**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-[(2E)-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$_2$Cl$_2$ 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)$_3$ ($\Phi_p = 0.40$ 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 Quany-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$_2$Cl$_2$ 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$_4$NClO$_4$). 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 \( \text{HOMO} = -e \left[ E_{\text{ox}} + 4.8 \text{ V} \right] \) and \( \text{LUMO} = -e \left[ E_{\text{red}} + 4.8 \text{ V} \right] \), respectively, where \( E_{\text{ox}} \) and \( E_{\text{red}} \) 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 \( \Omega \) per square) and subsequently baked at 120 \( ^\circ \text{C} \) 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 \( ^\circ \text{C} \) 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 \( \times 10^{-4} \) 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.

![Scheme S1](image)

Reagents and conditions: (i) 4-toluene sulfonyl chloride, Et$_3$N, CH$_2$Cl$_2$, room temperature; (ii) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$(aq), THF, 70 °C; (iii) iridium(III) chloride trihydrate, water, 2-methoxyethanol, reflux, and then silver trifluoromethanesulfonate, K$_2$CO$_3$, ligand, mesitylene, reflux; (iv) NaOH, CH$_2$Cl$_2$, methanol, room temperature.

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

![Scheme S2](image)

Reagents and conditions: (i) 4-iodoanisole, CuI, *trans*-1,2-cyclohexanediamine, K$_3$PO$_4$, 1,4-dioxane, reflux; (ii) KI, KIO$_3$, CH$_3$COOH, 90 °C; (iii) carbozole, CuI, *trans*-1,2-cyclohexanediamine, K$_3$PO$_4$, 1,4-dioxane, reflux; (iv) BBr$_3$, CHCl$_3$, 0 °C; (v) 1,4-dibromobutane, K$_2$CO$_3$, DMF, 70 °C; (vi) Mg, THF, reflux, then HPO(OEt)$_2$, 25
°C; (vii) 4-iodoanisole, Pd(OAc)$_2$, 1,4-bis(diphenylphosphino)butane (dppb), (i-Pr)$_2$NEt, DMSO, 90 °C; (viii) diphenylphosphine oxide, Pd(OAc)$_2$, dppb, (i-Pr)$_2$NEt, DMSO, 90 °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 °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(PPh₃)₄ (34.6 mg, 0.03 mmol), aqueous solution of Na₂CO₃ (2M, 1.5 mL), THF (2.5 mL) was heated at 70 ℃ under argon for 12 h. Then the reaction was quenched with water and extracted with dichloromethane. The combined organic layers were dried over Na₂SO₄, filtered, and then the solvent was completely removed. The crude product was purified by silica gel column chromatography with petroleum ether: CH₂Cl₂ = 2:1 as the eluent to afford product (260 mg) in a yield of 74%. ¹H NMR (400 MHz, CDCl₃) [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), IrCl₃·3H₂O (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, K₂CO₃ (5.2 g, 37.9 mmol), AgSO₃CF₃ (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: CH₂Cl₂ = 1:1 as the eluent to give product (5.6 g) in a total yield of 30%. ¹H NMR (400 MHz, CDCl₃) [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 CH₂Cl₂ (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$_2$Cl$_2$: ethyl acetate = 5:1 as the eluent in a yield of 83%. $^1$H NMR (400 MHz, $d_6$-DMSO) [ppm]: $\delta$ 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$_3$, $\delta$ (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$_6$IrN$_3$O$_3$: 811.1 Found: 811.1 [M$^+$]. Anal. calcd for C$_{33}$H$_{18}$F$_6$IrN$_3$O$_3$: 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$_3$PO$_4$ (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$_2$SO$_4$. 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]: $\delta$ 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]: $\delta$ 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$_3$PO$_4$ (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$_2$SO$_4$. The pure product (1.75 g) was obtained by column chromatography using petroleum ether: THF = 2:1 as eluent in a yield of 58%. ¹H 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 ºC, 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%. ¹H 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$_2$CO$_3$ (1.73 g, 12.5 mmol) was added to DMF (25 mL) and heated at 70 ºC for 6 h. After that, the mixture was poured into water, extracted with CH$_2$Cl$_2$ and dried over Na$_2$SO$_4$. The pure product (1.5 g) was obtained by column chromatography using petroleum ether: CH$_2$Cl$_2$ = 3:1 as eluent in a yield of 83%. ¹H 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 NH₄Cl aqueous was added slowly. The mixture was extracted with ethyl acetate and the organic phase was washed with NaHCO₃ aqueous and brine, then it was dried over Na₂SO₄. 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. ¹H NMR (400 MHz, CDCl₃) [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). ³¹P NMR (161 MHz, CDCl₃, 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 Na₂SO₄. 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%. ¹H NMR (400 MHz, CDCl₃) [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). ³¹P NMR (161 MHz, CDCl₃, 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 (dpbb) (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 CH₂Cl₂, washed with water completely and dried with Na₂SO₄. The pure product (260 mg) was obtained by column chromatography using CH₂Cl₂: methanol = 50:1 as eluent in a yield of 80%. ¹H NMR (400 MHz, CDCl₃) [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\(_3\), \( \delta \)): 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\(_4\)P\(_3\): 708.2; Found: 709.2 [M+H]\(^+\).

**Compound 13:** A solution of 12 (113 mg, 0.2 mmol) in dry CH\(_2\)Cl\(_2\) (2 mL) was cooled to 0 \(^\circ\)C, and BBr\(_3\) (32 \( \mu \)L 1 M solution in CH\(_2\)Cl\(_2\), 0.3 mmol) was added dropwise. After stirring for 2 h 0 \(^\circ\)C, the reaction was carefully quenched with methanol, followed by adding a saturated solution of NaHCO\(_3\). Then the mixture was extracted with CH\(_2\)Cl\(_2\), washed with water and dried with Na\(_2\)SO\(_4\). 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]: \( \delta \) 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\(_3\), \( \delta \)): 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\(_2\)CO\(_3\) (3.9 g, 28.8 mmol) was added to DMF (50 mL) and heated at 70 \(^\circ\)C for 10 h. After cooling to room temperature, the mixture was poured into water, extracted with CH\(_2\)Cl\(_2\) and dried with Na\(_2\)SO\(_4\). The pure product (3.8 g) was obtained by column chromatography using CH\(_2\)Cl\(_2\): methanol = 50:1 as eluent in a yield of 64%. \(^1\)H NMR (400 MHz, CDCl\(_3\)) [ppm]: \( \delta \) 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\(_3\), \( \delta \)): 28.56 (br, 2P), 27.87 (br, 1P).

**B-TCz2TPO1:** A mixture of 9 (86.9 mg, 120 \( \mu \)mol), 4 (49 mg, 60 \( \mu \)mol), Cs\(_2\)CO\(_3\) (64.5 mg, 198 \( \mu \)mol) was added to DMF (4 mL) and heated at 80 \(^\circ\)C for 9 h. Then 14 (59.7 mg, 72 \( \mu \)mol) 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 (59 mg) was obtained by column chromatography using petroleum ether: CH$_2$Cl$_2$ = 50:1 as eluent in a yield of 35%. $^1$H NMR (400 MHz, CDCl$_3$) [ppm]: $\delta$ 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$_3$, $\delta$ (vs. fluorobenzene)): 4.13-4.10 (m, 3F), 2.07-2.01 (m, 3F). $^{31}$P NMR (161 MHz, CDCl$_3$, $\delta$): 28.64 (br, 2P), 27.90 (br, 1P). MALDI-TOF MS: calcd for C$_{171}$H$_{123}$F$_6$IrN$_9$O$_9$P$_3$: 2846.9; Found: 2846.8 [M$^+$]. Anal. calcd for C$_{171}$H$_{123}$F$_6$IrN$_9$O$_9$P$_3$: 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$_2$CO$_3$ (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$_2$Cl$_2$ = 50:1 as eluent in a yield of 25%. $^1$H NMR (400 MHz, CDCl$_3$) [ppm]: $\delta$ 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$_3$, $\delta$ (vs. fluorobenzene)): 4.08-4.05 (m, 3F), 2.03-1.99 (m, 3F). $^{31}$P NMR (161 MHz, CDCl$_3$, $\delta$): 28.52 (br, 2P), 27.82 (br, 1P). MALDI-TOF MS: calcd for C$_{171}$H$_{123}$F$_6$IrN$_6$O$_{12}$P$_6$: 2950.8 Found: 2950.8 [M$^+$]. Anal. calcd for C$_{171}$H$_{123}$F$_6$IrN$_6$O$_{12}$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), Cs₂CO₃ (430 mg, 1.32 mmol) was added to DMF (15 mL) and heated at 80 °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 vacuum. The pure product (332 mg) was obtained by column chromatography using petroleum ether: CH₂Cl₂ = 6:1 as eluent in a yield of 85%. ¹H NMR (400 MHz, CDCl₃) [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). ¹⁹F NMR (376 MHz, CDCl₃, δ (vs. fluorobenzene)): 3.29 (d, J = 9.9 Hz, 3F), 1.53 (d, J = 9.3 Hz, 3F). MALDI-TOF MS: calcd for C₄₅H₄₂F₆IrN₃O₃: 979.3 Found: 979.3 [M⁺]. Anal. calcd for C₄₅H₄₂F₆IrN₃O₃: 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 $-\text{OCH}_2$- (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 $\text{B-TCz1TPO2}$. 
Figure S5. TGA (a) and DSC curves (b) of Ir dendrimers.
Figure S6. UV-visible absorption spectra in CH$_2$Cl$_2$ 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$_2$Cl$_2$ 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.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (100 nm)</td>
<td></td>
</tr>
<tr>
<td>LiF (0.5 nm)</td>
<td></td>
</tr>
<tr>
<td>Tm3PyPB (42 nm)</td>
<td></td>
</tr>
<tr>
<td>TPCz (8 nm)</td>
<td></td>
</tr>
<tr>
<td>EML (40 nm)</td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS (45 nm)</td>
<td></td>
</tr>
<tr>
<td>ITO</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td></td>
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</tbody>
</table>
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.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{abs}$&lt;sup&gt;a&lt;/sup&gt; [nm]</th>
<th>$\lambda_{em}$&lt;sup&gt;b&lt;/sup&gt; [nm]</th>
<th>$\Phi_{PL}$&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$\tau_{av}$&lt;sup&gt;d&lt;/sup&gt; [μs]</th>
<th>HOMO&lt;sup&gt;e&lt;/sup&gt; [eV]</th>
<th>LUMO&lt;sup&gt;e&lt;/sup&gt; [eV]</th>
<th>$T_d$ [°C]</th>
<th>$T_g$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B-G0</strong></td>
<td>264, 348, 381, 419, 447</td>
<td>467, 490</td>
<td>0.57</td>
<td>0.11</td>
<td>-5.23</td>
<td>-2.26</td>
<td>355</td>
<td>n.d.</td>
</tr>
<tr>
<td><strong>B-TCz2TPO1</strong></td>
<td>264, 343, 384, 417, 448</td>
<td>467, 490</td>
<td>0.59</td>
<td>0.66</td>
<td>-5.28</td>
<td>-2.48</td>
<td>425</td>
<td>220</td>
</tr>
<tr>
<td><strong>B-TCz1TPO2</strong></td>
<td>265, 344, 383, 418, 448</td>
<td>467, 490</td>
<td>0.53</td>
<td>0.56</td>
<td>-5.28</td>
<td>-2.48</td>
<td>414</td>
<td>198</td>
</tr>
</tbody>
</table>

<sup>a</sup> Measured in 10<sup>-5</sup> M dichloromethane solution; <sup>b</sup> Measured in 10<sup>-5</sup> M toluene solution; <sup>c</sup> Measured in N<sub>2</sub>-saturated toluene solution with Ir(ppy)<sub>3</sub> ($\Phi_{PL} = 0.40$) as the reference; <sup>d</sup> Measured in neat films under N<sub>2</sub> excited at 355 nm and the lifetimes are obtained as an average value by a biexponential fit of emission decay curves; <sup>e</sup> 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.

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

$^a$ 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 ($\eta_c$), power efficiency ($\eta_p$) and external quantum efficiency (EQE), respectively; $^d$ EQE roll-off at 1000 cd/m$^2$; $^e$ CIE at 8 V.