

Electronic supplementary information (ESI) for

Self-Host Heteroleptic Green Iridium Dendrimers: Achieving Efficient Non-doped Device Performance Based on A Simple Molecular Structure†

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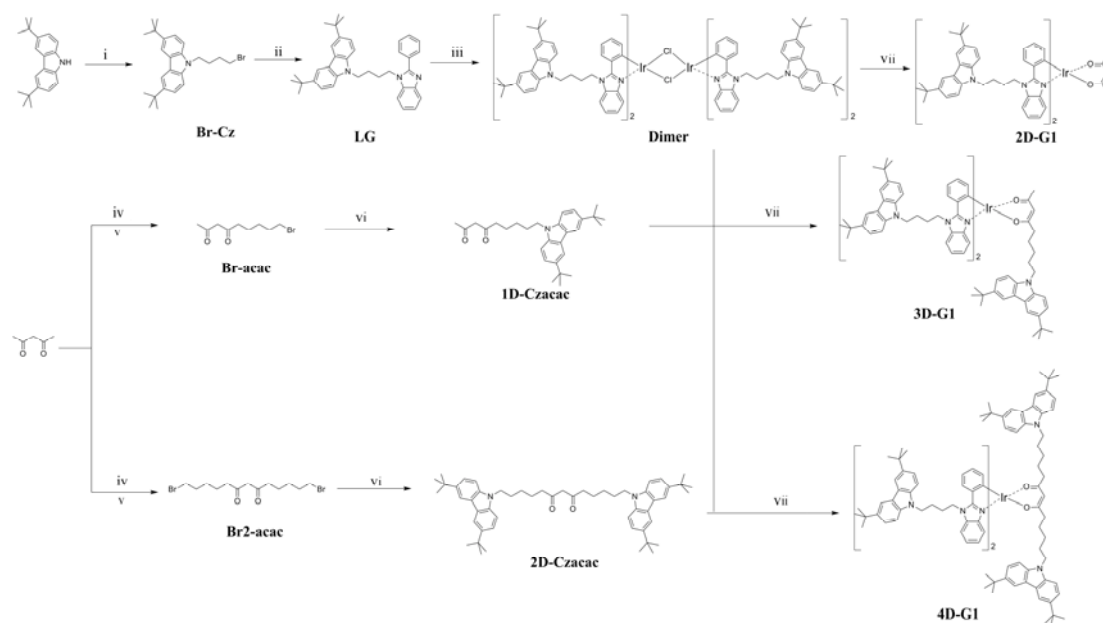
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Experimental

General information: ¹H NMR spectra were recorded with Bruker Avance 300 NMR spectrometer. MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) mass spectra were performed on AXIMA CFR MS apparatus (COMPACT). The elemental analysis (EA) was performed using a Bio-Rad elemental analysis system. 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 dichloromethane for UV/Vis absorption and toluene for photoluminescence with a concentration of 10⁻⁵ M. Thin films on quartz for spectroscopic measurements were prepared by spin-coating. Solution PL quantum efficiency was measured in N₂-saturated toluene by a relative method using *fac*-Ir(ppy)₃ ($\Phi_p = 0.40$ in toluene) as the standard. Phosphorescence spectra at 77 K were measured in toluene. The triplet energies were estimated as the maximum of the first vibronic mode ($S_0^{v=0} \leftarrow T_1^{v=0}$) of the corresponding phosphorescence spectra at 77 K. The PL decay curves were obtained from a Lecroy Wave Runner 6100 digital

oscilloscope (1 GHz) by using a tunable laser (pulse width = 4 ns, gate = 50 ns) as an excitation source (Continuum Sunlite OPO). And the lifetimes were obtained by single exponential fit of emission decay curves. Cyclic voltammetry experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The measurements were carried out with a conventional three-electrode system consisting of a platinum working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$). Ferrocene was used as a standard to calibrate the system.

Device fabrication and testing: To fabricate the OLEDs, 50 nm thick PEDOT:PSS films were first deposited on pre-cleaned ITO-coated glass substrates, and then cured at 120 °C in air for 1 h. The emissive layer was then prepared by spin-coating a chlorobenzene solution of the dendrimer at a concentration of 10 mg/mL. Successively, a 60 nm thick TPBI film was deposited, followed by deposition of the LiF/Al (1 nm/100 nm) cathode at a base pressure of less than 10^{-6} torr through a shadow mask with an array of 14 mm^2 openings. 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 2400/2000 source meter and a calibrated silicon photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.



Scheme S1. Synthesis of the self-hosted heteroleptic Ir dendrimers. Reagents and conditions: i) 1,4-dibromobutane, $\text{KOH}/n\text{-Bu}_4\text{NBr}$, toluene/ H_2O , reflux; ii) 2-phenyl-1*H*-benzoimidazole, NaH , DMF/THF , reflux; iii) $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, 2-ethoxyethanol/ H_2O , reflux; iv) 4-phenoxybutyl bromide, $\text{NaH}/n\text{-BuLi}$, THF , 0°C & r.t.; v) BBr_3 , DCM , -78°C & r.t.; vi) 3,6-di-*t*-butyl-9*H*-carbazole, $\text{NaH}/t\text{-BuOK}$, THF , 0°C & r.t.; vii) Na_2CO_3 , 2-ethoxyethanol/ CHCl_3 , 100°C .

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. All chemical reactions were carried out under an inert atmosphere. The intermediates 2-phenyl-1*H*-benzoimidazole,¹ and 3,6-di-*t*-butyl-9*H*-carbazole² were prepared according to the literature procedures.

The synthesis of the C^N ligand

9-(4-bromobutyl)-3,6-di-*t*-butyl-9*H*-carbazole(Br-Cz**):** A mixture of 3,6-di-*t*-butyl-9*H*-carbazole (5.6 g, 20 mmol), 1,4-dibromobutane (17.3 g, 80 mmol), potassium hydroxide (5.6 g, 100 mmol), tetrabutyl ammonium bromide (0.6 g, 2 mmol), toluene (80 mL), and water (12 mL) was refluxed for 12 h under argon. After

cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been completely removed, the excess 1,4-dibromobutane was distilled, then the residue was purified by column chromatography on silica gel with petroleum/ethylacetate(10:1) as the eluent to give the product 9-(4-bromobutyl)-3,6-di-*t*-butyl-9*H*-carbazole (7.5 g, 91%). ¹H NMR (300 MHz, CDCl₃) δ 8.14 (d, *J* = 1.7 Hz, 2H), 7.55 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 2.04-2.11 (m, 2H), 1.93-1.98 (m, 2H), 1.45 (s, 18H).

LG: A mixed solution of N,N-dimethylformamide (DMF, 60 mL) and tetrahydrofuran (THF, 120 mL) was added dropwise over 20 min to a stirred mixture of 2-phenyl-1*H*-benzoimidazole (4.7 g, 24 mmol) and sodium hydride (4.6 g, 0.2 mol). After that, the solution of the 9-(4-bromobutyl)-3,6-di-*t*-butyl-9*H*-carbazole (9.9 g, 24 mmol) dissolved in DMF (15 mL) and THF (30 mL) was slowly added dropwise. When the addition was completed, the resulting solution was refluxed for 24 h under argon. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel with DCM/ethylacetate (6:1) as the eluent to give the main ligand (9.2 g, 72%). ¹H NMR (300 MHz, CDCl₃) δ 8.09 (s, 2H), 7.83-7.80 (m, 1H), 7.60-7.57 (m, 2H), 7.48-7.39 (m, 5H), 7.30-7.23 (m, 3H), 7.15 (d, *J* = 8.7 Hz, 2H), 4.16 (br, 4H), 1.80 (br, 4H), 1.45 (s, 18H).

The synthesis of the O[^]O ligands

General synthetic method for the bromo-β-diketones: Acetylacetone (10.0 mmol) was added carefully dropwise over 15 min to the stirred suspension of the sodium hydride (11.5 mmol) in THF (50 mL) at 0 °C. The resultant mixture was stirred for 30 min at 0 °C. Butyllithium (20.0 or 40.0 mmol) was added dropwise over 30 min to the

stirred mixture at 0 °C. After 30 min, a solution of 4-phenoxybutyl bromide (22.5 or 45.0 mmol) in THF (5 or 10 mL) was added dropwise to the solution at 0 °C. When the addition is completed, the result solution was stirred for 2 h at 0 °C and for a further 2 h at room temperature, after which it was quenched with aqueous ammonium chloride. The mixture was acidified with concentrated hydrochloric acid to pH 1 and the aqueous phase was separated and extracted with dichloromethane. The combined organic layers were washed with brine and dried with anhydrous Na₂SO₄, and the solvent was evaporated in vacuo. The crude product was purified by distillation under reduced pressure to afford the phenoxy- β -diketones.

The phenoxy- β -diketone (15 mmol) was dissolved in 200 mL of dichloromethane in a 500 ml 3-neck round-bottom flask, and the flask was placed in an acetone-dry ice bath at -78 °C. Then boron tribromide (17.25 or 33.75 mmol) was added carefully to the stirred solution through an addition funnel. When the addition was completed, the reaction mixture was allowed to stir for 2 h at -78 °C, and then for a further 1 day at r.t., then a clear, brownish yellow solution was obtained. The reaction mixture was hydrolyzed carefully by 100 mL water. The organic layer was separated with a separator funnel. The organic layers was washed twice with water, then washed with aqueous sodium carbonate, and dried with anhydrous Na₂SO₄. Finally the solvent was evaporated to give the pure product.

Br-acac: This compound as a pale yellow oil was obtained with the yield of 94%. ¹H NMR (300 MHz, CDCl₃) δ 15.45 (s, 0.8H), 5.47 (s, 0.8H), 3.54 (s, 0.4H), 3.39 (t, J = 6.6 Hz, 2H), 2.52 (t, J = 7.2 Hz, 0.4H), 2.28 (t, J = 7.5 Hz, 1.6H), 2.01 (s, 3H), 1.80-1.90 (m, 2H), 1.53-1.67 (m, 2H), 1.40-1.51 (m, 2H).

Br2-acac: This compound as a pale yellow oil was obtained with the yield of 98%. ¹H NMR (300 MHz, CDCl₃) δ 15.45 (s, 0.8H), 5.47 (s, 0.8H), 3.54 (s, 0.4H), 3.39 (t, J = 6.6 Hz, 4H), 2.52 (t, J = 7.2 Hz, 0.8H), 2.28 (t, J = 7.5 Hz, 3.2H), 1.81-1.91 (m, 4H), 1.56-1.67 (m, 4H), 1.41-1.51 (m, 4H).

General synthetic method for the O[^]O ligands³: In one 3-neck round-bottom flask, the reactant bromo- β -diketones (1.0 mmol) was added carefully dropwise to the stirred suspension of the sodium hydride (1.1 mmol) in THF (10 mL) at 0 °C. Then the prepared sodium salt was transferred to another 3-neck round-bottom flask, in which potassium tert-butanolate (2.5 mmol) and 3,6-di-*t*-butyl-9*H*-carbazole (1.5 mmol, or 2.5 mmol) were dissolved in THF (15 mL, or 30 mL; and have been stirred at room temperature for 2 h) through a double pointed metal cannula needle at 0 °C. The reaction was stirred for 2 h at 0 °C, and a further 2 h at room temperature. After that, the reaction was quenched with aqueous ammonium chloride. Subsequently, the mixture was acidified with concentrated hydrochloric acid to pH 1 and the aqueous phase was separated and extracted with DCM. The combined organic layers were washed with brine and dried with anhydrous Na₂SO₄, and the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel.

1D-Czacac: This compound, as white solid in a yield of 85%, was obtained from the reactant 3,6-di-*t*-butyl-9*H*-carbazole and **Br-acac**. ¹H NMR (300 MHz, CDCl₃) δ 15.42 (s, 0.8H), 8.09 (d, $J=1.7$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 5.34 (s, 0.8H), 4.24 (t, $J = 7.1$ Hz, 2H), 3.44 (s, 0.4H), 2.43 (t, $J = 7.2$ Hz, 0.8H), 2.16 (t, $J = 7.2$ Hz, 1.2H), 1.96 (s, 3H), 1.92 – 1.83 (m, 2H), 1.69 – 1.58 (m, 2H), 1.39 (s, 20H).

2D-Czacac: This compound, as white solid in a yield of 80%, was obtained from the reactant 3,6-di-*t*-butyl-9*H*-carbazole and **Br2-acac**. ¹H NMR (300 MHz, CDCl₃) δ 15.42 (s, 0.8H), 8.09 (d, $J = 1.5$ Hz, 4H), 7.49 (dd, $J = 8.4, 1.8$ Hz, 4H), 7.28 (d, $J = 8.7$ Hz, 4H), 5.34 (s, 0.8H), 4.24 (t, $J = 6.9$ Hz, 4H), 3.44 (s, 0.4H), 2.43 (t, $J = 7.5$ Hz, 0.8H), 2.21 (t, $J = 7.8$ Hz, 3.2H), 1.83-1.92 (m, 4H), 1.58-1.68 (m, 4H), 1.45 (s, 36H), 1.36-1.44 (m, 4H).

The synthesis of the dendrimers

The chloro-bridged iridium dimer: A mixture of main ligand **LG**, iridium chloride trihydrate, 2-ethoxyethanol, and water was refluxed under argon for 24 h. After cooled to room temperature, the precipitate was collected by filtration and washed with water and ethanol. Then the crude product was purified by column chromatography on silica gel with DCM as eluent to give the chloro-bridged iridium dimer.

General synthetic method for the dendrimers: To the solution of the obtained chloro-bridged iridium dimer in 2-ethoxyethanol and chloroform, the ancillary ligand, and sodium carbonate were added. The mixture was stirred at 100 °C for 24 h under argon. After cooling to room temperature, water was added. The mixture was extracted with DCM, and the organic phase was washed with water, dried over anhydrous sodium sulfate, and then filtered. After the solvent was removed, the residue was purified by column chromatography on alkaline alumina with DCM and petroleum as eluent to afford the pure product.

Dendrimer 2D-G1: This compound was obtained as yellow-green solid from the C^N ligand **LG** and O^O ligand acetylacetonate, in a yield of 80%. ¹H NMR (300 MHz, CDCl₃) δ 8.12 (d, *J* = 9.0 Hz, 4H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.54-7.48 (m, 6H), 7.36-7.17 (m, 10H), 6.77 (t, *J* = 7.5 Hz, 2H), 6.54 (t, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 7.8 Hz, 2H), 5.10 (s, 1H), 4.55 (br, 4H), 4.26 (br, 4H), 2.13 (br, 8H), 1.69 (s, 6H), 1.45 (s, 36H). Anal. Calc. for C₇₉H₈₇N₆O₂Ir: C 70.56, H 6.52, N 6.25; Found C 70.31, H 6.57, N 5.92. MALDI-TOF (*m/z*): 1344.6 [M⁺].

Dendrimer 3D-G1: This compound was obtained as yellow-green solid from the C^N ligand **LG** and O^O ligand **1D-Czacac**, in a yield of 81%. ¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 1.8 Hz, 6H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.54-7.48 (m, 4H), 7.31-7.20 (m, 10H), 7.09-7.02 (m, 4H), 6.77 (t, *J* = 7.5 Hz, 2H), 6.54 (t, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 7.8 Hz, 2H), 5.10 (s, 1H), 4.56 (br, 2H), 4.26-4.00 (m, 8H), 3.68-3.44 (m, 2H), 2.22 (s, 6H), 1.95-1.86 (m, 4H), 1.54 (s, 3H), 1.45 (s, 60H). Anal.

Calc. for C₁₀₃H₁₁₈N₇O₂Ir: C 73.71, H 7.09, N 5.84; Found C 73.78, H 7.07, N 5.68.
MALDI-TOF (m/z): 1677.8 [M⁺].

Dendrimer 4D-G1: This compound was obtained as yellow-green solid from the C^N ligand **LG** and O^O ligand **2D-Czacac**, in a yield of 90%. ¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 1.8 Hz, 8H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.54-7.48 (m, 10H), 7.31-7.20 (m, 6H), 7.09-7.02 (m, 6H), 6.89 (t, *J* = 4.8 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 2H), 6.54 (t, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 7.8 Hz, 2H), 5.10 (s, 1H), 4.26-4.00 (m, 8H), 3.68-3.44 (m, 4H), 2.35 (s, 4H), 2.22 (s, 4H), 1.95-1.86 (m, 4H), 1.58 (s, 4H), 1.45 (s, 76H), 1.34 (s, 4H). Anal. Calc. for C₁₂₇H₁₄₉N₈O₂Ir: C 75.82, H 7.47, N 5.57; Found C 75.80, H 7.73, N 5.49. MALDI-TOF (m/z): 2011.1 [M⁺].

References:

1. D. W. Hein, R. J. Alheim and J. J. Leavitt, *J. Am. Chem. Soc.*, 1957, **79**, 427.
2. F. A. Neugebauer, H. Fisher, S. Bamberger and H. O. Smith, *Chem. Ber.*, 1972, **105**, 2686.
3. L. Chen, J. Ding, Y. Cheng, L. Wang, X. Jing and F. Wang, *Tetrahedron Lett.*, 2010, **51**, 4612.

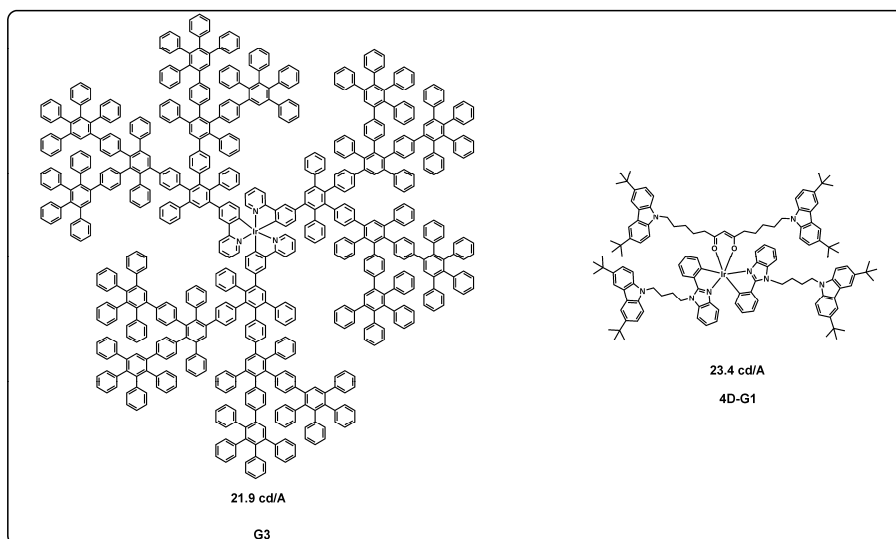


Fig. S1 The comparison of the molecular structure complexity as well as non-doped device performance between 4D-G1 and G3.

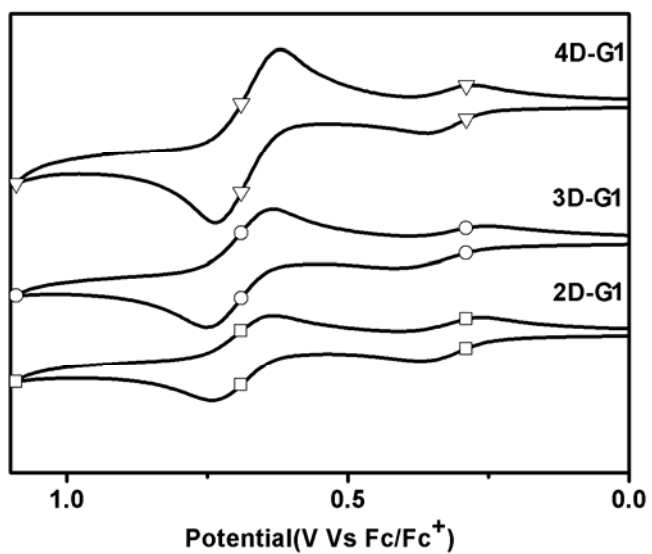


Fig. S2 The cyclic voltammograms of the dendrimers 3D-G1 and 4D-G1 compared with 2D-G1.

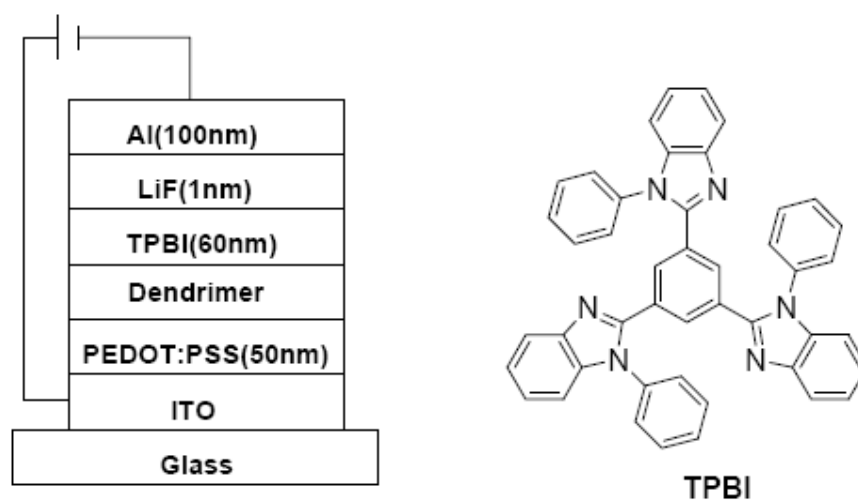


Fig. S3 Schematic diagram of EL device configuration and the molecular structure of the relevant compound used in the device.

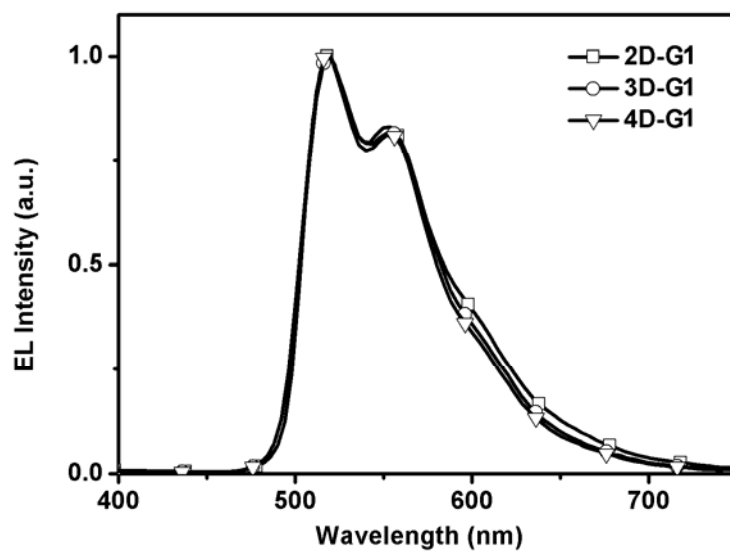


Fig. S4 EL spectra of non-doped devices at a driving voltage of 9 V.

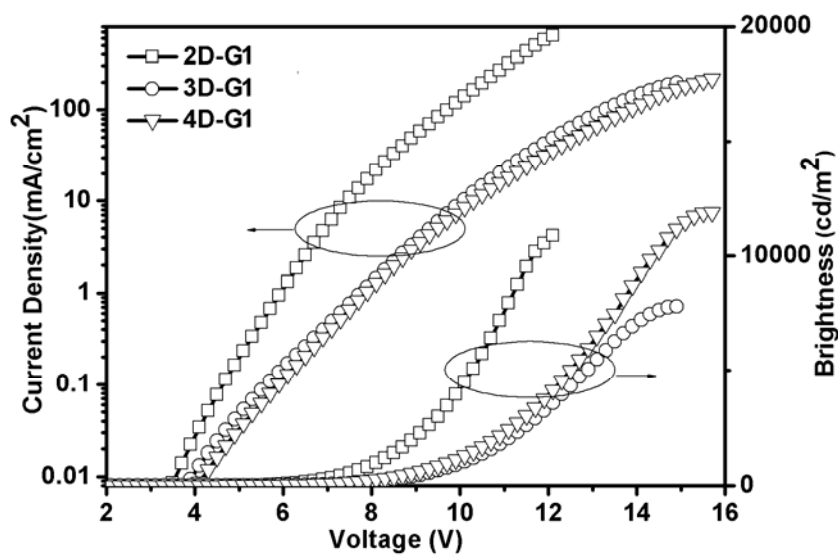


Fig. S5 The current density-voltage-luminescence characteristics for 2D-G1, 3D-G1 and 4D-G1.

Table S1. Photophysical and Electrochemical Properties of the Dendrimers

	λ_{abs} ^[a] [nm]	$\lambda_{\text{em}}/\Phi_{\text{p}}$ ^[b] [nm]	λ_{em} ^[c] [nm]	T_1 ^[d] [eV]	τ_1 ^[e] [μs]	E_{g} ^[f] [eV]	HOMO ^[g] [eV]	LUMO ^[h] [eV]
2D-G1	240, 298, 351, 412, 492	509/0.37	521	2.44	0.04	2.43	-5.11	-2.68
3D-G1	240, 298, 351, 412, 490	510/0.37	520	2.44	0.26	2.43	-5.11	-2.68
4D-G1	240, 298, 351, 412, 492	510/0.37	520	2.44	0.37	2.43	-5.11	-2.68

[a] Measured in CH_2Cl_2 at 298 K at a concentration of 10^{-5} M; [b] Measured in toluene at 298 K at a concentration of 10^{-5} M and an excitation wavelength of 410 nm; [c] Neat-film data measured at 298 K. PL spectra were measured with an excitation wavelength of 409 nm; [d] Estimated from the highest energy peak of the phosphorescence spectra at 77 K; [e] Measured in solid films at 298 K in argon and the lifetimes are obtained by single exponential fit of emission decay curves; [f] E_{g} : optical band gap estimated from the onset of the absorption edge; [g] HOMO = $-e (E^{\text{ox}} + 4.8 \text{ V})$, where E^{ox} was taken from the onset of the first oxidation potential; [h] LUMO = HOMO + E_{g} .

Table S2. Non-Doped Device Performance of the Dendrimers

	$V_{\text{turn-on}}$ [a] [V]	Brightness [b] [cd/m ²]	η_l [b] [cd/A]	η_p [b] [lm/W]	EQE [b] [%]	λ_{max} [nm]	CIE [x, y]
2D-G1	3.8	10890	6.7	6.1	1.9	518	(0.35, 0.60)
3D-G1	3.9	8000	14.3	12.2	4.0	518	(0.35, 0.60)
4D-G1	3.9	11880	23.4	16.3	6.6	518	(0.35, 0.60)

[a] At a brightness of 1 cd/m²; [b] The maximum values for brightness, luminous efficiency (η_l) power efficiency (η_p), and external quantum efficiency (EQE).