Supporting Information

Dendron Engineering in Self-Host Blue Iridium DendrimerstowardsLow-Voltage-DrivingandPower-EfficientNondoped Electrophosphorescent Devices

Yang Wang, Shumeng Wang, Junqiao Ding,* Lixiang Wang,* Xiabin Jing, and Fosong Wang

[*] Prof. L. Wang, Prof. X. Jing, Prof. F. Wang, Prof. J. Ding, Y. Wang, S. Wang State Key Laboratory of Polymer Physics and Chemistry Changchun Institute of Applied Chemistry, Chinese Academy of Sciences Changchun 130022 (P. R. China)
E-mail: junqiaod@ciac.ac.cn; lixiang@ciac.ac.cn
Y. Wang, S. Wang
University of the Chinese Academy of Sciences
Beijing 100049 (P. R. China)

Experimental

Measurements and Characterization: ¹H NMR, ¹⁹F NMR and ³¹P NMR spectra were recorded by Bruker Avance NMR spectrometer. The elemental analysis was performed using a Bio-Rad elemental analysis system. MALDI/TOF (Matrix assisted laser desorption ionization/Time-offlight) mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT) with 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 using a Perkin-Elmer-TGA 7 and Perkin-Elmer-DSC 7 system, respectively. The UV-vis absorption and photoluminescence (PL) spectra were measured by a Perkin-Elmer Lambda 35 UV/Vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. The phosphorescence spectra were measured at 77 K in toluene with a concentration of 10⁻⁴ M. The PL quantum yield was measured in argon-saturated toluene with the typical blue phosphor FIrpic ($\Phi_p = 0.83$) as the reference.^[1] The transient PL spectra were measured in argon atmosphere excited by 355 nm pulse with ca. 3 ns width from a Quanty-Ray DCR-2 pulsed Nd:YAG laser. And the average lifetimes were estimated according to the equation: $\tau_{av} = (A_1\tau_1^2 + C_1^2)^2$ $A_2\tau_2^2$ /($A_1\tau_1 + A_2\tau_2$). Cyclic voltammetry (CV) experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The measurements were carried out in CH₂Cl₂ for anodic sweeping and in N,N-dimethylformamide (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-Bu₄NClO₄). All potentials were calibrated against the ferrocene/ferrocenium couple. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were determined by the equation HOMO = e [$E_{\text{ox, onset}}$ + 4.8 V] and LUMO = -e [$E_{\text{red, onset}}$ + 4.8 V], where $E_{\text{ox, onset}}$ and $E_{\text{red, onset}}$ were the potential onset obtained from the first oxidation and reduction waves, respectively.

Device fabrication and testing: To fabricate nondoped s-PhOLEDs, a 45-nm-thick poly(3,4ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) film was firstly deposited on the pre-cleaned ITO-glass substrates (20 Ω per square) and baked at 120 °C for 40 min. Then the EML with a thickness of about 40 nm was spin-coated from a chlorobenzene solution onto the PEDOT: PSS layer and annealed at 100 °C for 30 min to remove the residual solvent in N₂ atmosphere. Subsequently, a 8 nm thick TPCz and a 42 nm thick Tm3PyPB were evaporated in succession as the hole blocking and electron transporting layer at a pressure less than 4.0×10^{-4} Pa. Finally, a 0.5 nm thick LiF and 100 nm thick Al were evaporated as the cathode. The active area of all the devices was 14 mm². According to a similar procedure, in addition, the hole-only devices were fabricated with a configuration of ITO/PEDOT:PSS (45 nm)/B-POCz, B-CzCz or B-CzTA (80 nm)/Au (75 nm). 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 calibrated by a silicon photodiode. All the measurements were carried out at room temperature under ambient conditions. The external quantum efficiency (EQE) was 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. The para-hydroxyl-substituted blue Ir core *p*-OH-dfppyIr was prepared according to

the literature procedure.^[2]



Scheme S1. Synthesis of Ir dendrimer B-POCz. Reagents and conditions: (i) 4-iodoanisole, CuI, K_3PO_4 , *trans*-1,2-cyclohexanediamine, 1,4-dioxane, reflux; (ii) KI, KIO₃, CH₃COOH, 90 °C; (iii) diphenylphosphaneoxide, Pd(OAc)₂, N,N-diisopropylethylamine, 1,4bis(diphenylphosphino)butane, DMSO, 110 °C; (iv) BBr₃, CH₂Cl₂, 0 °C; (v) 1,4-dibromobutane, K_2CO_3 , DMF, 70 °C; (vi) Cs₂CO₃, DMF, 70 °C.



Scheme S2. Synthesis of Ir dendrimer B-CzCz. Reagents and conditions: (i) 4-iodoanisole, CuI,
K₃PO₄, *trans*-1,2-cyclohexanediamine, 1,4-dioxane, reflux; (ii) KI, KIO₃, CH₃COOH, 90 °C; (iii)
carbazole, CuI, K₃PO₄, *trans*-1,2-cyclohexanediamine, 1,4-dioxane, reflux; (iv) BBr₃, CHCl₃, 0 °C;
(v) 1,4-dibromobutane, K₂CO₃, DMF, 70 °C; (vi) Cs₂CO₃, DMF, 70 °C..



Scheme S3. Synthesis of Ir dendrimer B-CzTA. Reagents and conditions: (i) 4-iodoanisole, Pd(OAc)₂, P(*t*-Bu)₃, NaO'Bu, toluene, 110 °C; (ii) NBS, DMF, 0 °C; (iii) carbazole, CuI, L-proline, K₂CO₃, DMSO, 150 °C; (iv) BBr₃, CH₂Cl₂, 0 °C; (v) 1,4-dibromobutane, K₂CO₃, DMF, 70 °C; (vi) Cs₂CO₃, DMF, 70 °C.

Synthetic procedures

Compound 1: A mixture of carbazole (16.7 g, 0.1 mol), 4-iodoanisole (28 g, 0.12 mol), trans-1,2-cyclohexanediamine (0.8 mL, 5 mmol), K_3PO_4 (50 g, 0.24 mol) and CuI (1.9 g, 0.01 mol) was dissolved in 1,4-dioxane (300 mL) and heated to reflux under argon atmosphere for 24 h. Then the crude mixture was filtered, added with CH_2Cl_2 and washed with diluted aqua ammonia, 1M hydrochloric acid, saturated salt water and water successively. The extracted organic layer was combined and evaporated under vacuum to remove most of organic solvent. The pure product can be obtained by recrystallization from ethyl acetate as a white solid (22.8 g, 84%). ¹H NMR (400 MHz, CDCl3) [ppm]: δ 8.14 (d, J = 7.7 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.42-7.37 (m, 2H), 7.33-7.27 (m, 4H), 7.11 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H).

Compound **2**: Compound **1** (13.6 g, 50 mmol) was dissolved in acetic acid (150 mL) at 90 °C. Then KI (12.4 g, 75 mmol) and KIO₃ (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. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.38 (s, 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).

Compound **POCz**: Compound **2** (3.2 g, 6 mmol), diphenylphosphaneoxide (3.6 g, 18 mmol), Pd(OAc)₂ (269 mg, 1.2 mmol), N,N-diisopropylethylamine (6.2 g, 48 mmol), 1,4bis(diphenylphosphino)butane (512 mg, 1.2 mmol) were added to 30 mL degassed DMSO under argon atmosphere. The reaction mixture was heated to 110 °C for 24 h. Then the mixture was poured into water, filtered, washed with water and dried in vacuum. The pure product (3.2 g) was obtained by column chromatography using ethyl acetate: methanol = 20:1 as the eluent in a yield of 80%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.48 (d, J = 12.2 Hz, 2H), 7.71-7.66 (m, 10H), 7.56-7.52 (m, 4H), 7.47-7.36 (m, 12H), 7.12 (d, J = 8.2 Hz, 2H), 3.92 (s, 3H).

Compound **POCz-OH**: A solution of **POCz** (1.68 g, 2.5 mmol) in dry CH_2Cl_2 (12 mL) was cooled to 0 °C, and BBr₃ (0.5 mL 1 M solution in CH_2Cl_2 , 5 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 NaHCO₃, filtering, washing with water completely and drying in vaccum. The pure product (1.2 g) was obtained in a yield of 73%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.39 (d, J = 12.4 Hz, 2H), 7.72-7.62 (m, 10H), 7.57-7.53 (m, 4H), 7.48-7.44 (m, 8H), 7.29 (dd, J = 8.5, 1.8 Hz, 2H), 7.11-7.04 (m, 4H).

Compound **POCz-O-C4H8Br**: A mixture of **POCz-OH** (1.06 g, 1.6 mmol), 1,4dibromobutane (0.77 mL, 6.4 mmol), K₂CO₃ (1.11 g, 8 mmol) was added to DMF (16 mL) and heated at 70 °C for 6 h. After that, the mixture was poured into water, extracted with CH₂Cl₂ and dried with Na₂SO₄. The pure product (600 mg) was obtained by column chromatography using petroleum ether: ethyl acetate = 1:20 as eluent in a yield of 50%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.44 (d, J = 12.3 Hz, 2H), 7.75-7.67 (m, 10H), 7.58-7.54 (m, 4H), 7.49-7.44 (m, 8H), 7.41-7.37 (m, 4H), 7.10 (d, J = 8.8 Hz, 2H), 4.10 (t, J = 5.9 Hz, 2H), 3.53 (t, J = 6.5 Hz, 2H), 2.17-2.09 (m, 2H), 2.06-1.99 (m, 2H).

B-POCz: A mixture of **POCz-O-C4H8Br** (262 mg, 0.33 mmol), *p*-OH-dfppyIr (81 mg, 0.1 mmol), Cs_2CO_3 (107 mg, 0.33 mmol) was added to DMF (6 mL) and heated at 80 °C for 18 h. After that, the mixture was poured into water, filtered and dried in vaccum. The pure product (200 mg) was obtained by column chromatography using petroleum ether: $CH_2Cl_2 = 50:1$ as eluent in a yield of 70%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.43 (d, J = 12.3 Hz, 6H), 7.80 (br, 3H), 7.74-7.66 (m, 30H), 7.56-7.52 (m, 12H), 7.47-7.43 (m, 24H), 7.40-7.35 (m, 12H), 7.31 (d, J = 6.2 Hz, 3H), 7.09 (d, J = 8.3 Hz, 6H), 6.50 (d, J = 5.9 Hz, 3H), 6.33 (m, 3H), 6.24 (d, J = 9.1 Hz, 3H),

4.17-4.12 (m, 12H), 2.05 (br, 12H). ¹⁹F NMR (376 MHz, CDCl₃, δ (vs. fluorobenzene)): 4.07 (d, J = 10.1 Hz, 3F), 2.00 (d, J = 9.8 Hz, 3F). ³¹P NMR (161 MHz, CDCl₃, δ): 30.17. MALDI-TOF MS: calcd for C₁₇₁H₁₂₉F₆IrN₁₂O₆P₆: 2951.9 Found: 2951.7 [M⁺]. Anal. calcd for C₁₇₁H₁₂₉F₆IrN₁₂O₆P₆: C 69.58, H 4.40, N 2.85 Found: C 69.66, H 4.43, N 2.80.

Compound CzCz: Carbazole (1.83 g, 11 mmol), compound 2 (2.6 g, 5 mmol), CuI (190 mg, 1 mmol), K₃PO₄ (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 Na₂SO₄. 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, CDCl₃) [ppm]: δ 8.30 (s, 2H), 8.19 (d, *J* = 7.7 Hz, 4H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.62-7.58 (m, 4H), 7.45-7.40 (m, 8H), 7.34-7.27 (m, 4H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 3H).

Compound **CzCz-OH**: This compound is synthesized according to a similar procedure described for **POCz-OH**. Yield: 97%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.30 (s, 2H), 8.19 (d, J = 7.7 Hz, 4H), 7.64-7.58 (m, 6H), 7.45-7.40 (m, 8H), 7.34-7.27 (m, 4H), 7.17 (d, J = 8.6 Hz, 2H).

Compound **CzCz-O-C4H8Br**: This compound is synthesized according to a similar procedure described for **POCz-O-C4H8Br**. Yield: 83%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.29 (s, 2H),

8.19 (d, *J* = 7.7 Hz, 4H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.62-7.58 (m, 4H), 7.44-7.40 (m, 8H), 7.33-7.27 (m, 4H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.18 (t, *J* = 5.9, 5.9 Hz, 2H), 3.58 (t, *J* = 6.5, 6.5 Hz, 2H), 2.23-2.15 (m, 2H), 2.12-2.05 (m, 2H).

B-CzCz. This dendrimer is synthesized according to a similar procedure described for **B-POCz**. Yield: 73%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.26 (s, 6H), 8.15 (d, J = 7.7 Hz, 12H), 7.82 (br, 3H), 7.59-7.52 (m, 18H), 7.41-7.35 (m, 24H), 7.32 (d, J = 6.3 Hz, 3H), 7.29-7.26 (m, 12H), 7.14 (d, J = 8.6 Hz, 6H), 6.46 (d, J = 5.5 Hz, 3H), 6.40-6.31 (m, 3H), 6.26 (d, J = 8.8 Hz, 3H), 4.15-4.13 (m, 12H), 2.05 (br, 12H). ¹⁹F NMR (376 MHz, CDCl₃, δ (vs. fluorobenzene)): 4.17 (d, J = 9.8 Hz, 3F), 2.05 (d, J = 9.8 Hz, 3F). MALDI-TOF MS: calcd. for C₁₇₁H₁₁₇F₆IrN₁₂O₆: 2742.0 Found: 2741.9 [M⁺]. Anal. calcd for C₁₇₁H₁₁₇F₆IrN₁₂O₆: C 74.90, H 4.30, N 6.13 Found: C 74.90, H 4.37, N 5.83.

Compound **3**: Diphenylamine (5.08 g, 30 mmol), 4-iodoanisole (10.5 g, 45 mmol), Pd(OAc)₂ (663 mg, 3 mmol), P(*t*-Bu)₃ (18.4 mL, 6 mmol, 1%), NaO'Bu (8.07 g, 84 mmol) were added to 120 mL degassed toluene under argon atmosphere. The reaction mixture was heated to reflux for 18 h. Then the mixture was filtered and concentrated. The pure product (3.1 g) was obtained by column chromatography using petroleum ether as eluent in a yield of 38%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 7.20 (t, J = 7.8 Hz, 4H), 7.07-7.01 (m, 6H), 6.95-6.93 (m, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H).

Compound 4: Compound 3 (3.02 g, 11 mmol) was dissolved with 80 mL DMF in an ice bath,

and was added with NBS (3.91 g, 22 mmol) slowly which was dissolved in 40 mL DMF before. The mixture was reacted for 3 h and then poured into water, extracted with CH_2Cl_2 and dried with Na_2SO_4 . The pure product (4.5 g) was obtained by column chromatography using petroleum ether as eluent in a yield of 95%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 7.30 (d, J = 8.9 Hz, 4H), 7.02 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 8.9 Hz, 4H), 6.84 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H).

Compound CzTA: Carbazole (4.2 g, 25 mmol), compound 4 (4,3 g, 10 mmol), CuI (342 mg, 2 mmol), K₂CO₃ (5.44 g, 40 mmol), L-proline (460 mg, 4 mmol) were added to 60 mL degassed DMSO under argon atmosphere. The reaction mixture was heated to 150 °C for 24 h. Then the mixture was poured into water and filtered. The filter cake was washed by dilute ammonia water, diluted hydrochloric acid, saturated brine successively and dried in vaccum. The pure product (2.7 g) was obtained by column chromatography using petroleum ether: $CH_2Cl_2 = 5:1$ as eluent in a yield of 45%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.15 (d, J = 7.8 Hz, 4H), 7.47-7.43 (m, 8H), 7.41 (dd, J = 8.2, 1.1 Hz, 4H), 7.34 (d, J = 8.8 Hz, 4H), 7.31-7.26 (m, 6H), 6.98 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H).

Compound **CzTA-OH**: This compound is synthesized according to a similar procedure described for **POCz-OH**. Yield: 88%. ¹H NMR (400 MHz, d_6 -DMSO) [ppm]: δ 9.57 (s, 1H), 8.24 (d, J = 7.7 Hz, 4H), 7.53 (d, J = 8.7 Hz, 4H), 7.47-7.40 (m, 8H), 7.32 (d, J = 8.8 Hz, 4H), 7.30-7.26 (m, 4H), 7.23 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H).

Compound CzTA-O-C4H8Br: This compound is synthesized according to a similar procedure

described for **POCz-O-C4H8Br**. Yield: 55%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.15 (d, J = 7.7 Hz, 4H), 7.47-7.44 (m, 8H), 7.42 (dd, J = 8.2, 0.9 Hz, 4H), 7.34 (d, J = 8.2 Hz, 4H), 7.30-7.27 (m, 6H), 6.97 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 5.8 Hz, 2H), 3.52 (t, J = 6.6 Hz, 2H), 2.14-2.07 (m, 2H), 2.02-1.95 (m, 2H).

B-CzTA: This dendrimer is synthesized according to a similar procedure described for **B-POCz**. Yield: 50%. ¹H NMR (400 MHz, CDCl₃) [ppm]: δ 8.14 (d, J = 7.7 Hz, 12H), 7.83-7.75 (m, 3H), 7.45-7.42 (m, 24H), 7.40 (dd, J = 8.2, 1.0 Hz, 12H), 7.33-7.27 (m, 33H), 6.94 (d, J = 8.8 Hz, 6H), 6.48 (dd, J = 6.3, 2.3 Hz, 3H), 6.35 (ddd, J = 13.0, 8.9, 2.4 Hz, 3H), 6.25 (dd, J = 9.1, 2.4 Hz, 3H), 4.12 (t, J = 5.3 Hz, 6H), 4.04 (br, 6H), 2.04-1.97 (m, 12H). ¹⁹F NMR (376 MHz, CDCl₃, δ (vs. fluorobenzene)): 4.04 (d, J = 9.9 Hz, 3F), 2.01 (d, J = 10.1 Hz, 3F). MALDI-TOF MS: calcd for C₁₇₁H₁₂₃F₆IrN₁₂O₆: 2746.9 Found: 2746.9 [M⁺]. Anal. calcd for C₁₇₁H₁₂₃F₆IrN₁₂O₆: C 74.74, H 4.51, N 6.12 Found: C 74.84, H 4.55, N 6.10.

References:

- [1] A. F. Rausch, M. E. Thompson, H. Yersin, J. Phys. Chem. A 2009, 113, 5927.
- [2] Y. Wang, Y. Lu, B. Gao, S. Wang, J. Ding, L. Wang, X. Jing and F. Wang, *Chem. Commun.***2016**, *52*, 11508.



Figure S1. (a) ¹H NMR spectrum, (b) ³¹P NMR spectrum and (c) MALDI-TOF spectrum of B-

POCz.



Figure S2. (a) ¹H NMR spectrum and (b) MALDI-TOF spectrum of B-CzCz.



Figure S3. (a) ¹H NMR spectrum and (b) MALDI-TOF spectrum of **B-CzTA**.



Figure S4. (a) Phosphorescent spectra with corresponding triplet energies of **B-G0** and dendron fragments (b) Molecular structures of **B-G0**, different dendrons and Ir dendrimers.



Figure S5. Molecular structures, simulated sizes of Ir-cored dendrimers performed by Gaussian 09 program package based on density function theory (DFT) using semi-empirical PM6 method with 6-31G* basis sets, and the HOMO/LUMO distribution based on B3LYP method.



Figure S6. The electrochemical spectra of Ir core and dendrimers in which anodic sweeping was measured in CH_2Cl_2 solution and cathodic sweeping was done in DMF solution, respectively.

	<i>E</i> _{ox,onset} [V vs Fc/Fc ⁺]	<i>E</i> _{red,onset} [V vs Fc/Fc ⁺]	HOMO [eV]	LUMO [eV]
B-G0	0.48	-2.54	-5.28	-2.26
POCz	0.94	-2.54	-5.74	-2.26
CzCz	0.60	-2.67	-5.40	-2.13
CzTA	0.33	-2.82	-5.13	-1.98

Table S1. The electrochemical data of Ir core and different dendrons.



Figure S7. From up to down, the atomic force microscopy (AFM) (5 μ m × 5 μ m) surface topographic and phase images of three self-host blue Ir dendrimers are presented in sequence.



Figure S8. (a) Thermal gravimetric analysis and (b) the second heating scans of differential scanning calorimetry curves for Ir dendrimers.



Figure S9. Absorption spectra in CH_2Cl_2 and PL spectra in toluene of **B-G0** at a concentration of 10^{-5} M.



Figure S10. Decay of PL intensity (excited at 355 nm) at room temperature for thin films of Ir dendrimers.



Figure S11. (a) Schematic diagram of device configuration and corresponding molecular structures and (b) energy levels of different layers with blue column standing for Ir core and purple column for different dendrons.



Figure S12. (a) Luminous efficiency *versus* brightness and (b) external quantum efficiency (EQE) *versus* brightness for Ir dendrimers.

Dendrimer	λ _{abs} ^a [nm]	λ _{em} ^b [nm]	$\Phi_P^{\ c}$	τ ^d [μs]	τ _{av} ^e [μs]	<i>T</i> _d [°C]	<i>T</i> g [°C]
B-POCz	277, 327, 383, 418, 449	466	0.80	0.79	0.28	419	197
B-CzCz	264, 343, 385, 418, 449	466	0.84	0.80	0.44	422	243
B-CzTA	294, 327, 384, 417, 448	466	0.79	0.75	0.34	420	192

Table S2. The photophysical and thermal data of self-host blue Ir dendrimers.

^aMeasured in 10⁻⁵ M dichloromethane solution; ^bMeasured in 10⁻⁵ M toluene solution; ^cMeasured in argon-saturated toluene solution with FIrpic ($\Phi_{PL} = 0.83$) as the reference; ^dMeasured in solutions under argon, excited at 355 nm. The lifetimes are obtained by a monoexponential fit of emission decay curves; ^eMeasured in neat films under argon excited at 355 nm and the lifetimes are obtained as an average value by a biexponential fit of emission decay curves.

Table S3. Nondoped device performance for self-host blue Ir dendrimers.

Dendrimer	V^{a} [V]	$\eta_{\rm p}{}^{\rm a}$ [lm/W]	η_{c}^{a} [cd/A]	EQE ª [%]	<i>L</i> ^b [cd/m ²]	CIE ° [x, y]
B-POCz	4.9/5.8/7.4	5.6/6.1/4.1	7.0/11.3/9.6	2.4/5.0/4.8	7030	(0.19, 0.34)
B-CzCz	3.2/4.0/5.0	15.6/16.1/11.9	14.1/20.5/18.9	6.6/9.5/8.8	9360	(0.17, 0.32)
B-CzTA	2.7/3.4/4.4	30.3/24.4/16.3	25.8/26.4/22.9	12.1/12.3/10.5	11260	(0.16, 0.32)

^a Data at 1, 100 and 1000 cd/m² for driving voltage (*V*), power efficiency (η_p), luminous efficiency (η_c) and external quantum efficiency (EQE), respectively; ^b The maximum brightness (*L*); ^c CIE at 10 V.