solution was added DMF (20 mL), CuI (3.5 g, 18.4 mmol) and **3** (1.5 g, 4.6 mmol). The resulting mixture was heated to reflux for 4 h under Ar atmosphere. The hot mixture was rapidly filtered and the filtrate was poured into water and extracted with dichloromethane. The combined organic layers were neutralized with 1 M HCl,

followed by washing with water and brine, drying with Na<sub>2</sub>SO<sub>4</sub>, and purifying by silica gel column chromatography using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 3:1 as eluent to give white product (950 mg) in a yield of 90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.49 (d, *J* = 2.5 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.05 (dd, *J* = 8.7, 2.5 Hz, 2H), 3.93 (s, 6H).

*Methyl 4-(3,6-dimethoxy-carbazol-9-yl)benzoate (5)*: **4** (9.7 g, 42 mmol), methyl 4-bromobenzoate (10.9 g, 51 mmol), potassium carbonate (14.8 g, 105 mmol), Pd(OAc)<sub>2</sub> (124 mg, 0.6 mmol), P(*t*-Bu)<sub>3</sub> (314 mg, 1.6 mmol) were added to 200 mL degassed toluene under argon atmosphere. The reaction mixture was heated to reflux for 16 h. Then the mixture was filtered, the solvent was removed by vacuum distillation, followed by adding 150 mL CH<sub>2</sub>Cl<sub>2</sub>. The crude product was washed with water, brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The pure product (13.0 g) was obtained by column chromatography using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 2:1 as eluent in a yield of 84%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.25 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 2.4 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 2H), 3.98 (s, 3H), 3.95 (s, 6H).

*Methyl 4-(3,6-dihydroxy-carbazol-9-yl)benzoate (6)*: A solution of **5** (2.2 g, 6.0 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was cooled to 0°C, and BBr<sub>3</sub> (2.4 mL 1 M solution in CH<sub>2</sub>Cl<sub>2</sub>, 24.0 mmol) was added dropwise. After stirring for 4 h 0 °C, the reaction was carefully quenched with methanol, followed by adding a saturated solution of

NaHCO<sub>3</sub>. Then the mixture was filtered, washed with water and dried in vacuum. Column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 3:1 as eluent provides the pure product (1.4 g) in a yield of 70%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sup>6</sup>, δ): 9.15 (s, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 2.4 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 2H), 3.87 (s, 3H).

*9-(4-(Hydroxymethyl)phenyl)-carbazole-3,6-diol (PC-OH)*: To a stirred solution of LiAlH<sub>4</sub> (455 mg, 12 mmol) in THF (40 mL) was added a solution of **6** in THF (20 mL). The mixture was heated to reflux for 12 h, and then 1 M HCl was added to quench the reaction. The acidic solution was extracted with ethyl acetate. The organic layers were combined and then dried with Na<sub>2</sub>SO<sub>4</sub>. The pure product (1.8 g) was obtained by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 4:1 as eluent in a yield of 96% in two steps. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sup>6</sup>, δ): 9.07 (s, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 2.3 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 2H), 4.61 (s, 2H), 3.60 (s, 1H). MALDI-TOF MS: calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>3</sub>: 305.1 found: 305.1 [M<sup>+</sup>].

*4-Methoxy-N-(2-nitrophenyl)benzenamine (7)*: 2-nitroaniline (1.4 g, 10 mmol), 4-iodoanisole (2.6 g, 11 mmol), CuI (190 mg, 1 mmol), K<sub>3</sub>PO<sub>4</sub> (6.3 g, 30 mmol), *trans*-1,2-cyclohexanediamine (0.1 mL, 0.5 mmol) were added to 25 mL degassed toluene under argon atmosphere. The reaction mixture was heated to reflux for 24 h. Then the mixture was filtered, the solvent was removed by vacuum distillation, followed by



adding 150 mL CH<sub>2</sub>Cl<sub>2</sub>. The crude product was washed with water, brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The pure product (1.75 g) was obtained by column chromatography using petroleum ether: ethyl acetate = 10:1 as eluent in a yield of 72%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 9.40 (m, 1H), 8.16 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.33-7.27 (m, 1H), 7.20-7.16 (m, 2H), 7.00-6.92 (m, 3H), 6.72-6.67 (m, 1H), 3.83 (s, 3H).

*N*-(4-methoxyphenyl)benzene-1,2-diamine (**8**): The mixture of **7** (3.9 g, 16 mmol), iron powder (4.5 g, 80 mmol), methanol (50 mL) and water (50 mL) was refluxed, then concentrated hydrochloric acid (10.4 mL) was added slowly. After that, the reaction was conducted for 2 h. After cooling to room temperature, the mixture was filtered, extracted with ethyl acetate and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained by removing the solvent for the next reaction without further purification.

*N*-(2-(4-methoxyphenylamino)phenyl)benzamide (**9**): The crude product **8** was charged in a round bottle, 30 mL Et<sub>3</sub>N and 15 mL CH<sub>2</sub>Cl<sub>2</sub> was then added, and the mixture was cooled to 0 °C. Benzoyl chloride (1.9 mL, 16 mmol) was dissolved in 15 mL CH<sub>2</sub>Cl<sub>2</sub> and then slowly added to the bottle. The reaction was conducted under argon atmosphere for 6 h. The crude product was obtained by removing the solvent for the next reaction without further purification.

*1*-(4-Methoxyphenyl)-2-phenyl-1*H*-benzo[*d*]imidazole (**10**): The crude product **9** was dissolved in acetic acid (30 mL) and refluxed for 8 h. The mixture was poured into

water, extracted with  $\text{CH}_2\text{Cl}_2$ , and dried with  $\text{Na}_2\text{SO}_4$ . The pure product (3.4 g) was obtained by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 as eluent in a yield of 71%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.89 (d,  $J = 7.9$  Hz, 1H), 7.60 (dd,  $J = 7.7, 1.6$  Hz, 2H), 7.36-7.28 (m, 5H), 7.25-7.20 (m, 3H), 7.03-6.99 (m, 2H), 3.89 (s, 3H).

*1-(4-Hydroxyphenyl)-2-phenyl-1H-benzo[d]imidazole (11)*: A solution of **10** (9.7 g, 32 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (100 mL) was cooled to 0 °C, and  $\text{BBr}_3$  (1 M solution in  $\text{CH}_2\text{Cl}_2$ , 6.5 mL, 64 mmol) was added dropwise. After stirring for 15 min at 0 °C, the mixture was reacted for 2 h at room temperature. Then the reaction was carefully quenched with methanol, followed by adding a saturated solution of  $\text{NaHCO}_3$ , filtering, washing with water and drying in vacuum. The pure product (8.9 g) was obtained in a yield of 98%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d^6$ ,  $\delta$ ): 9.92 (s, 1H), 7.74-7.71 (m, 1H), 7.54-7.50 (m, 2H), 7.37-7.31 (m, 3H), 7.26-7.09 (m, 5H), 6.89-6.85 (m, 2H). MALDI-TOF MS: calcd for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}$ : 286.1 found: 287.1  $[\text{M}+\text{H}]^+$ .

*HO-Ir(pbi)<sub>3</sub>*:  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (248 mg, 0.7 mmol) and **11** (421 mg, 1.5 mmol) were added in a 16 mL mixture of 2-methoxyethanol (12 mL) and water (4 mL). The mixture was refluxed for 24 h and then poured into water. The solid was collected by filtration and dried in vacuum to give the chloro-bridged dimer complex. Next, the crude dimer, silver trifluoroacetate (170 mg, 0.8 mmol), **11** (250 mg, 0.9 mmol) and 2-ethoxyethanol (15 mL) were heated at reflux for 24 h. After cooling to room

temperature, the mixture was poured into water, filtered, washed with water and dried in vacuum. The pure product (375 mg) was obtained by chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 15:1 as eluent in a total yield of 80%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sup>6</sup>, δ): 10.15 (s, 3H), 7.37 (d, *J* = 8.4 Hz, 3H), 7.16-7.00 (m, 15H), 6.89-6.82 (m, 3H), 6.70 (d, *J* = 7.5 Hz, 3H), 6.61-6.44 (m, 9H), 6.12 (d, *J* = 8.2 Hz, 3H). MALDI-TOF MS: calcd for C<sub>57</sub>H<sub>39</sub>IrN<sub>6</sub>O<sub>3</sub>: 1048.3 found: 1048.3 [M<sup>+</sup>]. Anal. calcd for C<sub>57</sub>H<sub>39</sub>IrN<sub>6</sub>O<sub>3</sub>: C 65.31, H 3.75, N 8.02 Found: C 65.40, H 3.77, N 8.00.

*General Procedure for the Williamson Reaction for the Synthesis of Dendrons **D2-OH** ~ **D4-OH**.*

A mixture of **Dn-Br** (2.1 equiv), **PC-OH** (1 equiv), potassium carbonate (3 equiv), and 18-crown-6 (0.2 equiv) in dry acetone was refluxed under argon atmosphere for 24 h. The mixture was cooled to room temperature and the crude product was purified by column chromatography on silica gel using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 1:3 as eluent.

**D2-OH**: Yield: 87%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.14 (d, *J* = 1.3 Hz, 4H), 7.73 (d, *J* = 8.4 Hz, 4H), 7.72 (s, 2H), 7.59 (m, 8H), 7.45 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.38 (m, 4H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 2H), 5.31 (s, 4H), 4.84 (s, 2H), 1.46 (s, 36H). MALDI-TOF MS: calcd for C<sub>73</sub>H<sub>73</sub>N<sub>3</sub>O<sub>3</sub>: 1039.5 found: 1038.6. Anal. calcd for C<sub>73</sub>H<sub>73</sub>N<sub>3</sub>O<sub>3</sub>: C, 84.28; H, 7.07; N, 4.04. Found: C, 84.18; H, 7.10; N, 3.95.

**D3-OH**: Yield: 60%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.14 (br s, 8H), 7.78-7.71 (m, 18H), 7.66-7.59 (m, 18H), 7.48-7.36 (m, 20H), 7.23-7.17 (m, 6H), 5.33 (s, 4H), 5.31

(s, 8H), 4.84 (s, 2H), 1.46 (s, 72H). MALDI-TOF MS: calcd for C<sub>165</sub>H<sub>157</sub>N<sub>7</sub>O<sub>7</sub>: 2350.1 found: 2350.1 [M<sup>+</sup>]. Anal. calcd for C<sub>165</sub>H<sub>157</sub>N<sub>7</sub>O<sub>7</sub>: C, 84.33; H, 6.73; N, 4.17. Found: C, 83.79; H, 6.98; N, 3.92.

**D4-OH**: Yield: 40%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.13 (br s, 16H), 7.74-7.59 (m, 80H), 7.43-7.36 (m, 40H), 7.20 (m, 14H), 5.29 (m, 28H), 4.82 (s, 2H), 1.45 (s, 144H). MALDI-TOF MS: calcd for C<sub>349</sub>H<sub>325</sub>N<sub>15</sub>O<sub>15</sub>: 4969.4 found: 4969.4 [M<sup>+</sup>]. Anal. calcd for C<sub>349</sub>H<sub>325</sub>N<sub>15</sub>O<sub>15</sub>: C, 84.35; H, 6.59; N, 4.23. Found: C, 84.35; H, 6.69; N, 4.04.

*General Procedure for the Synthesis of Dendrons D1-Br ~D4-Br.*

CBr<sub>4</sub> (1.5-2.0 equiv) was added to a solution of **Dn-OH** (1 equiv) in CH<sub>2</sub>Cl<sub>2</sub>, which was followed by addition of PPh<sub>3</sub> (1.5-2.0 equiv). The mixture was stirred at room temperature for 1 h, then the mixture was precipitated in methanol and filtered to give product which could be used in the next step without further purification.

**D1-Br**: CBr<sub>4</sub> (1.5 equiv) and PPh<sub>3</sub> (1.5 equiv) were used in the reaction. Yield: 93%.

**D2-Br**: CBr<sub>4</sub> (1.5 equiv) and PPh<sub>3</sub> (1.5 equiv) were used in the reaction. Yield: 90%.

**D3-Br**: CBr<sub>4</sub> (2.0 equiv) and PPh<sub>3</sub> (2.0 equiv) were used in the reaction. Yield: 88%.

**D4-Br**: CBr<sub>4</sub> (2.0 equiv) and PPh<sub>3</sub> (2.0 equiv) were used in the reaction. Yield: 88%.

*Mitsunobu Reaction for the Synthesis of Dendron D4-OH.*

To a cold (0°C), stirred solution of **D3-OH** (493 mg, 0.2 mmol), **6** (33 mg, 0.1 mmol), PPh<sub>3</sub> (55 mg, 0.2 mmol) and dry THF (3 mL) was added diisopropyl azodiformate (DIAD) (40 μL, 0.2 mmol) dropwise via syringe. After addition, the resulting mixture

was stirred for 9 h at 0 °C. Then the reaction mixture was poured into methanol, filtrated, washed with methanol and dried under vacuum to give the crude product for the next reaction without further purification.

To a stirred slurry of LiAlH<sub>4</sub> (7.6 mg, 0.2 mmol) and dry THF (12 mL) was slowly added crude product from the last step. The resulting mixture was allowed to react at room temperature for 4 h. The reaction was quenched with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel chromatography using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 1:3 as eluent to give white solid (310 mg) in a total yield of 62%.

*General Procedure for the Synthesis of Ir(III) Dendrimers.*

To a solution of **HO-Ir(pbi)<sub>3</sub>** (1 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (3.3 equiv) in DMF or mixture solvents of DMF and toluene were added **Dn-Br** (3.3 equiv). After heated at 100 °C for 12h, the mixture was poured into water and extracted with dichloromethane. The organic layer was carefully washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by chromatography on silica gel using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 1:1~2:1 as eluent. For **21NPC-G3** and **45NPC-G4**, further purification by a GPC column using toluene as eluent was carried out.

**3NPC-G1**: Yield: 82%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.14 (d, *J* = 1.6 Hz, 6H), 7.71 (d, *J* = 8.3 Hz, 6H), 7.63 (d, *J* = 8.3 Hz, 6H), 7.50 (d, *J* = 2.60 Hz, 3H), 7.47 (dd, *J* = 8.7, 1.9 Hz, 6H), 7.41 (d, *J* = 2.3 Hz, 3H), 7.38 (d, *J* = 8.7 Hz, 6H), 7.28 (dd, *J* = 8.7, 2.5 Hz, 3H), 7.24-7.20 (m, 3H), 7.07 (d, *J* = 4.0 Hz, 6H), 6.85-6.72 (m, 12H), 6.52 (t,

$J = 7.2$  Hz, 3H), 6.36 (d,  $J = 8.2$  Hz, 3H), 5.28 (s, 6H), 1.47 (s, 54H). MALDI-TOF MS: calcd for  $C_{138}H_{126}IrN_9O_3$ : 2149.9 found: 2150.0 [ $M^+$ ]. Anal. calcd for  $C_{138}H_{126}IrN_9O_3$ : C, 77.06; H, 5.90; N, 5.86. Found: C, 77.34; H, 5.90; N, 5.89.

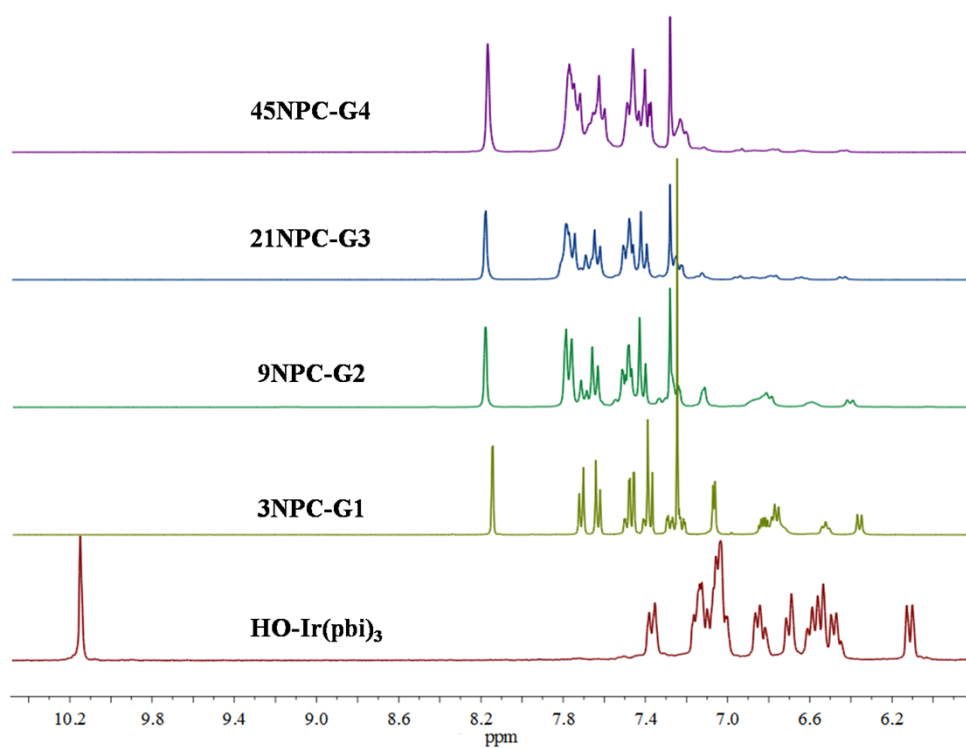
**9NPC-G2**: Yield: 63%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 8.17 (d,  $J = 1.6$  Hz, 12H), 7.79-7.61 (m, 45H), 7.54-7.39 (m, 39H), 7.33-7.30 (m, 3H), 7.27-7.24 (m, 3H), 7.12 (d,  $J = 2.8$  Hz, 6H), 6.91-6.78 (m, 12H), 6.62-6.56 (m, 3H), 6.40 (d,  $J = 8.0$  Hz, 3H), 5.35 (s, 12H), 5.32 (s, 6H), 1.50 (s, 108H). MALDI-TOF MS: calcd for  $C_{276}H_{252}IrN_{15}O_9$ : 4115.3 found: 4115.3 [ $M^+$ ]. Anal. calcd for  $C_{276}H_{252}IrN_{15}O_9$ : C, 80.42; H, 6.61; N, 4.99. Found: C, 80.18; H, 6.28; N, 4.99.

**21NPC-G3**: Yield: 70%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 8.17 (d,  $J = 1.2$  Hz, 12H), 7.79-7.62 (m, 102H), 7.54-7.38 (m, 75H), 7.33-7.30 (m, 3H), 7.26-7.22 (m, 18H), 7.12 (t,  $J = 7.6$  Hz, 6H), 6.96-6.76 (m, 12H), 6.64 (t,  $J = 7.2$  Hz, 3H), 6.44 (d,  $J = 8.0$  Hz, 3H), 5.36-5.33 (br, 42H), 1.50 (s, 216H). MALDI-TOF MS: calcd for  $C_{552}H_{504}IrN_{27}O_{21}$ : 8044.3 found: 8044.5 [ $M^+$ ]. Anal. calcd for  $C_{552}H_{504}IrN_{27}O_{21}$ : C, 82.42; H, 6.32; N, 4.70. Found: C, 82.31; H, 6.27; N, 4.61.

**45NPC-G4**: Yield: 60%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 8.17 (d,  $J = 1.2$  Hz, 48H), 7.77-7.59 (m, 225H), 7.49-7.37 (m, 147H), 7.26-7.20 (m, 42H), 7.12 (t,  $J = 7.6$  Hz, 6H), 6.96-6.75 (m, 12H), 6.64 (t,  $J = 7.2$  Hz, 3H), 6.44 (d,  $J = 8.0$  Hz, 3H), 5.37-5.24 (br, 90H), 1.48 (s, 432H). MALDI-TOF MS: calcd for  $C_{1104}H_{1008}IrN_{51}O_{45}$ : 15902.4 found: 15903.0 [ $M^+$ ]. Anal. calcd for  $C_{1104}H_{1008}IrN_{51}O_{45}$ : C, 83.38; H, 6.39; N, 4.49. Found: C, 83.23; H, 6.55; N, 4.14.

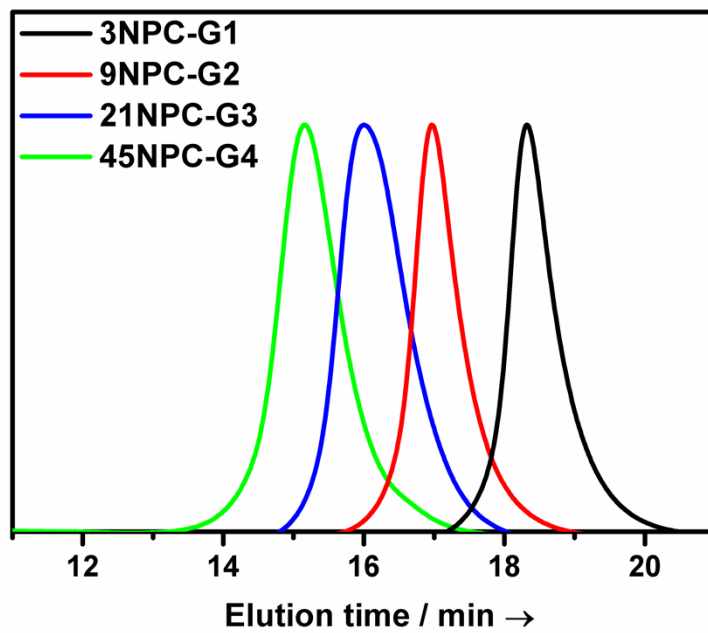
## References:

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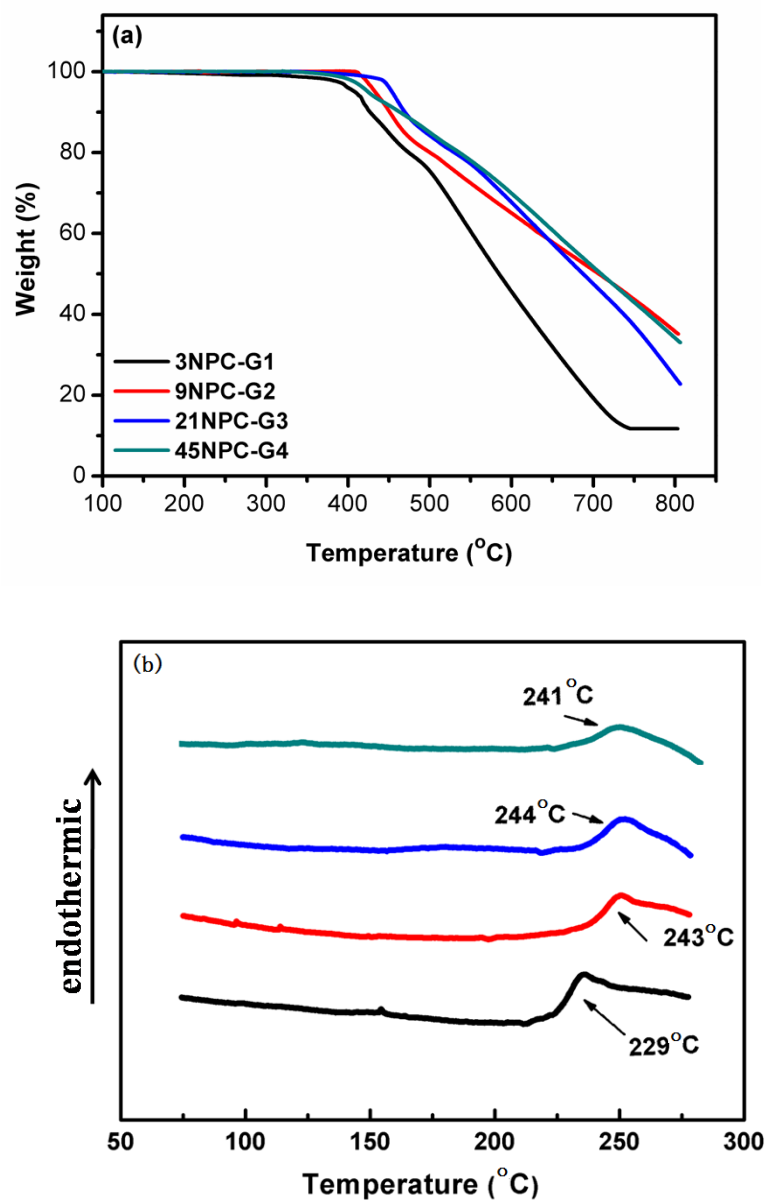


**Fig. S1** <sup>1</sup>H NMR spectra of HO-Ir(pbi)<sub>3</sub> and Ir dendrimers.

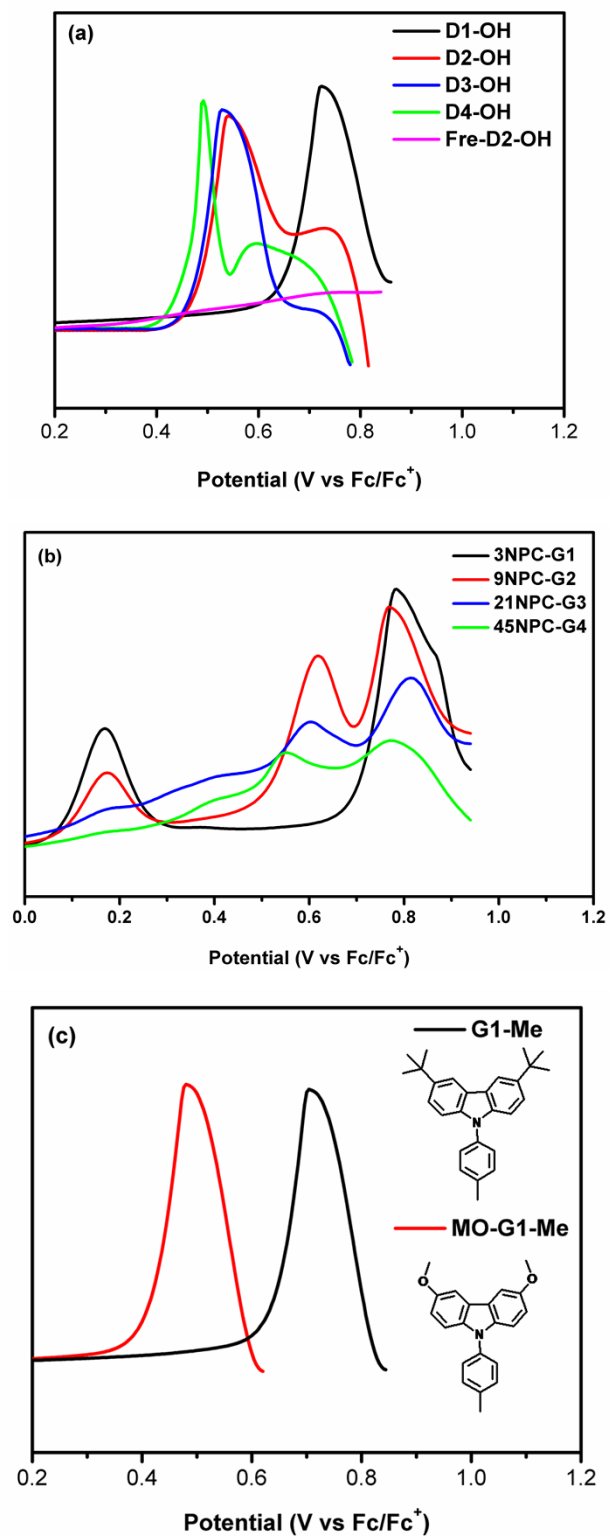




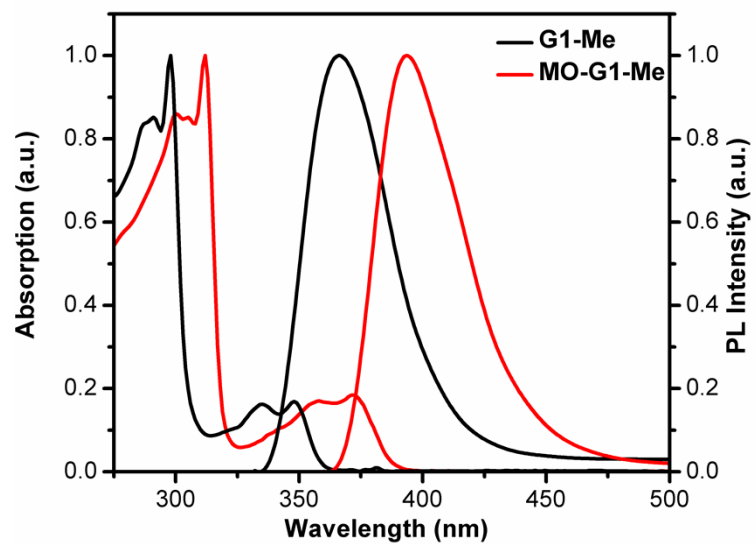
**Fig. S2** GPC analysis of Ir dendrimers.



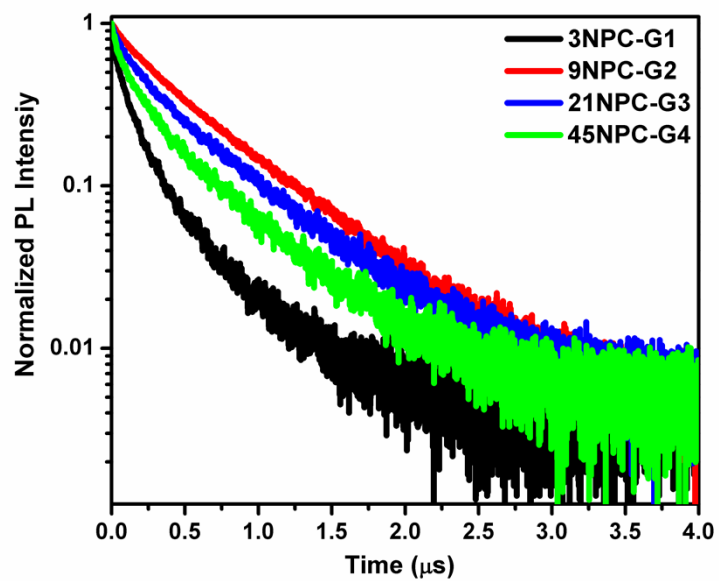
**Fig. S3** TGA (a) and DSC curves (b) for Ir dendrimers.



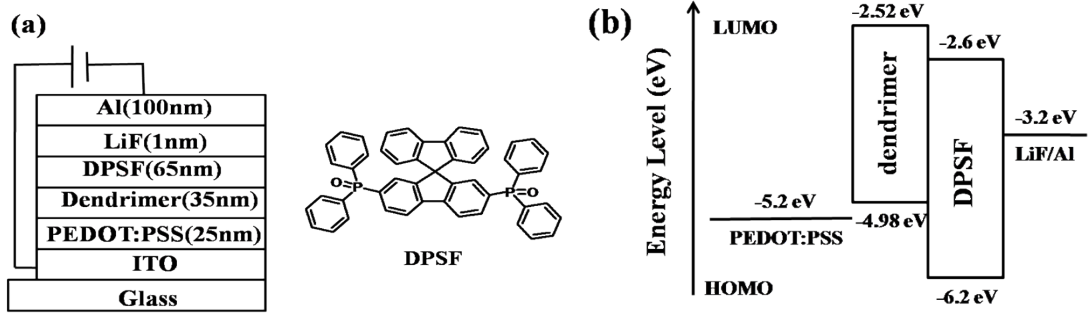
**Fig. S4** DPV curves of **D1-OH~D4-OH** compared with **Fre-D2-OH** (a), Ir dendrimers (b), and model compounds **G1-Me** and **MO-G1-Me** (c).



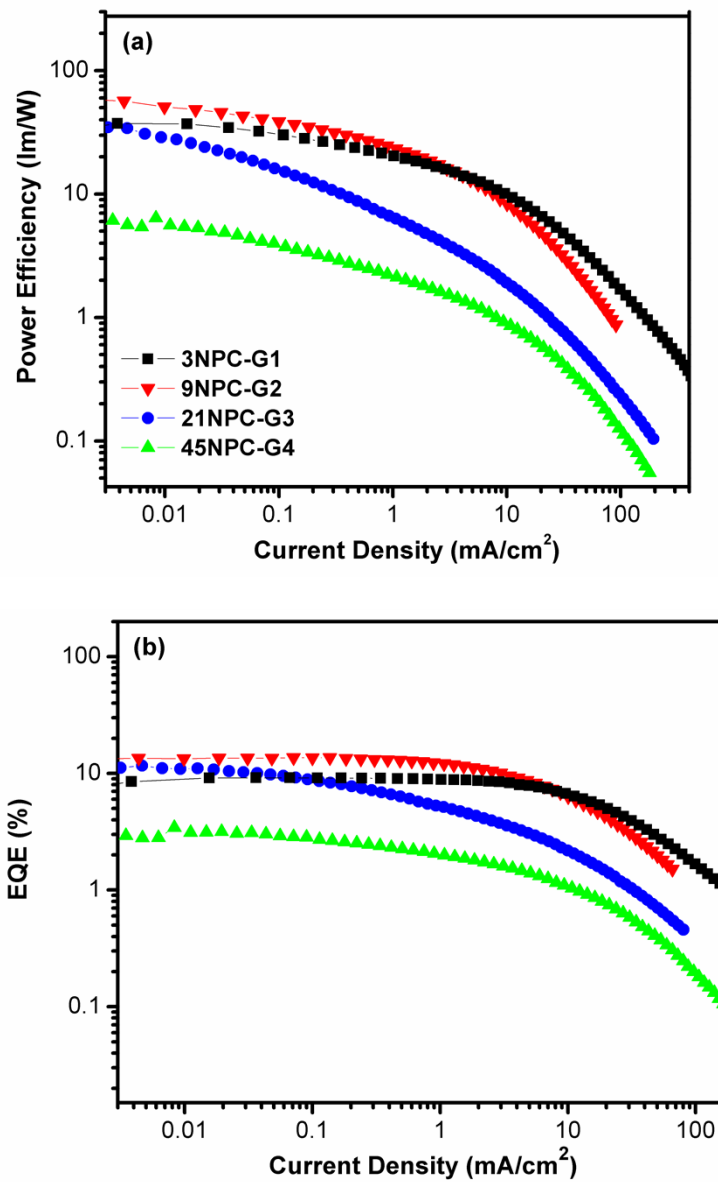
**Fig. S5** UV-vis absorption and PL spectra in solutions for model compounds **G1-Me** and **MO-G1-Me** ( $\lambda_{\text{ex}} = 298$  nm).



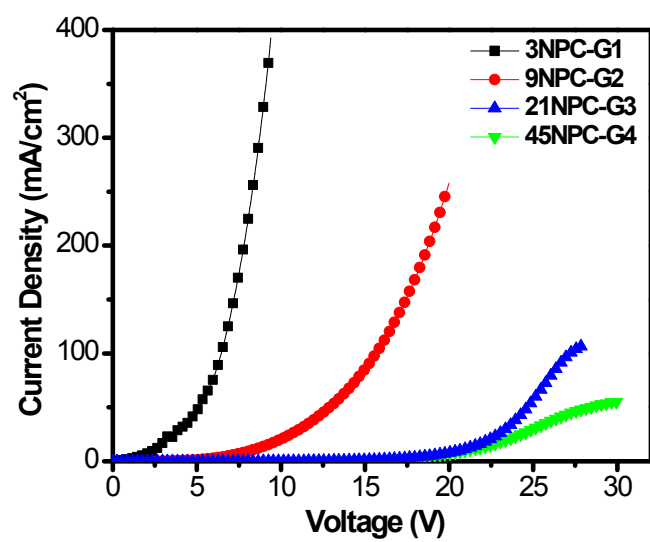
**Fig. S6** Transient PL spectra of Ir dendrimers in films measured under argon atmosphere ( $\lambda_{\text{ex}} = 355$  nm).



**Fig. S7** Schematic diagram of device configuration and molecular structures of the materials used in the device (a), and their energy levels (b).

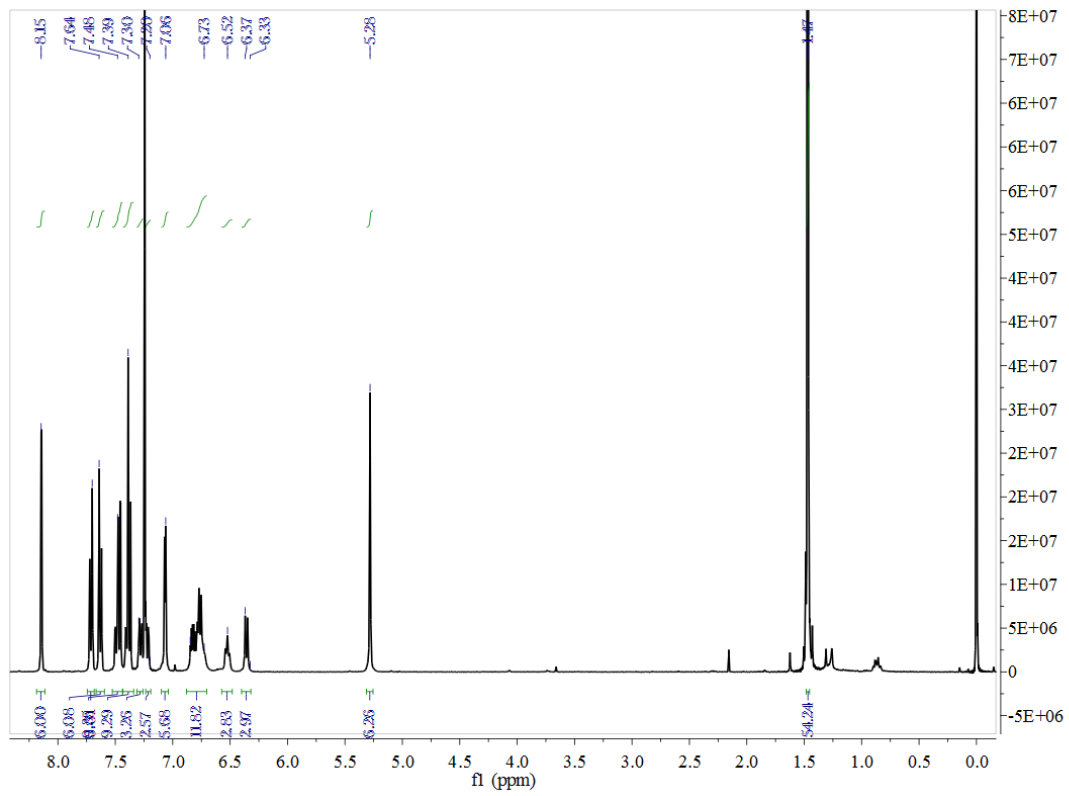


**Fig. S8** Power efficiency versus current density (a), and EQE versus current density (b) curves of Ir dendriemrs.

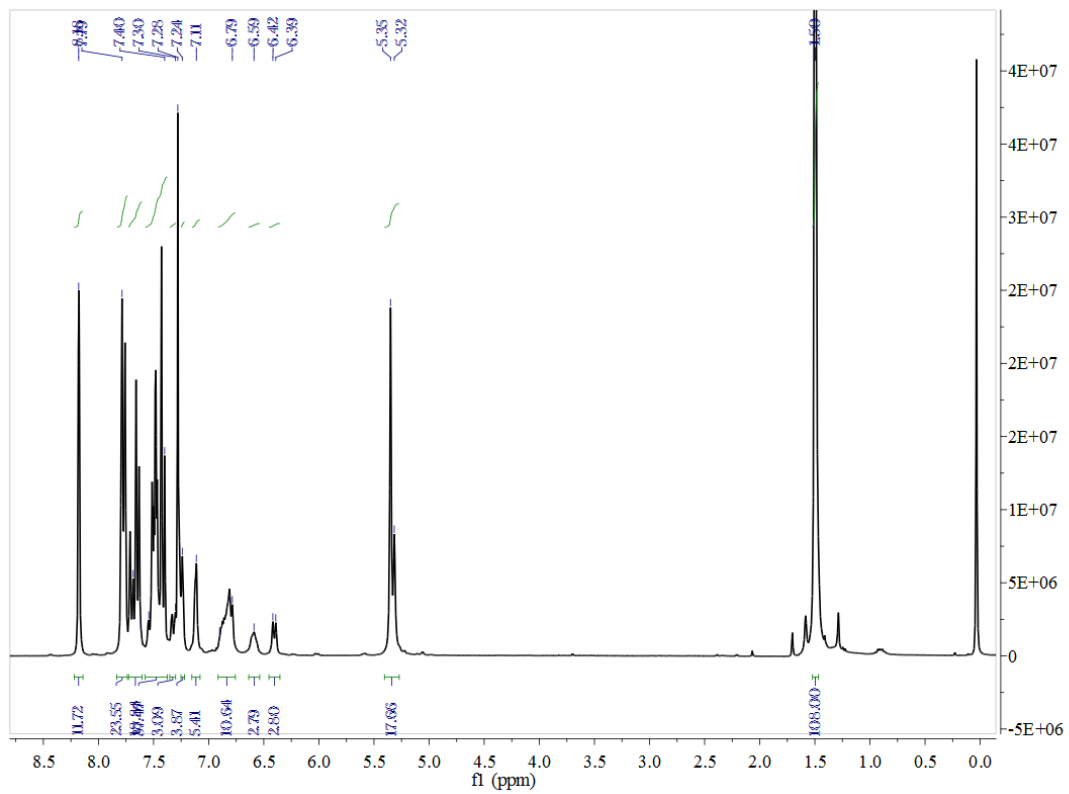


**Fig. S9** Current density — voltage characteristics of hole-only devices for Ir dendrimers.

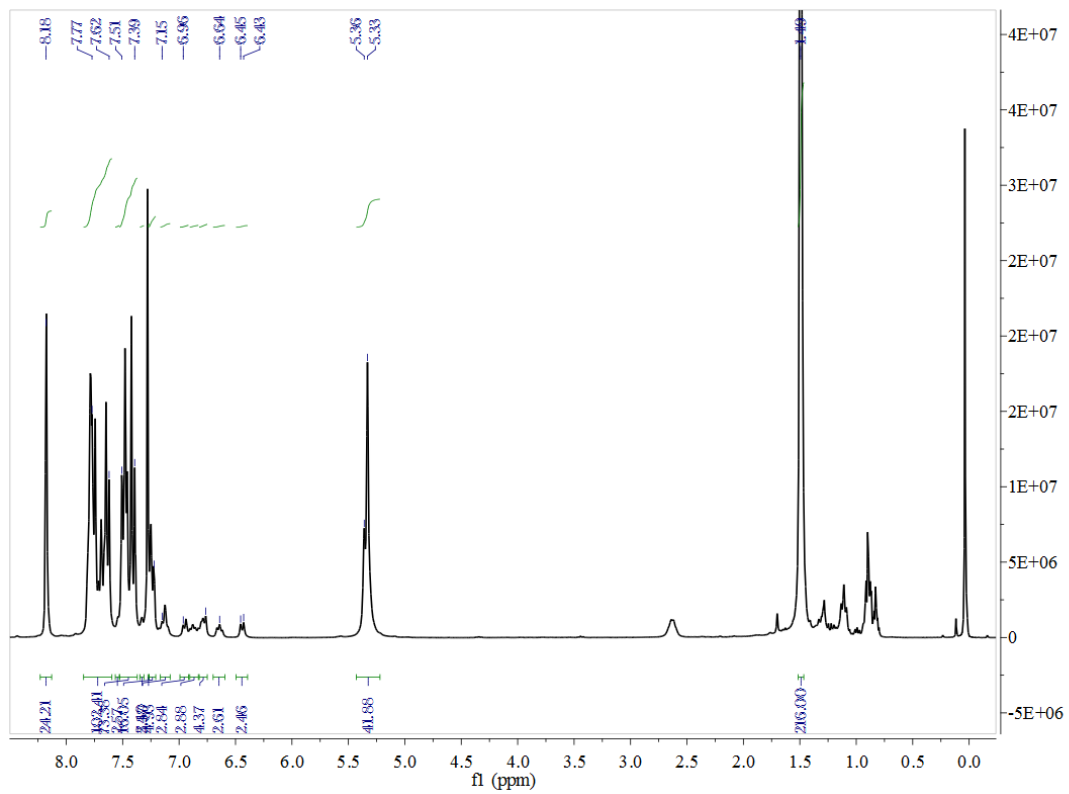




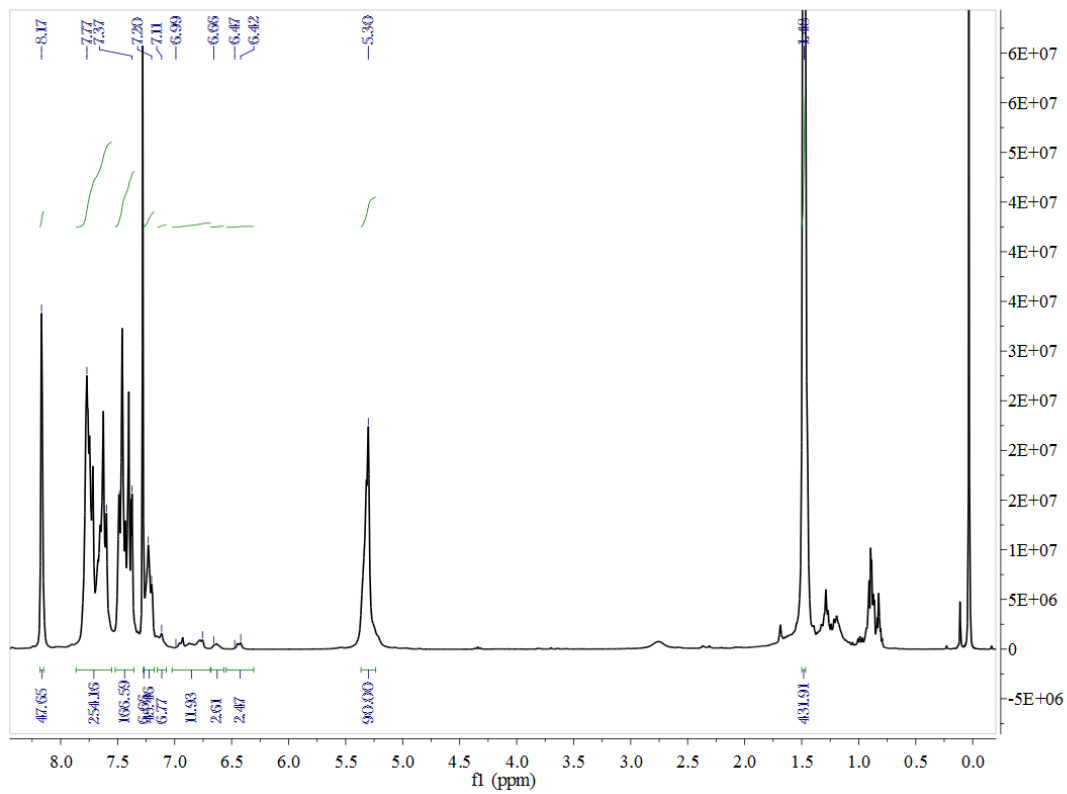
**Fig. S10**  $^1\text{H}$  NMR spectrum of 3NPC-G1.



**Fig. S11**  $^1\text{H}$  NMR spectrum of 9NPC-G2.



**Fig. S12** <sup>1</sup>H NMR spectrum of **21NPC-G3**.

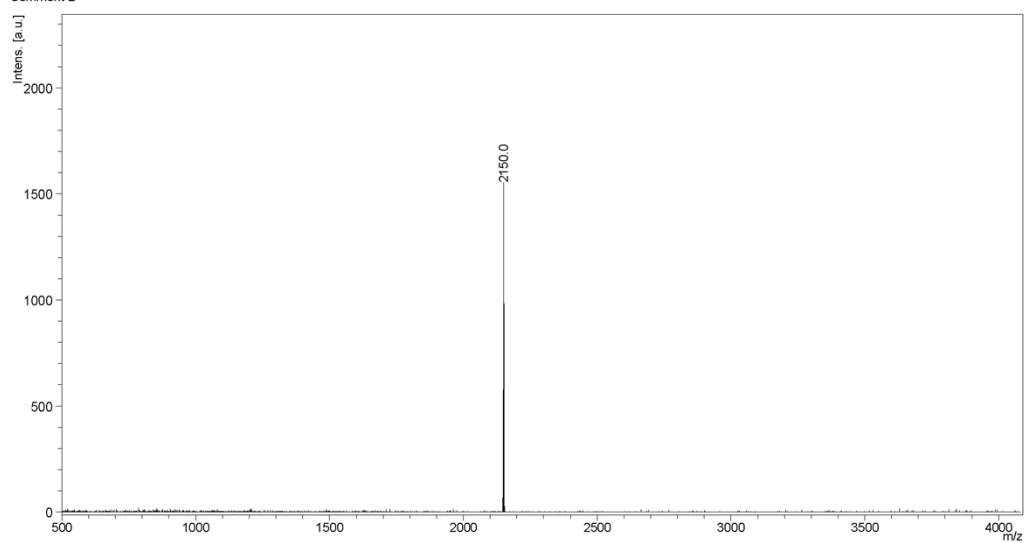


**Fig. S13** <sup>1</sup>H NMR spectrum of 45NPC-G4.

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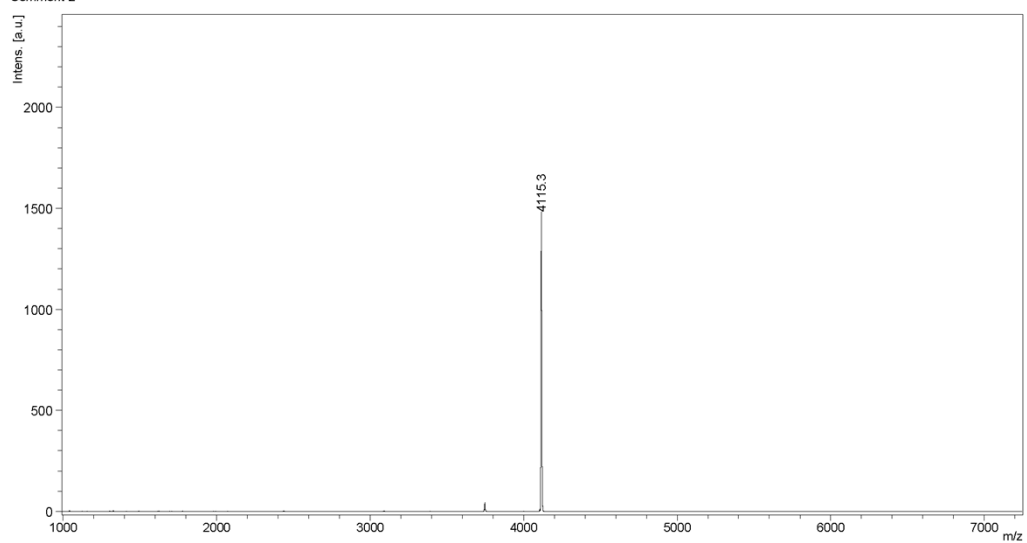
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**Fig. S14** MALDI-TOF spectrum of **3NPC-G1**.

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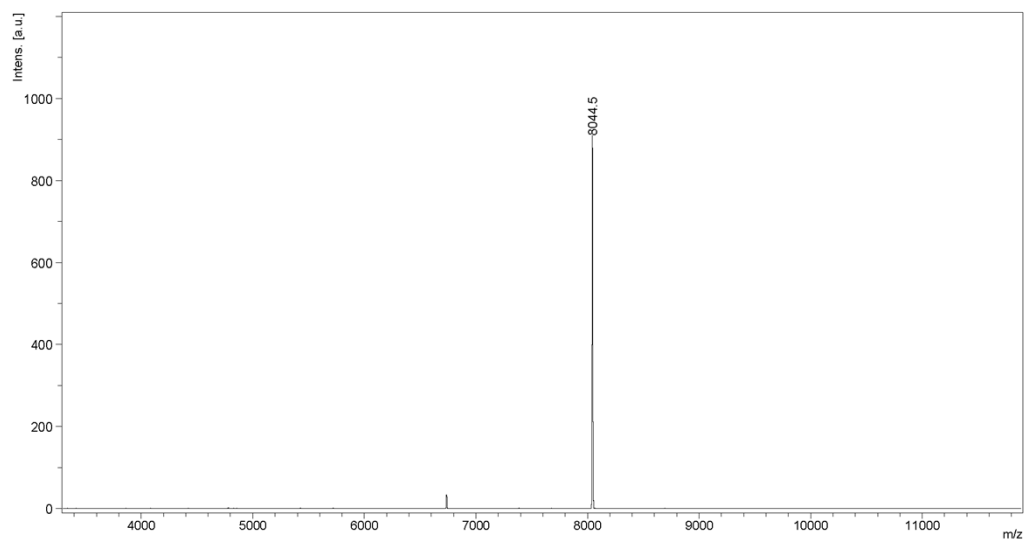
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**Fig. S15** MALDI-TOF spectrum of **9NPC-G2**.

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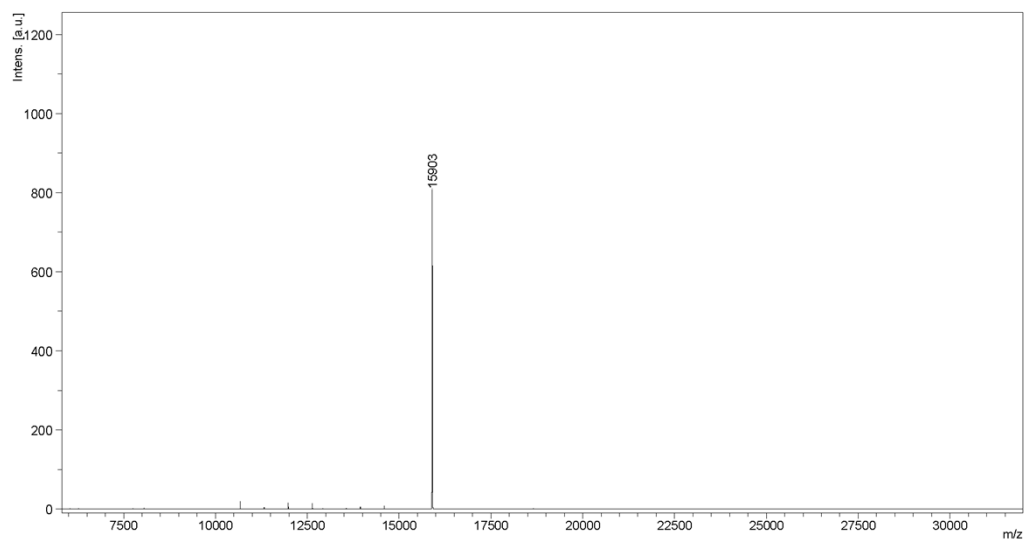
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**Fig. S16** MALDI-TOF spectrum of **21NPC-G3**.

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**Fig. S17** MALDI-TOF spectrum of **45NPC-G4**.



**Table S1.** Photophysical and electrochemical properties of model compounds **G1-Me** and **MO-G1-Me**.

	$\lambda_{\text{abs}} (\log \varepsilon)^{\text{a}}$ [nm]	$\lambda_{\text{em}}^{\text{b}}$ [nm]	$E_{1/2,\text{ox}}^{\text{c}}$ [V]
<b>G1-Me</b>	298, 347	366	0.70
<b>MO-G1-Me</b>	311, 370	394	0.48

<sup>a</sup> Measured in DCM at 298K with a concentration of  $10^{-6}$  M; <sup>b</sup> Measured in toluene at 298K with a concentration of  $10^{-5}$  M; <sup>c</sup> Measured in DCM solutions. The half-wave potential given is taken from DPV peaks.

**Table S2.** The fitting data of lifetimes for Ir dendrimers.

	$A_1$	$\tau_1$ [ $\mu\text{s}$ ]	$A_2$	$\tau_2$ [ $\mu\text{s}$ ]	R	$\tau_{\text{av}}$ [ $\mu\text{s}$ ]
<b>3NPC-G1</b>	0.90	0.04	0.10	0.26	0.999	0.14
<b>9NPC-G2</b>	0.74	0.61	0.26	0.16	0.999	0.57
<b>21NPC-G3</b>	0.58	0.56	0.42	0.11	0.999	0.50
<b>45NPC-G4</b>	0.61	0.08	0.39	0.47	0.998	0.39