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Supporting Information

Single Molecular Tuning of Charge Balance in Blue-Emitting Iridium Dendrimers for Efficient Nondoped Solution-Processed Phosphorescent OLEDs

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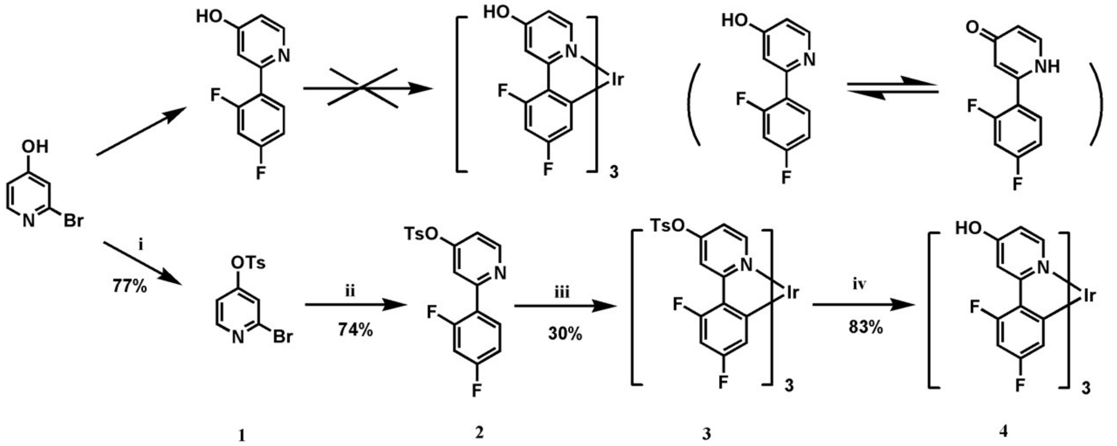
Experimental

Measurements and Characterization: ^{1}H NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded with Bruker Avance NMR spectrometer. The elemental analysis was performed using a Bio-Rad elemental analysis system. MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT) using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as the matrix. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a flow of nitrogen with Perkin-Elmer-TGA 7 and Perkin-Elmer-DSC 7 system, respectively. Atomic force microscope (AFM) measurements were performed on a Bruker Dimension ICON SPM. The nanoscope analysis software version 1.40 was used for image acquisition. The UV/Vis absorption and photoluminescence spectra were measured by a Perkin–Elmer Lambda 35 UV/Vis spectrometer and a Perkin–Elmer LS 50B spectrofluorometer, respectively. Solution spectra were recorded in CH_2Cl_2 for UV/Vis absorption and toluene for photoluminescence with a concentration of 10^{-5} M. All the above experiments and measurements were carried out at room temperature under ambient conditions. Solution PL quantum efficiency was measured in argon-saturated toluene by a relative method using *fac*-Ir(ppy)$_3$ (Φ_p = 0.40 in toluene) as the standard. 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 Quanty-Ray DCR-2 pulsed Nd:YAG laser. Moreover, the average lifetimes were calculated according to the equation: $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. Cyclic voltammetry experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The measurements were carried out in CH_2Cl_2 for anodic sweeping and in DMF for cathodic sweeping with a conventional three-electrode system consisting of a platinum working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate(*n*-Bu_4NClO_4). Ferrocene was used as a standard to calibrate the system. All potentials were calibrated against the ferrocene/ferrocenium couple. The HOMO and LUMO levels were calculated according to the equation HOMO = -e [E_{ox} + 4.8 V] and LUMO = -e [E_{red} + 4.8 V], respectively, where E_{ox} and E_{red} were the initial oxidation peak value and reduction peak value, respectively.

Device fabrication and characterization: To fabricate OLEDs, a 45-nm-thick poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) film was first deposited on the pre-cleaned ITO-glass substrates (20 Ω per square) and subsequently baked at 120 ^{o}C for 30 min. For the single-layer blue-emitting devices, Ir dendrimers from chlorobenzene solutions was spin-coated onto the PEDOT:PSS as the emissive layer (EML) and annealed at 100 ^{o}C for 30 min in argon atmosphere. The thickness of the EML was about 80 nm. Successively, a 0.5 nm-thick film of LiF, and a 100 nm-thick film of Al were thermally evaporated on top of the EML at a pressure of less than 8.0×10^{-4} Pa. The multilayer devices were fabricated by the same method, except that a 8 nm-thick film of TPCz and 42 nm-thick film of Tm3PyPB were evaporated before the deposition of LiF and Al. The active area of all the devices was 14 mm^2. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current density-voltage and brightness-voltage curves of the devices were measured using a Keithley 2400 source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions. The external quantum efficiencies were calculated from the brightness, current density and EL spectrum, assuming a Lambertian distribution.

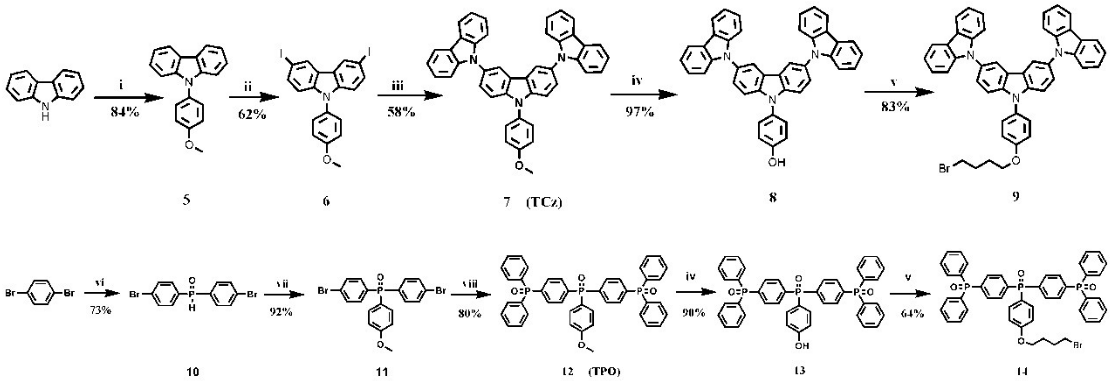
Synthesis: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures.

Scheme S1. Synthesis of the reactive Ir core containing three hydroxyl groups at the para positions relative to N atom.



Reagents and conditions: (i) 4-toluene sulfonyl chloride, Et_3N, CH_2Cl_2, room temperature; (ii) $Pd(PPh_3)_4$, $Na_2CO_3(aq)$, THF, 70 ^{o}C; (iii) iridium(III) chloride trihydrate, water, 2-methoxyethanol, reflux, and then silver trifluoromethanesulfonate, K_2CO_3, ligand, mesitylene, reflux; (iv) NaOH, CH_2Cl_2, methanol, room temperature.

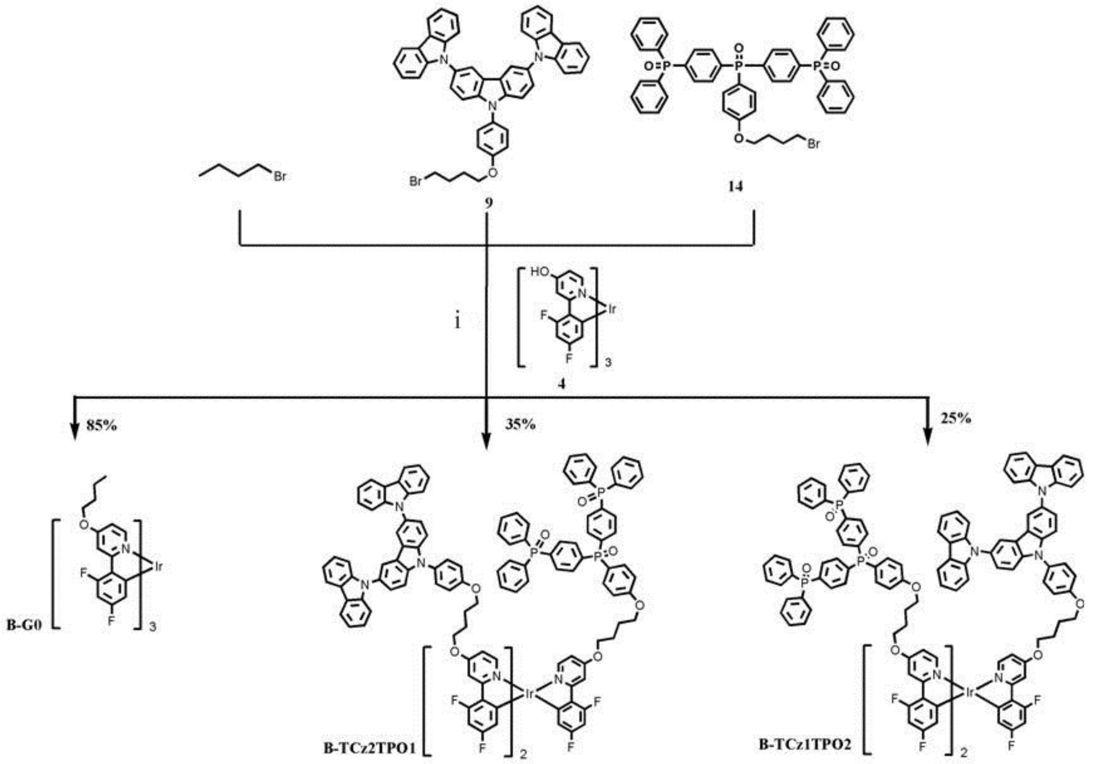
Scheme S2. Synthesis of the bromide p- and n-type dendrons.



Reagents and conditions: (i) 4-iodoanisole, CuI, *trans*-1,2-cyclohexanediamine, K_3PO_4, 1,4-dioxane, reflux; (ii) KI, KIO_3, CH_3COOH, 90 ^{o}C; (iii) carbozole, CuI, *trans*-1,2-cyclohexanediamine, K_3PO_4, 1,4-dioxane, reflux; (iv) BBr_3, $CHCl_3$, 0 ^{o}C; (v) 1,4-dibromobutane, K_2CO_3, DMF, 70 ^{o}C; (vi) Mg, THF, reflux, then $HPO(OEt)_2$, 25

^{o}C; (vii) 4-iodoanisole, Pd(OAc)$_2$, 1,4-bis(diphenylphosphino)butane (dppb), (*i*-Pr)$_2$NEt, DMSO, 90 ^{o}C; (viii) diphenylphosphine oxide, Pd(OAc)$_2$, dppb, (*i*-Pr)$_2$NEt, DMSO, 90 ^{o}C.

Scheme S3. Synthesis of the dendrimers **B-TCz2TPO1** and **B-TCz1TPO2** together with the model complex **B-G0**.



Reagents and conditions: (i) Cs$_2$CO$_3$, DMF, 80 ^{o}C.

Synthetic procedures

2-bromopyridin-4-yl 4-methylbenzenesulfonate (1): The mixture of 2-bromopyridin-4-ol (10 g, 57.4 mmol), 4-methylbenzene-1-sulfonyl chloride (16 g, 86.1 mmol), Et$_3$N (8 mL) and CH$_2$Cl$_2$ (200 mL) was stirred at room temperature for 2 h. Then the solvent was completely removed, and the residue was purified by column chromatography on silica gel using petroleum ether: CH$_2$Cl$_2$ = 5:1 as eluent to give the product (13 g) in 77% yield. ^{1}H NMR (400 MHz, CDCl$_3$) [ppm]: δ□8.33 (d, *J* = 5.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.02 (dd, *J* = 5.6, 2.1 Hz, 1H), 2.48 (s, 3H).

2-(2,4-difluorophenyl)pyridin-4-yl 4-methylbenzenesulfonate (2): A mixture of 2,4-difluorophenylboronic acid (473 mg, 1.5 mmol), **1** (314 mg, 1.0 mmol) and Pd(PPh$_3$)$_4$ (34.6 mg, 0.03 mmol), aqueous solution of Na_2CO_3 (2M, 1.5 mL), THF (2.5 mL) was heated at 70 ^oC under argon for 12 h. Then the reaction was quenched with water and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and then the solvent was completely removed. The crude product was purified by silica gel column chromatography with petroleum ether: CH_2Cl_2 = 2:1 as the eluent to afford product (260 mg) in a yield of 74%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.65 (d, *J* = 5.6 Hz, 1H), 8.02 (dt, *J* = 8.9, 8.9, 6.9 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 1.7, 1.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 5.6, 2.2 Hz, 1H), 7.00 (ddt, *J* = 8.8, 8.8, 2.5, 1.0 Hz, 1H), 6.89 (ddd, *J* = 11.3, 8.7, 2.5 Hz, 1H), 2.47 (s, 3H).

iridium complex (3): A mixture of **2** (11.53 g, 33.2 mmol), $IrCl_3 \cdot 3H_2O$ (5.6 g, 15.8 mmol), 2-ethoxyethanol (360 mL) and water (120 mL) was refluxed under argon for 24 h. Then the mixture was poured into water, filtered and dried in vacuum, the crude product was directly used for next step without further purification. Then, the mixture of the above-obtained chloride-bridged dimer, K_2CO_3 (5.2 g, 37.9 mmol), $AgSO_3CF_3$ (4.0 g, 18.9 mmol) and **2** (6.6 g, 18.9 mmol) was added with mesitylene (340 mL) under argon atmosphere. The mixture was stirred under reflux for 24 h. After that the mixture was filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether: CH_2Cl_2 = 1:1 as the eluent to give product (5.6 g) in a total yield of 30%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 7.81 (d, *J* = 3.2 Hz, 3H), 7.79 (d, *J* = 8.4 Hz, 6H), 7.37 (d, *J* = 8.2 Hz, 6H), 7.33 (d, *J* = 6.3 Hz, 3H), 6.86 (dd, *J* = 6.2, 2.4 Hz, 3H), 6.39 (m, 3H), 6.11 (dd, *J* = 9.0, 2.3 Hz, 3H), 2.47 (s, 9H).

iridium complex (4): A mixture of **3** (5.6 g, 4.4 mmol), NaOH (1.0 g, 26 mmol), methanol (10 mL) and CH_2Cl_2 (100 mL) was stirred at room temperature for 6 h. Then 1M HCl aqueous was added until PH = 7. The mixture was filtered, washed with saturated brine and dried in vacuum. The pure product (3.1 g) was obtained by column chromatography using CH_2Cl_2: ethyl acetate = 5:1 as the eluent in a yield of 83%. ^{1}H NMR (400 MHz, d_6-DMSO) [ppm]: δ 11.24 (s, 3H), 7.65 (t, J = 2.4, 2.4 Hz, 3H), 7.24 (d, J = 6.3 Hz, 3H), 6.70 (dd, J = 6.3, 2.4 Hz, 3H), 6.67-6.58 (m, 3H), 6.06 (dd, J = 9.1, 2.3 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, δ (vs. fluorobenzene)): 4.19 (d, J = 10.0 Hz, 3F), 2.17 (d, J = 9.9 Hz, 3F). MALDI-TOF MS: calcd for $C_{33}H_{18}F_6IrN_3O_3$: 811.1 Found: 811.1 [M^+]. Anal. calcd for $C_{33}H_{18}F_6IrN_3O_3$: C 48.89, H 2.24, N 5.18 Found: C 48.96, H 2.30, N 5.14.

9-(4-methoxyphenyl)-9H-carbazole (5): Carbazole (16.7 g, 0.1 mol), 4-iodoanisole (28 g, 0.12 mol), CuI (1.9 g, 0.01 mol), K_3PO_4 (50 g, 0.24 mol), *trans*-1,2-cyclohexanediamine (0.8 mL, 5 mmol) were added to 250 mL degassed 1,4-dioxane under argon atmosphere. The reaction mixture was heated to reflux for 24 h. Then the mixture was filtered, the filtrate was washed by dilute ammonia water, diluted hydrochloric acid, saturated brine successively and dried over Na_2SO_4. The pure product (22.8 g) was obtained by recrystallization from ethyl acetate in a yield of 84%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.14 (d, J = 7.7 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.42-7.37 (m, 2H), 7.33-7.24 (m, 4H), 7.11 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H).

3,6-diiodo-9-(4-methoxyphenyl)-9H-carbazole (6): Compound **5** (13.6 g, 50 mmol) was dissolved in acetic acid (150 mL) at 90 °C. Then KI (12.4 g, 75 mmol) and KIO_3 (8.0 g, 37.5 mmol) were added, and the system was maintained at 80 °C for 8 h. After that, the mixture was poured into water and filtered. The filter cake was recrystallized from ethanol to give 16 g (62 %) of a nude solid. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.38 (br, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H).

9-(3-(9H-carbazol-9-yl)-9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazole (7, TCz): Carbazole (1.83 g, 11 mmol), compound **6** (2.6 g, 5 mmol), CuI (190 mg, 1 mmol), K_3PO_4 (5.21 g, 25 mmol), *trans*-1,2-cyclohexanediamine (80 μL, 0.5 mmol) were added to 30 mL degassed 1,4-dioxane under argon atmosphere. The reaction mixture was heated to reflux for 24 h. Then the mixture was filtered, the filtrate was washed by dilute ammonia water, diluted hydrochloric acid, saturated brine successively and dried over Na_2SO_4. The pure product (1.75 g) was obtained by column chromatography using petroleum ether: THF = 2:1 as eluent in a yield of 58%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.30 (br, 2H), 8.19 (d, *J* = 7.7 Hz, 4H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.62-7.58 (m, 4H), 7.43-7.40 (m, 8H), 7.33-7.29 (m, 4H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 3H).

4-(3,6-di(9H-carbazol-9-yl)-9H-carbazol-9-yl)phenol (8): A solution of **7** (1.69 g, 2.8 mmol) in dry $CHCl_3$ (18 mL) was cooled to 0 °C, and BBr_3 (0.56 mL 1 M solution in $CHCl_3$, 5.6 mmol) was added dropwise. After stirring for 15 min at this temperature, 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 $NaHCO_3$, filtering, washing with water completely and drying in vacuum. The pure product (1.6 g) was obtained in a yield of 97%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.29 (br, 2H), 8.19 (d, *J* = 7.7 Hz, 4H), 7.64-7.58 (m, 6H), 7.44-7.41 (m, 8H), 7.33-7.29 (m, 4H), 7.17 (d, *J* = 8.6 Hz, 2H).

9-(9-(4-(4-bromobutoxy)phenyl)-3-(9H-carbazol-9-yl)-9H-carbazol-6-yl)-9H-carbazole (9): A mixture of **8** (1.47 g, 2.5 mmol), 1,4-dibromobutane (1.21 ml, 10 mmol), K_2CO_3 (1.73 g, 12.5 mmol) was added to DMF (25 mL) and heated at 70 °C for 6 h. After that, the mixture was poured into water, extracted with CH_2Cl_2 and dried over Na_2SO_4. The pure product (1.5 g) was obtained by column chromatography using petroleum ether: CH_2Cl_2 = 3:1 as eluent in a yield of 83%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.27 (br, 2H), 8.16 (d, *J* = 7.7 Hz, 4H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.59-7.55 (m, 4H), 7.42-7.37 (m, 8H), 7.30-7.27 (m, 4H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.16 (t, *J* = 5.8 Hz, 2H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.20-2.13 (m, 2H), 2.09-2.03 (m, 2H).

Compound 10: The mixture of 1,4-dibromobenzene (10.9 g, 46.5 mmol) and magnesium (1.1 g, 55.9 mmol) was heated to 60 °C in THF (75 mL) for 2 h to form Grignard reagent and then cooled to room temperature. Diethylphosphite (1.8 mL, 14.1 mmol) was added dropwise to the mixture and stirred at room temperature for 2 h. After that NH_4Cl aqueous was added slowly. The mixture was extracted with ethyl acetate and the organic phase was washed with $NaHCO_3$ aqueous and brine, then it was dried over Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:2 as eluent to give the product (3.6 g) in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.04 (d, *J* = 486.9 Hz, 1H), 7.67 (dd, *J* = 8.4, 2.2 Hz, 4H), 7.55 (dd, *J* = 13.2, 8.4 Hz, 4H). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 19.07.

Compound 11: **10** (1.8 g，5 mmol), *p*-iodoanisole (1.8 g，7.5 mmol), *N*-methylmorpholine (0.9 mL，8 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.2 g，1 mmol) was added consecutively to 15 mL toluene under argon. The mixture was refluxed for 8 h. After cooling to room temperature, the obtained suspension was washed with 1 M HCl and brine and dried with Na_2SO_4. The pure product (2.1 g) was obtained by column chromatography using petroleum ether: ethyl acetate = 2:1 as eluent in a yield of 92%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 7.61 (dd, *J* = 8.4, 2.2 Hz, 4H), 7.57-7.47 (m, 6H), 6.98 (dd, *J* = 8.8, 2.2 Hz, 2H), 3.86 (s, 3H). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 27.90.

Compound 12 (TPO): **11** (210 mg，0.4 mmol),diphenylphosphine oxide (273 mg，1.4 mmol), N,N-diisopropylethylamine (465 mg，3.6 mmol), $Pd(OAc)_2$ (20.2 mg，90 μmol) and 1,4-bis(diphenylphosphino)butane (dppb) (38.4 mg，90 μmol) was added consecutively to 10 mL DMSO under argon. The mixture was heated for 12 h. After cooling to room temperature, the mixture was poured into water, extracted with CH_2Cl_2, washed with water completely and dried with Na_2SO_4. The pure product (260 mg) was obtained by column chromatography using CH_2Cl_2: methanol = 50:1 as eluent in a yield of 80%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 7.77-7.72 (m, 7H), 7.68-7.63 (m, 8H), 7.59-7.53 (m, 6H), 7.50-7.45 (m, 9H), 6.98 (dd, *J* = 8.8, 2.2 Hz, 2H), 3.85 (s, 3H). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 28.47 (d, *J* = 14.2 Hz, 2P), 27.84 (d, *J* = 7.2 Hz, 1P). MALDI-TOF MS: calcd for $C_{43}H_{35}O_4P_3$: 708.2; Found: 709.2 $[M+H]^+$.

Compound 13: A solution of **12** (113 mg，0.2 mmol) in dry CH_2Cl_2 (2 mL) was cooled to 0 °C, and BBr_3 (32 μL 1 M solution in CH_2Cl_2, 0.3 mmol) was added dropwise. After stirring for 2 h 0 °C, the reaction was carefully quenched with methanol, followed by adding a saturated solution of $NaHCO_3$. Then the mixture was extracted with CH_2Cl_2, washed with water and dried with Na_2SO_4. The product (100 mg) was obtained after removing all solvent and drying in vacuum in a yield of 90%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 7.73 (dd, *J* = 8.8, 5.5 Hz, 8H), 7.65 (ddd, *J* = 11.5, 7.0, 4.3 Hz, 8H), 7.57 (t, *J* = 7.2 Hz, 4H), 7.52-7.45 (m, 8H), 7.36 (dd, *J* = 11.8, 8.5 Hz, 2H), 6.98 (dd, *J* = 8.5, 2.1 Hz, 2H). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 29.48 (br, 2P), 28.89 (br, 1P).

Compound 14: A mixture of **13** (5 g，7.2 mmol), 1,4-dibromobutane (4.4 mL，36 mmol), K_2CO_3 (3.9 g，28.8 mmol) was added to DMF (50 mL) and heated at 70 °C for 10 h. After cooling to room temperature, the mixture was poured into water, extracted with CH_2Cl_2 and dried with Na_2SO_4. The pure product (3.8 g) was obtained by column chromatography using CH_2Cl_2: methanol = 50:1 as eluent in a yield of 64%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 7.78-7.70 (m, 8H), 7.68-7.63 (m, 8H), 7.59-7.52 (m, 6H), 7.50-7.45 (m, 8H), 6.96 (dd, *J* = 8.8, 2.2 Hz, 2H), 4.04 (t, *J* = 5.9 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 2.09-2.02 (m, 2H), 1.99-1.92 (m, 2H). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 28.56 (br, 2P), 27.87 (br, 1P).

B-TCz2TPO1: A mixture of **9** (86.9 mg，120 μmol), **4** (49 mg，60 μmol), Cs_2CO_3 (64.5 mg，198 μmol) was added to DMF (4 mL) and heated at 80 °C for 9 h. Then **14** (59.7 mg，72 μmol) was added to the mixture and reacted for another 12h. After cooling to room temperature, the mixture was poured into water, filtered and dried in vaccum. The pure product (59 mg) was obtained by column chromatography using petroleum ether: CH_2Cl_2 = 50:1 as eluent in a yield of 35%. ^1H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.26 (d, *J* = 1.4 Hz, 4H), 8.15 (d, *J* = 7.7 Hz, 8H), 7.83-7.81 (m, 2H), 7.77-7.70 (m, 9H), 7.67-7.62 (m, 8H), 7.60-7.53 (m, 17H), 7.51-7.44 (m, 9H), 7.41-7.36 (m, 16H), 7.33-7.24 (m, 11H), 7.17 (dd, *J* = 8.84, 4.4 Hz, 4H), 6.93 (dd, *J* = 8.7, 1.9 Hz, 2H), 6.49 (dt, *J* = 6.1, 2.5 Hz, 2H), 6.42 (dd, *J* = 6.4, 2.4 Hz, 1H), 6.38-6.31 (m, 3H), 6.27-6.22 (m, 3H), 4.19-4.16 (m, 8H), 4.07-4.01 (m, 4H), 2.07 (br, 8H), 1.95 (br, 4H). ^{19}F NMR (376 MHz, $CDCl_3$, δ (vs. fluorobenzene)): 4.13-4.10 (m, 3F), 2.07-2.01 (m, 3F). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 28.64 (br, 2P), 27.90 (br, 1P). MALDI-TOF MS: calcd for $C_{171}H_{123}F_6IrN_9O_9P_3$: 2846.9; Found: 2846.8 [M^+]. Anal. calcd for $C_{171}H_{123}F_6IrN_9O_9P_3$: C 72.14, H 4.35, N 4.43; Found: C 72.18, H 4.50, N 4.35. Purity (determined by HPLC): 99.3%.

B-TCz1TPO2: A mixture of **14** (614 mg，0.7 mmol), **4** (300 mg，370 μmol), Cs_2CO_3 (398 mg，1.2 mmol) was added to DMF (15 mL) and heated at 80 °C for 9 h. Then **9** (321 mg，0.4 mmol) was added to the mixture and reacted for another 12h. After cooling to room temperature, the mixture was poured into water, filtered and dried in vaccum. The pure product (210 mg) was obtained by column chromatography using petroleum ether: CH_2Cl_2 = 50:1 as eluent in a yield of 25%. ^1H NMR (400 MHz, $CDCl_3$) [ppm]: δ 8.26 (d, *J* = 1.0 Hz, 2H), 8.15 (d, *J* = 7.7 Hz, 4H), 7.82 (br, 2H), 7.77-7.72 (m, 18H), 7.67-7.62 (m, 17H), 7.59-7.54 (m, 16H), 7.49-7.45 (m, 17H), 7.39-7.36 (m, 8H), 7.32-7.28 (m, 6H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.95-6.93 (m, 4H), 6.52 (d, *J* = 4.5 Hz, 1H), 6.45 (t, *J* = 5.4 Hz, 2H), 6.38-6.30 (m, 3H), 6.26-6.23 (m, 3H), 4.21-4.19 (m, 4H), 4.10-4.04 (m, 8H), 2.10 (br, 4H), 1.97 (br, 8H). ^{19}F NMR (376 MHz, $CDCl_3$, δ (vs. fluorobenzene)): 4.08-4.05 (m, 3F), 2.03-1.99 (m, 3F). ^{31}P NMR (161 MHz, $CDCl_3$, δ): 28.52 (br, 2P), 27.82 (br, 1P). MALDI-TOF MS: calcd for $C_{171}H_{129}F_6IrN_6O_{12}P_6$: 2950.8 Found: 2950.8 [$M^+$]. Anal. calcd for $C_{171}H_{129}F_6IrN_6O_{12}P_6$: C 69.58, H 4.40, N 2.85 Found: C 69.68, H 4.42, N 2.80. Purity (determined by HPLC): 98.9%.

B-G0: A mixture of **4** (324 mg, 0.4 mmol), Cs_2CO_3 (430 mg, 1.32 mmol) was added to DMF (15 mL) and heated at 80 ^{o}C for 2 h. Then 1-bromobutane (194 μL, 1.8 mmol) was added to the mixture and reacted for another 12 h. After cooling to room temperature, the mixture was poured into water, filtered and dried in vaccum. The pure product (332 mg) was obtained by column chromatography using petroleum ether: CH_2Cl_2 = 6:1 as eluent in a yield of 85%. ^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: δ 7.78-7.77 (m, 3H), 7.27 (d, J = 6.3 Hz, 3H), 6.48 (dd, J = 2.6, 6.4Hz, 3H), 6.38-6.32 (m, 3H), 6.25 (dd, J = 2.5, 9.2 Hz, 3H), 4.05 (t, J = 6.4Hz, 6H), 1.74-1.84 (m, 6H), 1.43-1.55 (m, 6H), 1.43-1.55 (m, 6H), 0.98 (t, J = 7.3 Hz, 9H). ^{19}F NMR (376 MHz, $CDCl_3$, δ (vs. fluorobenzene)): 3.29 (d, J = 9.9 Hz, 3F), 1.53 (d, J = 9.3 Hz, 3F). MALDI-TOF MS: calcd for $C_{45}H_{42}F_6IrN_3O_3$: 979.3 Found: 979.3 [M^+]. Anal. calcd for $C_{45}H_{42}F_6IrN_3O_3$: C 55.21, H 4.32, N 4.29 Found: C 55.22, H 4.36, N 4.27.

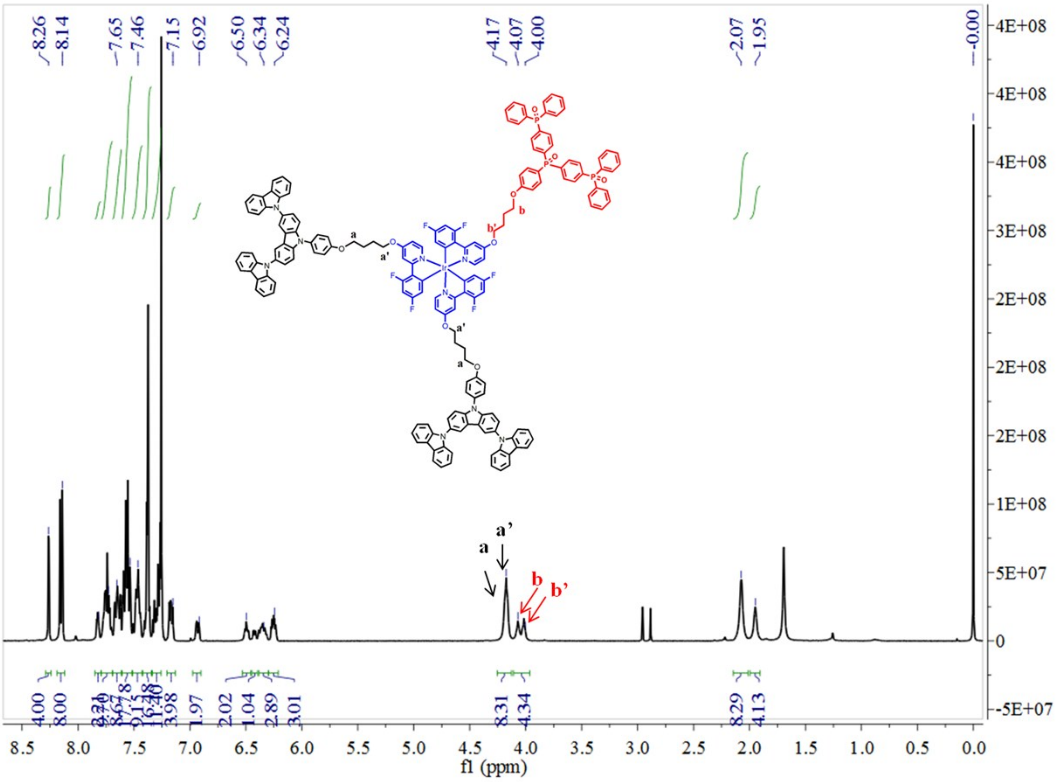


Figure S1. ^{1}H NMR spectrum of **B-TCz2TPO1**. The multiple peak at 4.17 ppm is attributed to protons of -OCH$_2$- (a and a′) from **TCz**, and the signal at 4.00-4.07 ppm is assigned to those (b and b′) from **TPO**. The ratio of the integral of protons a and a′ with that of protons b and b′ is 2:1, indicating that content ratio of **TCz** and **TPO** dendron is 2:1.

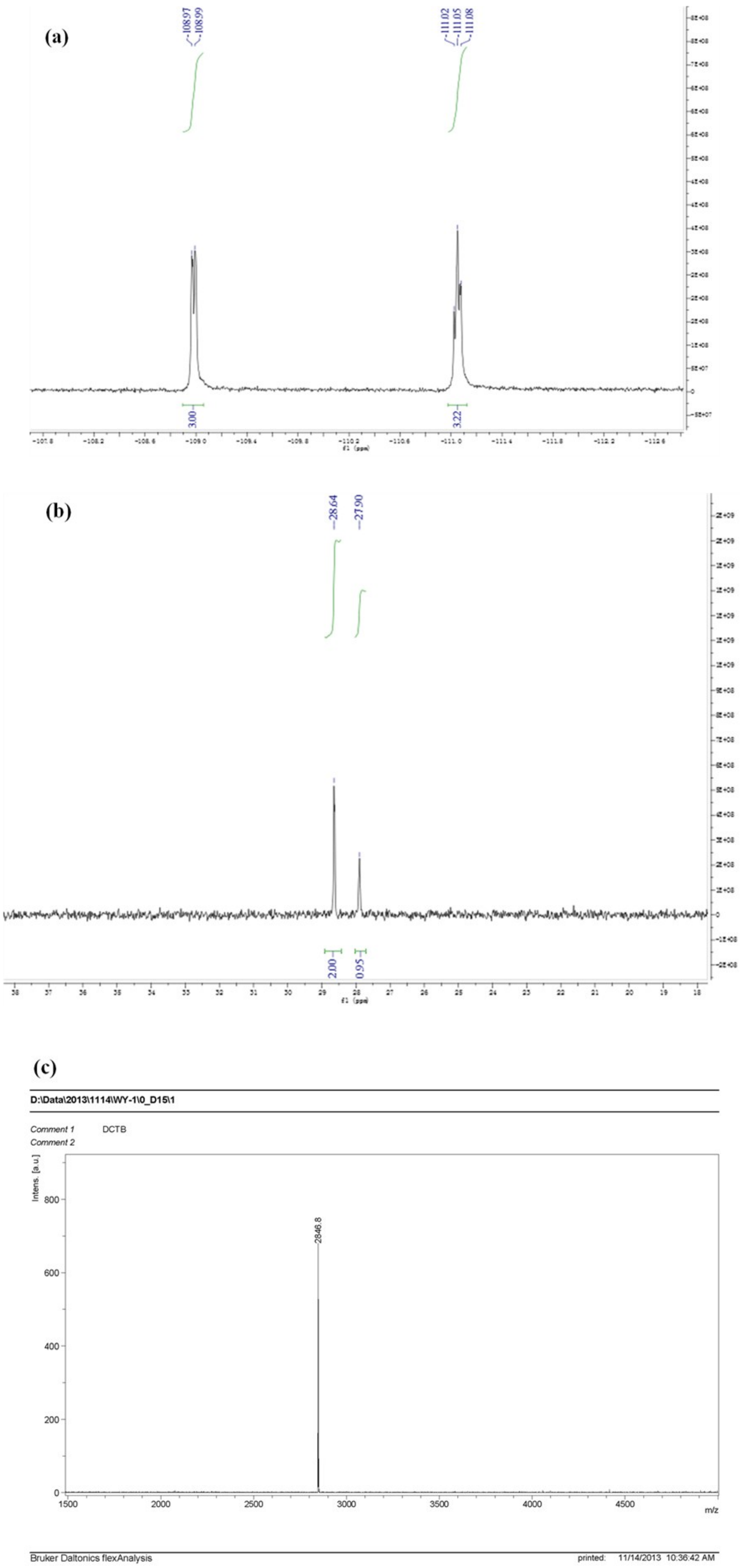


Figure S2. ^{19}F NMR (a), ^{31}P NMR (b) and MALDI-TOF spectrum (c) of the dendrimer **B-TCz2TPO1**.

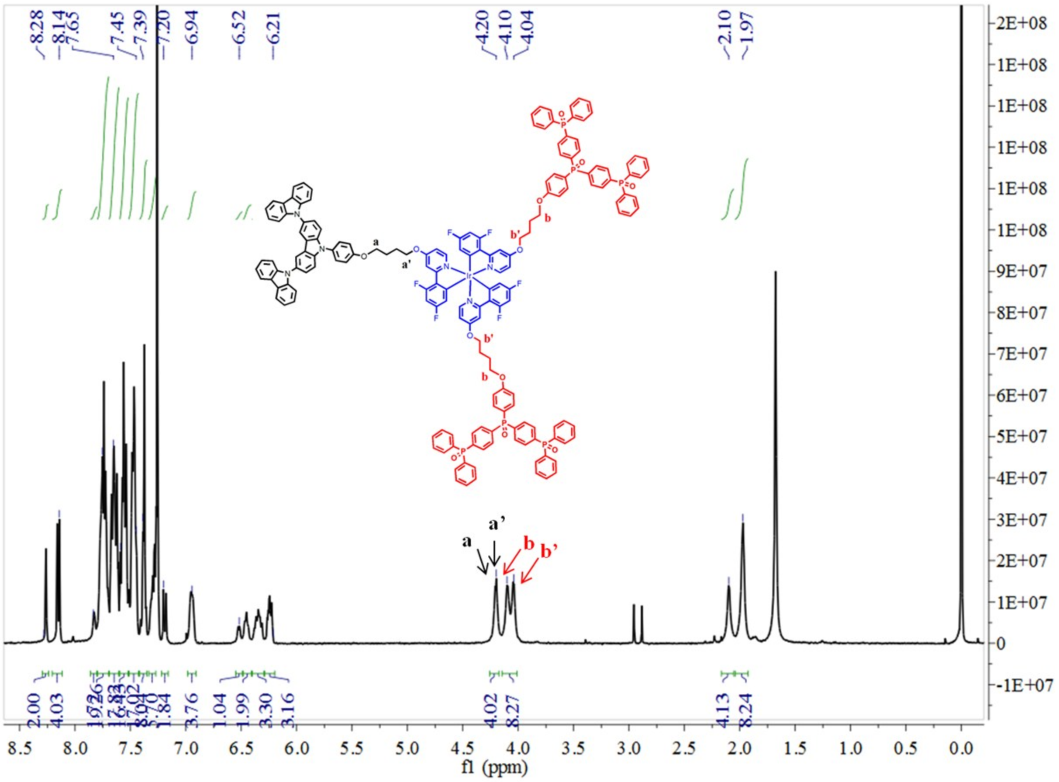


Figure S3. ^{1}H NMR spectrum of **B-TCz1TPO2**. The multiple peaks at 4.20 ppm is attributed to protons of -OCH$_2$- (a and a′) from **TCz** and the signal at 4.04-4.10 ppm is assigned to those (b and b′) from **TPO**. The ratio of the integral of protons a and a′ with that of protons b and b′ is 1:2, indicating that content ratio of **TCz** and **TPO** dendron is 1:2.

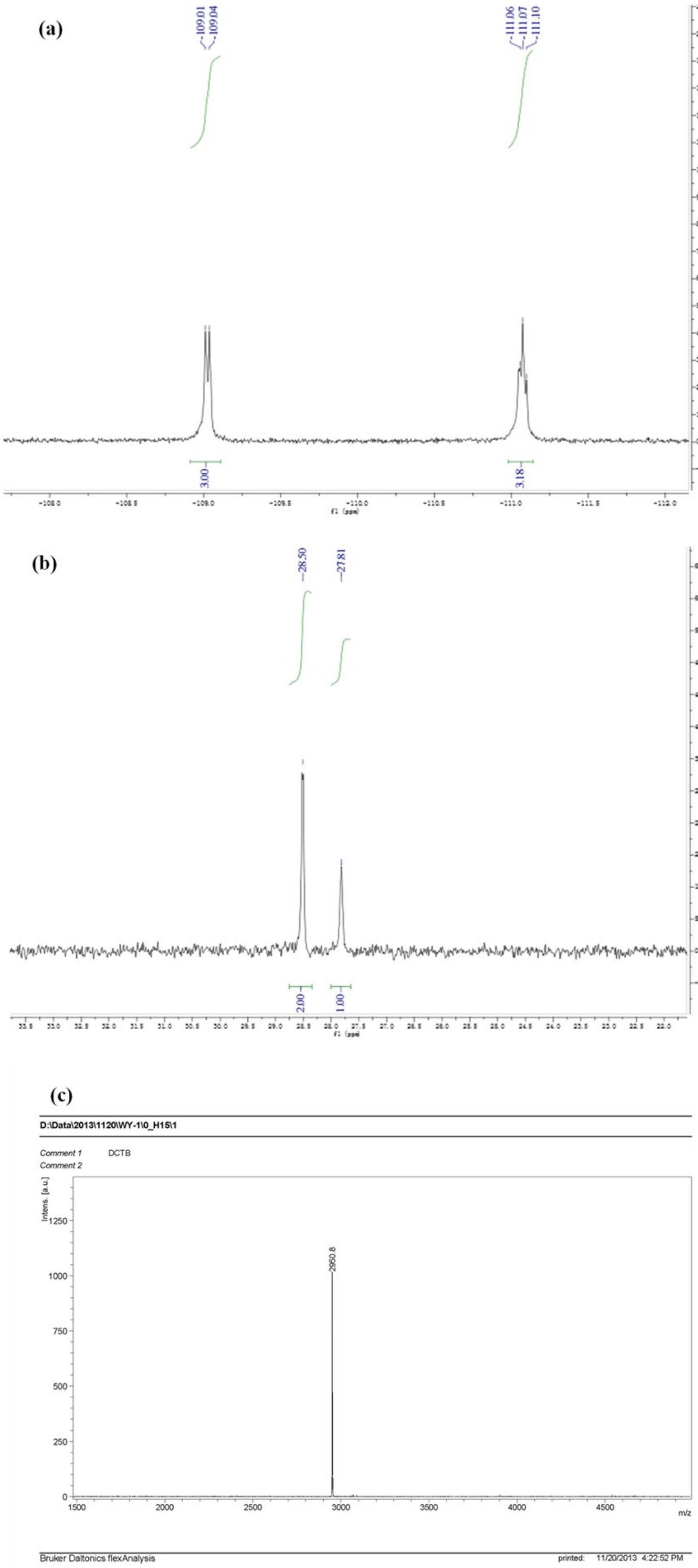


Figure S4. ^{19}F NMR (a), ^{31}P NMR (b) and MALDI-TOF spectrum (c) of the dendrimer **B-TCz1TPO2**.

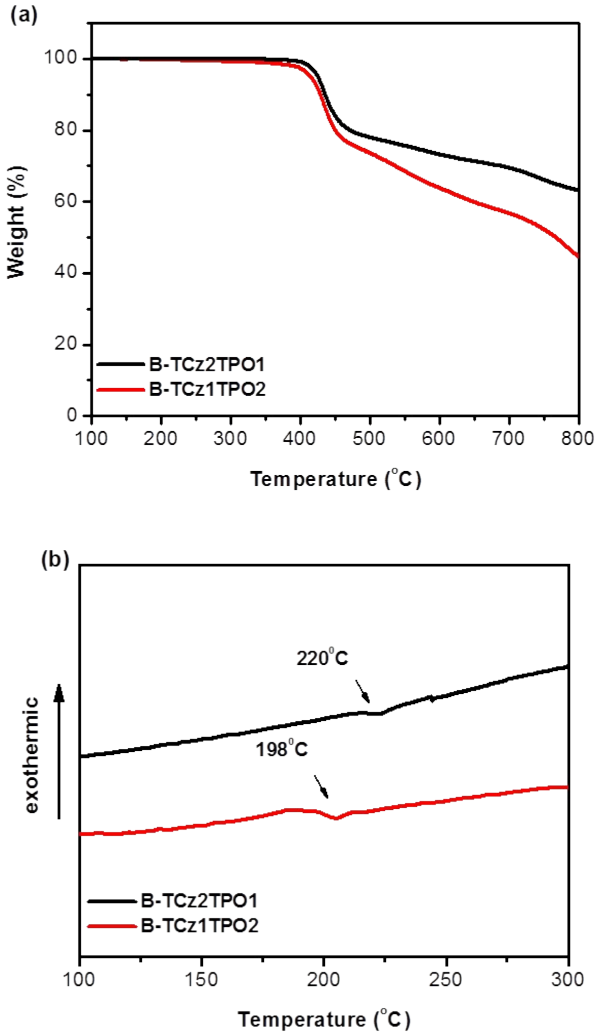


Figure S5. TGA (a) and DSC curves (b) of Ir dendrimers.

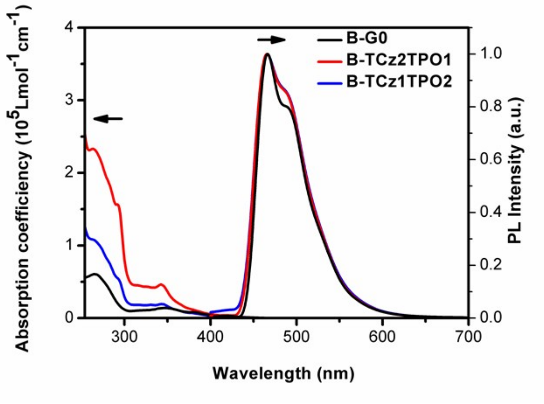


Figure S6. UV-visible absorption spectra in CH_2Cl_2 and PL spectra in toluene of the dendrimers **B-TCz2TPO1** and **B-TCz1TPO2** in comparison to the model complex **B-G0** without any dendrons.

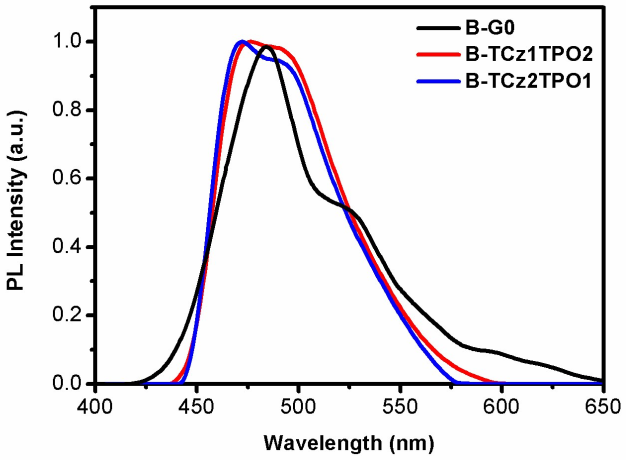


Figure S7. PL spectra of Ir dendrimers **B-TCz2TPO1** and **B-TCz1TPO2** in neat films compared with **B-G0**.

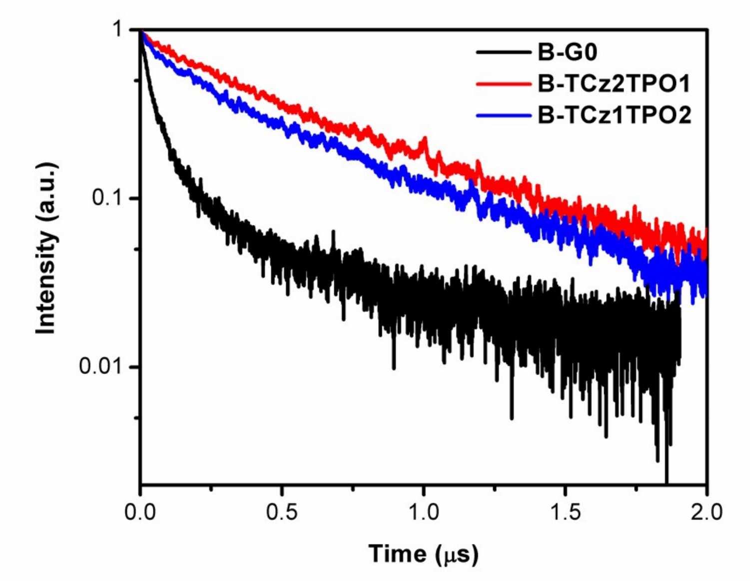


Figure S8. Decay of PL intensity (excited at 355 nm) at room temperature for thin films of Ir dendrimers compared with **B-G0**.

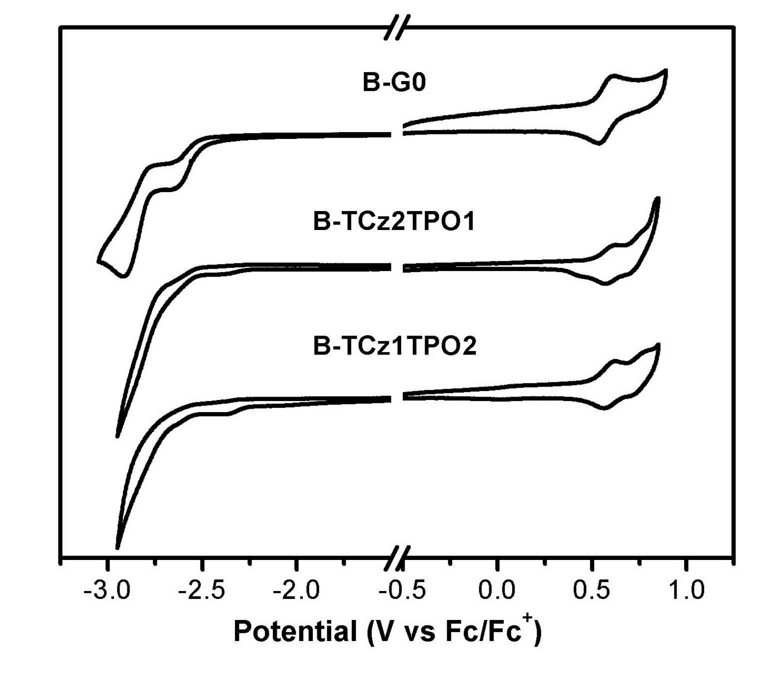


Figure S9. The electrochemical spectra of Ir dendrimers measured in CH_2Cl_2 solution (anodic sweeping) and DMF solution (cathodic sweeping), respectively.

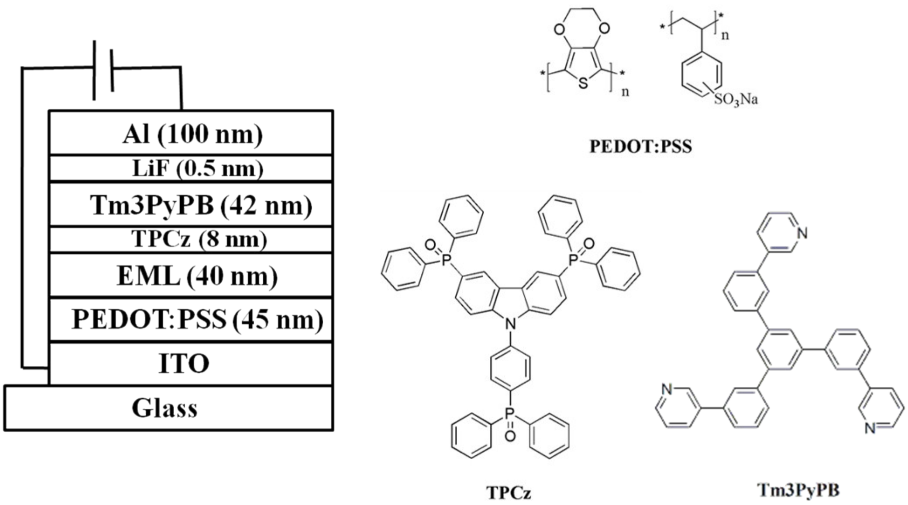


Figure S10. Schematic diagram of device configuration and molecular structures of the materials used in the device.

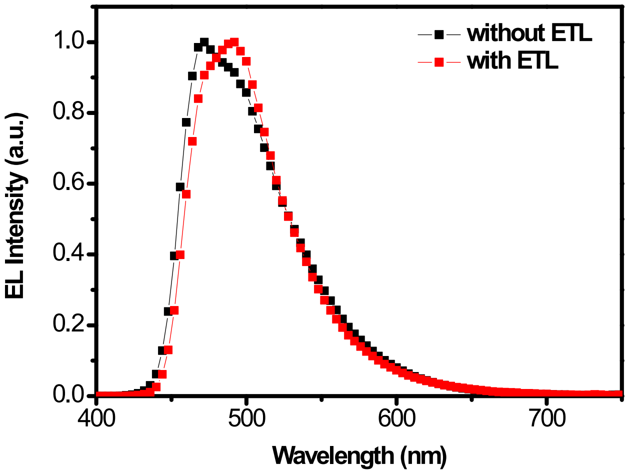


Figure S11. Comparison of EL spectra for B-TCz2TPO1 based devices with and without ETL.

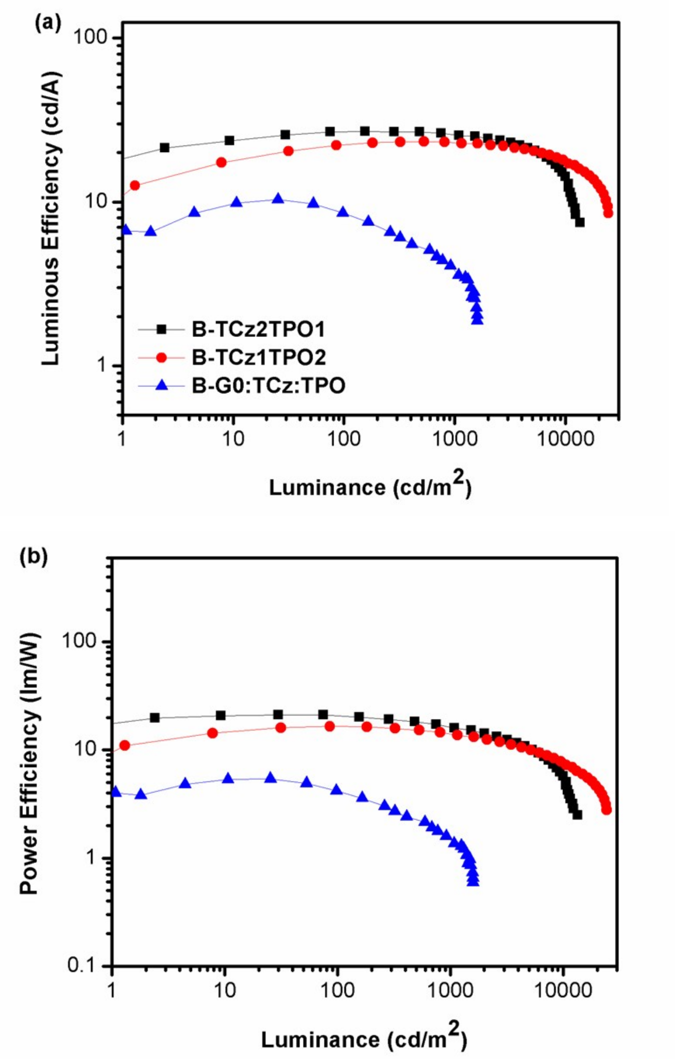


Figure S12. Luminous efficiency (a) and power efficiency as a function of luminance (b) for the undoped s-PhOLEDs of the dendrimers **B-TCz2TPO1** and **B-TCz1TPO2** compared with the corresponding physical blending **B-G0**: **TCz**: **TPO** (1: 2: 1).

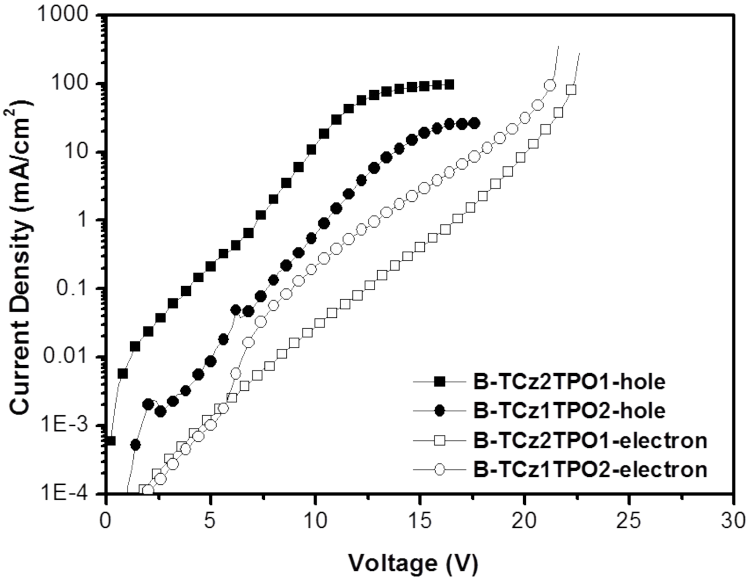


Figure S13. Current density versus voltage curves of hole- and electron-only devices for Ir dendrimers.

Table S1. The photophysical, electrochemical, and thermal data of Ir dendrimers.

	λ_{abs} [a] [nm]	λ_{em} [b] [nm]	Φ_{PL} [c]	τ_{av} [d] [μs]	HOMO [e] [eV]	LUMO [e] [eV]	T_d [°C]	T_g [°C]
B-G0	264, 348, 381, 419, 447	467, 490	0.57	0.11	-5.23	-2.26	355	n.d.
B-	264, 343, 384, 417, 448	467, 490	0.59	0.66	-5.28	-2.48	425	220
B-	265, 344, 383, 418, 448	467, 490	0.53	0.56	-5.28	-2.48	414	198

[a] Measured in 10^{-5} M dichloromethane solution; [b] Measured in 10^{-5} M toluene solution; [c] Measured in N_2-saturated toluene solution with $Ir(ppy)_3$ (Φ_{PL} = 0.40) as the reference; [d] Measured in neat films under N_2 excited at 355 nm and the lifetimes are obtained as an average value by a biexponential fit of emission decay curves; [e] HOMO = - e(E_{ox}^{onset} + 4.8 V), LUMO = - e(E_{red}^{onset} + 4.8 V), where E_{ox}^{onset} and E_{red}^{onset} represent for the onset oxidation and reduction potential, respectively.

Table S2. Device performance of the undoped s-PhOLEDs.

EML	V_{on} [a] [V]	L [b] [cd/m^2]	η_c [c] [cd/A]	η_p [c] [lm/W]	EQE [c] [%]	Roll-off [d]	CIE [e] [x, y]
B-G0:**TCz**:**TPO**	5.2	1610	10.3, 3.6	5.4, 1.4	4.8, 1.7	65%	(0.17, 0.28)
B-TCz2TPO1	3.4	13500	26.9, 25.5	21.2, 16.0	11.5, 10.9	5%	(0.18, 0.37)
B-TCz1TPO2	3.6	24360	23.3, 22.7	16.6, 13.7	10.0, 9.8	2%	(0.18, 0.36)

[a] Turn-on voltage at a brightness of 1 cd/m^2; [b] The maximum brightness (L); [c] Maximum data and data at 1000 cd/m^2 for luminous efficiency (η_c), power efficiency (η_p) and external quantum efficiency (EQE), respectively; [d] EQE roll-off at 1000 cd/m^2; [e] CIE at 8 V.