Electronic Supplementary Information

Highly efficient single-layer white polymer light-emitting devices employing triphenylamine-based iridium dendritic complexes as orange emissive component

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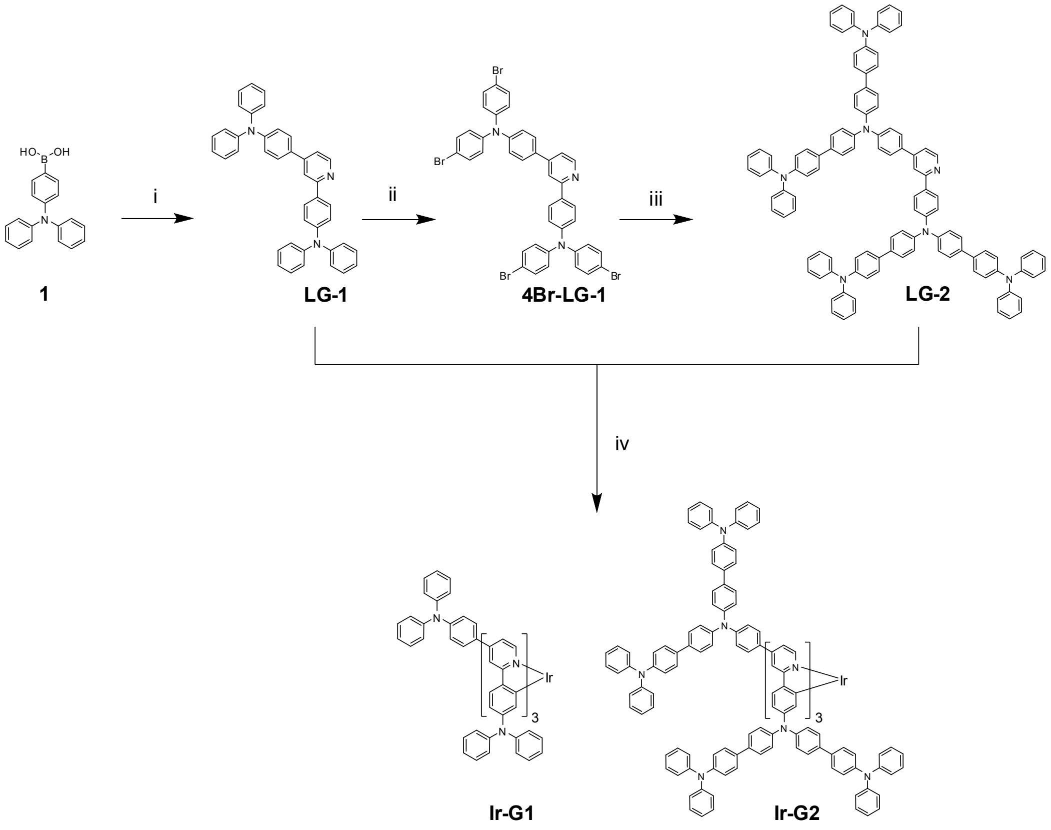
Materials and Synthesis: Starting chemicals and reagents were purchased from commercial sources and used as received without further purification. Solvents for synthesis were purified according to standard procedures prior to use. All reactions were performed under an inner argon atmosphere. Synthesis of 4-(diphenylamino)phenylboronic acid (**1**) was performed following the literature procedure.[1]

^{1}H-NMR and ^{13}C-NMR spectra were measured on a MECUYR-VX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. MALDI-TOF mass spectra were performed on Bruker BIFLEX III TOF mass spectrometer.



Scheme S1. Synthetic routes of the dendritic Ir(III) complexes **Ir-G1** and **Ir-G2**. Reagents and conditions: i) $Pd(PPh_3)_4$, toluene, ethanol, 2M Na_2CO_3, 2,4-dibromopyridine, 110°C; ii) NBS, DMF, 0°C; iii) $Pd(PPh_3)_4$, toluene, 2M Na_2CO_3, **1**; iv) $Ir(acac)_3$, glycerol, 2-(2-methoxyethoxy)ethanol, *o*-dichlorobenzene, 230°C.

Synthesis of **LG-1**: To a well degassed solution of 2,4-dibromopyridine (1.69 g, 7.15 mmol), **1** (5.40 g, 18.60 mmol), and 2M Na_2CO_3 (45 mL, 22.50 mmol) in a mixed solvents of toluene (135 mL) and ethanol (45 mL), $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol) was added. The resulting mixture was stirred and heated to reflux at 110°C for 48 h under argon atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure and taken up with CH_2Cl_2. The organic layer was washed with brine and water sequentially and dried over anhydrous Na_2SO_4. After filtered, the solvent was evaporated to dryness and subjected to column chromatography on silica gel with petroleum/ethyl acetate (5:1, v/v) as the eluent to give the product (3.53 g) in a yield of 87% as off white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.65 (d, *J* = 5.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.83 (s, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 5.1 Hz, 1H), 7.29-7.24 (m, 8H), 7.16 (d, *J* = 7.5 Hz, 12H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 162.8, 155.1, 154.2, 152.8, 152.6, 136.8, 134.8, 134.6, 133.2, 133.1, 130.3, 130.1, 128.9, 128.6, 128.3, 124.3, 122.7; MALDI-TOF: calcd for $C_{41}H_{31}N_3$, 565.7; found, 565.05. Anal. calcd for $C_{41}H_{31}N_3$: C 87.05, H 5.52, N 7.43; found: C 86.84, H 5.58, 7.33.

Synthesis of **4-Br-LG-1**: A solution of NBS (2.62 g, 14.74 mmol) in DMF (30 mL) was slowly added to a mixture of **LG-1** (1.99 g, 3.51 mmol) in DMF (30 mL) with several drops of acetic acid at 0°C under argon atmosphere. The resulting mixture was allowed to slowly warmed up to room temperature to stir for another 18 h. To the solution, H_2O (300 mL) was added and then extracted with CH_2Cl_2 (300 mL). The organic layer was washed with $NaHCO_3$ saturated solution, and dried over anhydrous Na_2SO_4. After removal of solvent, the resulting solid was recrystallized from CH_2Cl_2 and ethanol twice to give light yellow powder (2.47 g) in a yield of 80%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.67 (d, *J* = 5.1 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.82 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.40-7.35 (m, 9H), 7.15 (d, *J* = 8.7 Hz, 4H), 7.00-6.97 (m, 8H); ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 162.07, 154.7, 153.5, 152.9, 151.0, 150.8, 138.9, 137.5, 137.4, 133.0, 131.0, 130.8, 128.6, 124.2, 122.5, 121.3, 121.0; MALDI-TOF: calcd for $C_{41}H_{27}Br_4N_3$, 881.29; found, 881.65.

Synthesis of **LG-2**: According to the similar procedure to the preparation of **LG-1**, **LG-2** was synthesized by the suzuki-cross coupling between **4Br-LG-1** and **1** using toluene as solvent to give a yield of 86%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.67 (d, *J* = 5.4 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.87 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52-7.45 (m, 16H), 7.39 (d, *J* = 5.1 Hz, 1H), 7.28-7.20 (m, 32H), 7.14 (d, *J* = 9.0 Hz, 20H), 7.04 (t, *J* = 7.5 Hz, 8H); ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 153.8, 152.6, 151.9, 150.8, 140.9, 139.5, 134.2, 132.9, 132.3, 130.1, 129.9, 129.3, 129.0, 128.1, 127.9; MALDI-TOF: calcd for $C_{113}H_{83}N_7$, 1538.92; found, 1538.33; Anal. cacld for $C_{113}H_{83}N_7$: C 88.19, H 5.44, N 6.37; found: C 87.70, H 5.50, N 6.33.

Preparation of **Ir-G1**: **LG-1** (0.96 g, 1.70 mmol) and $Ir(acac)_3$ (0.25 g, 0.50 mmol) were added to a 50 mL of round-necked flask. Thereafter, distilled *o*-dichlorobenzene (5 mL) was first added to the mixture. After the ligand was completely dissolved, 2-(2-methoxyethoxy)ethanol (10 mL) and glycerol (20 mL) were added to the flask. The mixture was refluxed at 230^{o}C for 24 h. After completion, *o*-dichlorobenzene was removed under reduced pressure. The mixture was poured into H_2O and extracted with CH_2Cl_2. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified through column chromatography with petroleum/CH_2Cl_2 (1:1, v/v) as eluent to afford **Ir-G1** (0.95 g) as red powder with a yield of 95%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.85 (s, 3H), 7.61 (s, 3H), 7.52 (d, *J* = 8.0 Hz, 6H), 7.38 (d, *J* = 9.0 Hz, 3H), 7.29 (d, *J* = 9.0 Hz, 14H), 7.16-7.09 (m, 28H), 6.98 (s, 6H), 6.85-6.80 (m, 16H), 6.64 (s, 5H), 6.25 (d, *J* = 7.8 Hz, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 166.57, 149.19, 148.44, 147.91, 147.49, 147.28, 138.06, 131.42, 130.61, 129.67, 128.81, 127.85, 125.77, 125.01, 124.62, 123.85, 123.06, 122.37, 118.51, 114.85; MALDI-TOF: calcd for $C_{123}H_{90}IrN_9$, 1886.31; found, 1886.0; Anal. calcd for $C_{123}H_{90}IrN_9$: C 78.32, H 4.81, N 6.68; found: C 78.28, H 4.88, N 6.86.

Preparation of **Ir-G2**: **Ir-G2** was prepared following the procedure described for **Ir-G1**. The product was obtained as orange-red powder (0.84 g) with a yield of 98%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.89 (s, 3H), 7.67 (s, 3H), 7.59 (d, *J* = 9.0 Hz, 6H), 7.51-7.43 (m, 28H), 7.25 (d, *J* = 6.9 Hz, 80H), 7.20-7.11 (m, 46H), 7.04-6.91 (m, 58H), 6.81 (d, *J* = 8.7 Hz, 16H), 6.25-6.20 (m, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.97, 147.18, 146.57, 146.13, 136.08, 135.23, 134.66, 129.52, 127.79, 127.63, 127.42, 126.96, 125.33, 124.61,124.39, 124.22, 123.15, 122.83; MALDI-TOF: calcd for $C_{339}H_{246}IrN_{21}$, 4805.94; found, 4805.8; Anal. calcd for $C_{339}H_{246}IrN_{21}$: C 84.72, H 5.16, N 6.12; found: C 84.47, H 5.31, N 6.11.

Photophysical and Electrochemical Measurements

Uv-visible absorption spectra were conducted on a Shimadzu UV-2500 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The solution PL quantum efficiencies were measured by a relative method using *fac*-Ir(ppy)$_3$ (Φ_{FL} = 0.4, in toluene).[2] The lifetimes of phosphorescence in toluene solutions were measured by exciting the materials with 350 nm from a Hydrogen lamp on a FLS 920 Combined steady-state and Life-time spectrometer. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) with a CHI voltammetric analyzer. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min^{-1} from room temperature to 400 °C under a flow of nitrogen. The glass transition temperature (T_g) was determined from the second heating scan. The T_g of **Ir-G1** appear at 217.2°C which is as high as that of Wong's second-generation Ir(III) dendrimer (T_g)[3] and no T_g was detected for **Ir-G2**.

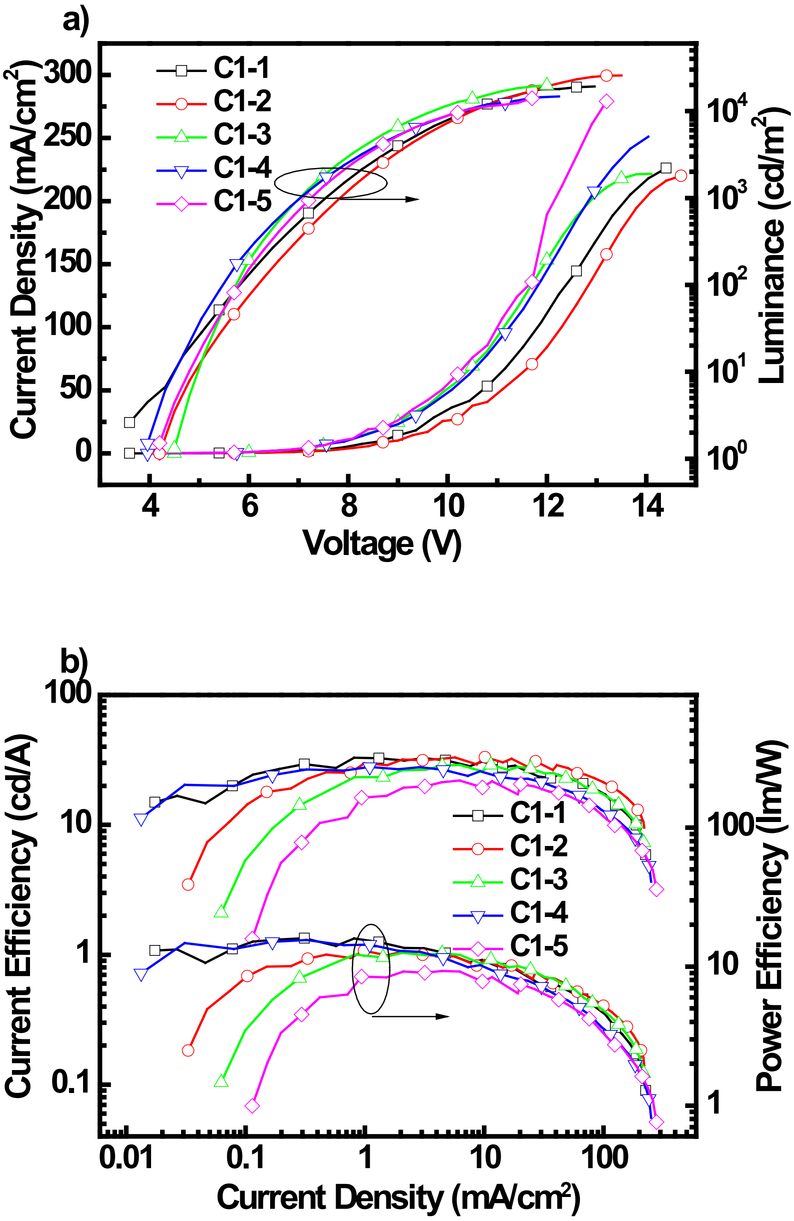
Table S1. The photophysical and electrochemical data of the dendrimers.

	λ_{abs} ^{a} (nm)	λ_{em} ^{b} (nm)	λ_{em} ^{c} (nm)	Φ_{FL} ^{b,d} (%)	Φ_{FL} ^{c,e} (%)	τ ^{f} (μs)	HOMO ^{g}/LUMO ^{g} (eV) $_{exp}$
Ir-G1	304 (0.7)，376 (1.2)	561	571	29	20	0.11	4.72/2.39
Ir-G2	308 (2.3)，370 (3.2)	562	568	40	37	0.10	4.92/2.48

[a] Measured in toluene at 298 K with a concentration of 10^{-5} M. [b] Measured in toluene at 298 K with a concentration of 10^{-5} M and the excitation wavelength of 380 nm. [c] Neat film data measured at 298 K, which were prepared by drop-coating on quartz substrates with the excitation wavelength of 380 nm for the PL spectra. [d] Measured with a relative method at 298 K in N$_2$-saturated toluene solutions using Ir(ppy)$_3$ (Φ = 40% in toluene) as the calibration standard and the excitation wavelength of 360 nm. [e] Measured with an integrating sphere

under an excitation wavelength of 380 nm. [f] Measured in toluene with a concentration of 10^{-6} M at 298 K in the air and the lifetime were obtained by monoexponential fit of emission decay curves for **Ir-G1** and **Ir-G2**. [g] The HOMO energies were estimated from the onset of oxidation potentials and the LUMO energies were deduced from the energy gap (E_g) and HOMO.

Current density–voltage–luminance characteristics and efficiencies versus current density curves for the Devices C and D based on Ir-G1.



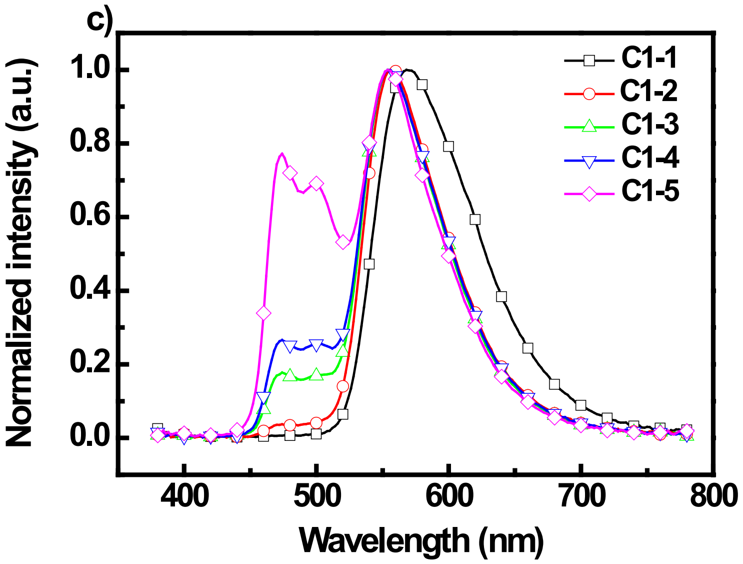
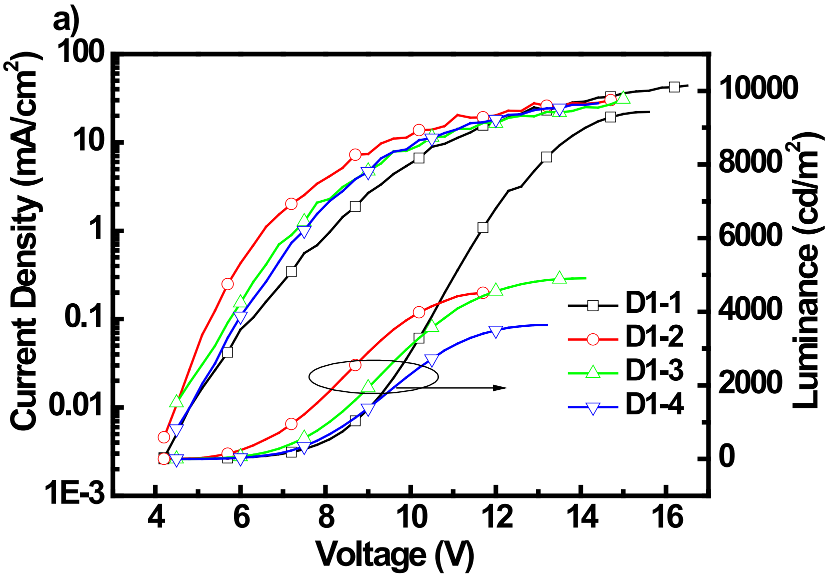


Fig. S1 Characteristics of devices C with the structure of ITO/PEDOT:PSS (P4083, 50 nm)/ PVK (72 wt%): OXD-7 (21 wt%): Ir dopant (FIrpic 7 wt%; FIrpic: **Ir-G1** = 1:1, 5:1, 15:1, 30:1, 40:1) (70 nm)/Ba (4 nm)/Al (150 nm). a) Current density-voltage-luminance characteristics. b) Current efficiency and power efficiency *versus* current density curves. c) EL spectra recorded at 1 mA cm^{-2}.



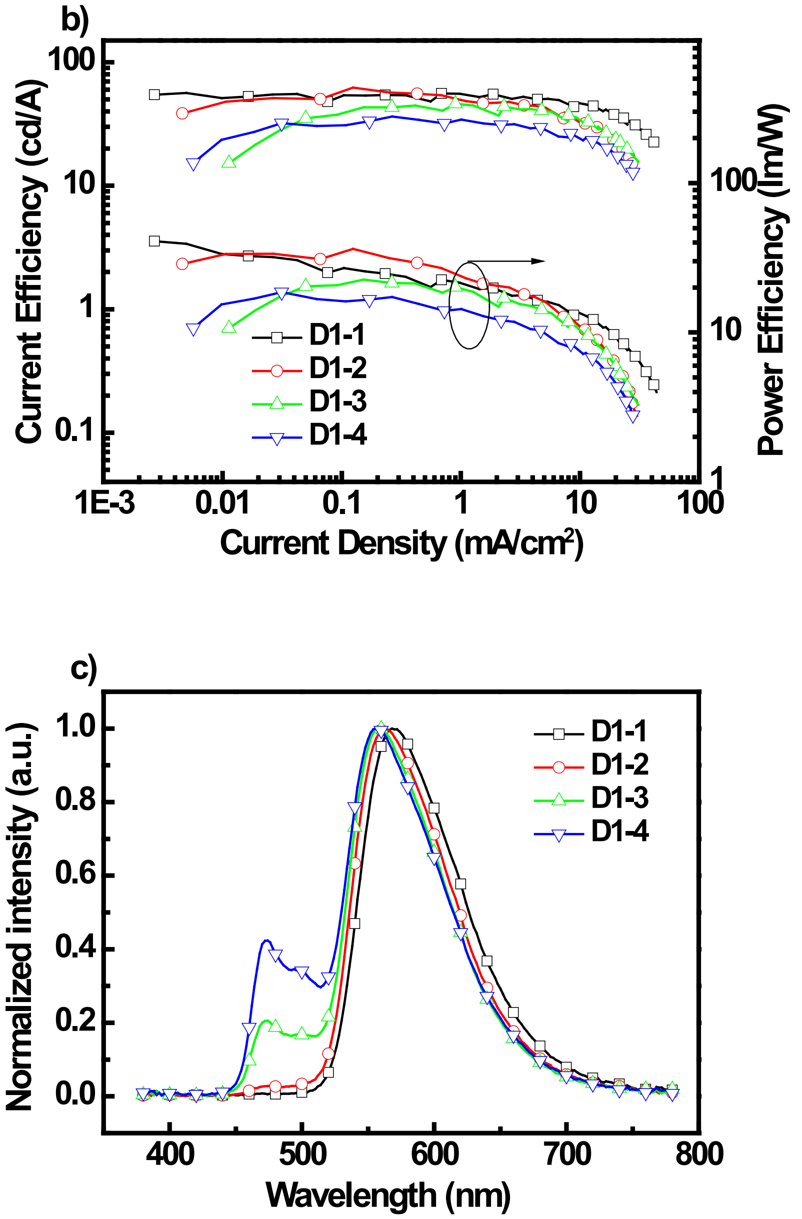


Fig. S2 Characteristics of devices D with the structure of ITO/PEDOT:PSS (P8000, 50 nm)/ PVK (72 wt%): OXD-7 (21 wt%): Ir dopant (FIrpic 7 wt%; FIrpic: **Ir-G1** = 1:1, 5:1, 15:1, 30:1) (70 nm)/Ba (4 nm)/Al (150 nm). a) Current density-voltage-luminance characteristics. b) Current efficiency and power efficiency *versus* current density curves. c) EL spectra recorded at 1 mA cm^{-2}.

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[2] K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.,* 1985, **107**, 1431.

[3] G. Zhou, W.-Y. Wong, B. Yao, Z. Xie, L. Wang, *Angew. Chem. Int. Ed.,* 2007, **46**, 1149.