Electronic Supplementary Information

Iridium phosphors with peripheral triphenylamine encapsulation: highly efficient solution-processed red electrophosphorescence

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Experimental Section

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. 3-bromo-*N*,*N*-diphenylaniline and bis(4-bromophenyl)amine were prepared according to previously reported procedures.[1]

N,N-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline ***(1)***: To a solution of 3-bromo-*N*,*N*-diphenylaniline (3.43 g, 10.5 mmol) in tetrahydrofuran (THF, 110 mL) at -78 °C, *N*-butyllithium (2.3 M in hexane; 5.5 mL, 12.6 mmol) was added dropwise under argon. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.1 mL, 14.7 mmol) was added to the mixture after the stirring was continued for one hour. The resulting mixture was kept stirring at -78 °C for further one hour before it was warmed to room temperature slowly. Thereafter, the reaction mixture was quenched with water and extracted with diethyl ether. The combined organic phases was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum/ ethyl acetate (6:1, v/v) to give a white solid. Yield: 3.12 g (80%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.50 (d, *J* = 6.9 Hz, 2H), 7.26-7.18 (m, 6H), 7.08-6.96 (m, 5H), 1.35 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.89, 147.19, 131.04, 129.67, 129.06, 128.78, 128.26, 123.62, 122.23, 83.68, 24.78; MALDI-TOF: Calcd. for $C_{24}H_{26}BNO_2$ 371.3; Found 371.0.

$N^{4'}$-(3'-(diphenylamino)biphenyl-4-yl)-N^3,N^3-diphenylbiphenyl-3,4'-diamine (**2**): To a well degassed solution of bis(4-bromophenyl)amine (2.98 g, 9.1 mmol), **1** (7.79 g, 21.0 mmol), and 2M Na_2CO_3 (18 mL, 36 mmol) in toluene (54 mL), $Pd(PPh_3)_4$ (0.63 g, 0.55 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 chloroform ($CHCl_3$). 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/$CHCl_3$ (2:1, v/v) as the eluent to afford a white solid. Yield: 4.65 g (78%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.38 (s, 2H), 7.25-7.20 (m, 14H), 7.15-7.11 (m, 14H), 7.06-7.00 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.20, 147.75, 141.74, 133.45, 129.54, 129.18, 127.84, 124.10, 122.65, 122.44, 122.10, 120.85, 117.88; MALDI-TOF: Calcd. for $C_{48}H_{37}N_3$ 655.8; Found 655.3.

*$N^{4'}$-(3-bromophenyl)-$N^{4'}$-(3'-(diphenylamino)biphenyl-4-yl)-N^{3},N^{3}-diphenylbiphenyl-3,4'-diamine (**3**)*: Potassium *tert*-butoxide (0.89 g, 8.0 mmol) was added to a 100 mL round-necked flask containing **2** (3.48 g, 5.3 mmol), 1-bromo-3-iodobenzene (1.81 g, 6.4 mmol) and CuI (0.10 g, 0.53 mmol) under a flow of argon. And then (±)-*trans*-1,2-diaminocyclohexane (127 μL, 1.06 mmol) and 1,4-dioxane (20 mL) were added with syringe in sequence. The mixture was heated to 110°C with good stirring overnight under argon atmosphere. After cooling, H_2O (100 mL) was added and the mixture was extracted with $CHCl_3$. The organic layer was combined and washed with H_2O and then dried over anhydrous Na_2SO_4. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum/$CHCl_3$ (2:1, v/v), then the crude product was recrystallized from dichloromethane (CH_2Cl_2) and ethanol to give a white powder. Yield: 3.65 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.30 (s, 2H), 7.25-7.21 (m, 18H), 7.16-7.11 (m, 12H), 7.04-7.01 (s, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.90, 146.67, 130.23, 128.52, 124.58, 123.73; MALDI-TOF: Calcd. for $C_{54}H_{40}BrN_3$ 810.8; Found 811.0.

*$N^{4'}$-(3'-(diphenylamino)biphenyl-4-yl)-N^{3},N^{3}-diphenyl-$N^{4'}$-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)biphenyl-3,4'-diamine (**4**)*: Compound **4** was synthesized following the same procedure for **1** to give a white solid. Yield: 1.32 g (70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.50 (s, 2H), 7.34-7.25 (m, 19H), 7.20-7.13 (m, 9H), 7.05-7.01 (m, 9H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.22, 147.76, 147.06, 146.77, 141.68, 134.54, 131.41, 130.17, 129.52, 129.18, 128.93,

128.65, 127.63, 124.13, 123.56, 122.67, 122.27, 120.97, 83.77, 24.81; MALDI-TOF: Calcd. for $C_{60}H_{52}BN_3O_2$ 857.9; Found 857.3.

3,3'-(pyridine-2,4-diyl)bis(N,N-diphenylaniline) ***(L1)***: To a well degassed solution of 2,4-dibromopyridine (2.11 g, 8.9 mmol), **1** (9.2 g, 24.8 mmol), and 2M Na_2CO_3 (26 mL, 52 mmol) in a mixed solvents of toluene (80 mL) and ethanol (26 mL), $Pd(PPh_3)_4$ (0.63 g, 0.55 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/$CHCl_2$ (2:1, v/v) as the eluent to afford a white solid. Yield: 3.88 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.61 (s, 2H), 7.34-7.25 (m, 12H), 7.13-7.02 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.61, 149.78, 148.91, 148.59, 148.28, 147.68, 147.40, 140.69, 139.49, 129.85, 129.56, 129.29, 129.14, 124.96, 124.30, 124.02, 123.10, 122.81, 122.61, 121.90, 121.56, 120.94, 120.16, 118.65; MALDI-TOF: Calcd. for $C_{41}H_{31}N_3$ 565.7; Found 566.2; Anal. Calcd. for $C_{41}H_{31}N_3$: C 87.05, H 5.52, N 7.43; Found: C 87.48, H 5.16, N 7.24.

$N^{4'}$,$N^{4''}$-(3,3'-(pyridine-2,4-diyl)bis(3,1-phenylene))bis($N^{4'}$-(3'-(diphenylamino)biphenyl-4-yl)-N^3,N^3-diphenylbiphenyl-3,4'-diamine) ***(L2)***: The dendritic ligand **L2** was synthesized according to the similar procedure for the preparation of **L1**. Yield: 1.32 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.61 (s,

2H), 7.37-7.34 (m, 10H), 7.31-7.29 (m, 6H), 7.26-7.23 (m, 20H), 7.23-7.20 (m, 10H), 7.12-7.10 (m, 20H), 7.01-6.99 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.42, 149.80, 148.84, 148.19, 147.69, 146.83, 146.55, 141.55, 141.43, 140.69, 139.57, 135.40, 134.90, 129.53, 129.16, 127.83, 127.72, 125.35, 124.09, 123.19, 122.66, 122.23, 121.45, 120.97, 120.26, 118.67; MALDI-TOF: Calcd. for $C_{113}H_{83}N_7$ 1538.9; Found 1538.6; Anal. Cacld. for $C_{113}H_{83}N_7$: C 88.19, H 5.44, N 6.37; Found: C 87.75, H 5.63, N 6.00.

*Preparation of **R1***: **L1** (1.32 g, 2.34 mmol) and $Ir(acac)_3$ (0.34 g, 0.69 mmol) were added to a 50 mL round-necked flask. Thereafter, distilled *o*-dichlorobenzene (6 mL) was first added to the mixture. After the ligand was completely dissolved, 2-(2-methoxyethoxy)ethanol (12 mL) and glycerol (18 mL) were added to the flask. The mixture was refluxed at 230 ^{o}C for 48 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 (3:4, v/v) as eluent to afford **R1** as red powder. Yield: 1.21 g with a yield of 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (s, 3H), 7.58 (d, *J* = 7.5 Hz, 3H), 7.46 (d, *J* = 7.5 Hz, 3H), 7.29 (s, 3H), 7.23-7.14 (m, 30H), 7.10-7.07 (m, 12H), 7.02-6.99 (m, 24H), 6.83 (d, *J* = 7.8 Hz, 6H), 6.71 (d, *J* = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.28, 161.09, 157.72, 148.94, 148.39, 148.10, 147.66, 144.97, 139.23, 138.07, 130.17, 130.02, 129.26, 129.04, 124.78, 124.21, 123.53, 123.01, 122.75, 122.01, 121.39, 121.10, 120.63, 117.38; MALDI-TOF: Calcd. for $C_{123}H_{90}IrN_9$ 1886.3; Found 1886.5; Anal. Calcd. for $C_{123}H_{90}IrN_9$: C 78.32, H 4.81, N 6.68; Found: C 78.32, H 4.67, N 6.59.

R2: This compound was prepared according to the procedure for the synthesis of **R1**. Yield: 0.34 g (39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 3H), 7.52-7.51 (m, 6H), 7.40-7.30 (m, 60H), 7.27-7.17 (m, 60H), 7.15-7.03 (m, 30H), 6.81-6.79 (m, 36H), 6.62-6.43 (m, 36H), 6.24-6.15 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.45, 148.06, 147.89, 147.30, 146.01, 144.36, 142.08, 141.29, 139.27, 136.31, 133.87, 129.43, 128.25, 127.72, 125.49, 124.73, 124.40, 122.91, 122.56, 121.90, 121.14, 117.72; MALDI-TOF: Calcd. for $C_{339}H_{246}IrN_{21}$ 4805.9; Found 4805.6; Anal. Calcd. for $C_{339}H_{246}IrN_{21}$: C 84.72, H 5.16, N 6.12; Found: C 84.32, H 4.81, N 5.67.

Measurements and Characterization: ^{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. Mass spectra were measured on a Voyager-DE STR MALDI-TOF instrument, using α-cyano-4-hydroxyclinnamic acid (CHCA) as a matrix. UV-vis absorption spectra were conducted on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescent (PL) spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The solid state PL quantum efficiencies (PLQYs) were measured using an integration sphere. The measurements follow the method that reported by Prof. R. H. Friend.[2] For comparison, we also tested the solid state PLQYs of $Ir(piq)_3$ under the same condition. The values in neat film and the same polymer matrix were 3% and 46%, respectively.[3] All PLQYs are ± 5%. The lifetimes of phosphors in thin films were measured by exciting the materials from a Hydrogen lamp on a FLS 920 Combined steady-state and life-time spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 ^{o}C min^{-1} from room temperature to 400 ^{o}C under a flow of nitrogen. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 15 ^{o}C min^{-1} from 25 to 800 ^{o}C. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium–ferrocene (Fc$^+$/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s^{-1}. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

1. Z. H. Li and M. S. Wong, *Org. Lett.;* 2006, **8**, 1499.

2. (a) J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.,* 1997, **9**, 230; (b) Y.-C. Chiu, J.-Y. Hung, Y. Chi, C.-C. Chen, C.-H. Chang, C.-C. Wu, Y.-M. Cheng, Y.-C. Yu, G.-H. Lee and P.-T. Chou, *Adv. Mater.,* 2009, **21**, 2221.

3. (a) H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, *Coord. Chem. Rev.,* 2011, **255**, 2622; (b) J. C. Deaton, R. H. Young, J. R. Lenhard, M. Rajeswaran and S. Huo, *Inorg. Chem.,* 2010, **49**, 9151.

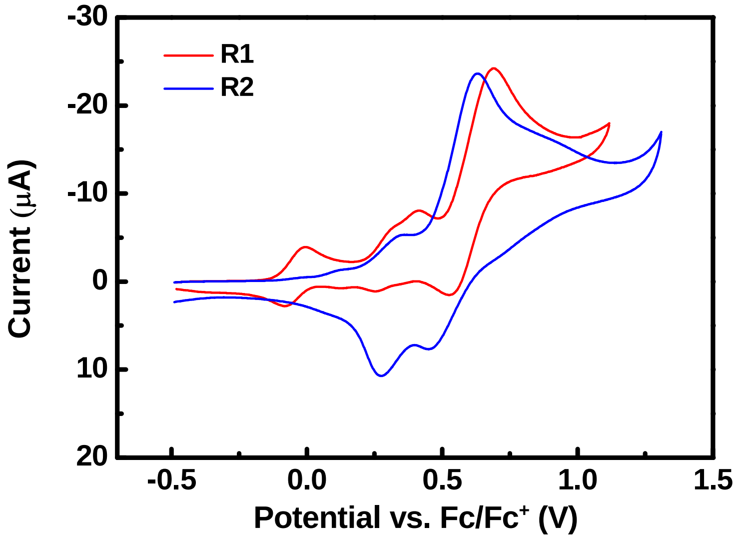

Fig. S1 Cyclic voltammograms of **R1** and **R2** in CH_2Cl_2 for oxidation.

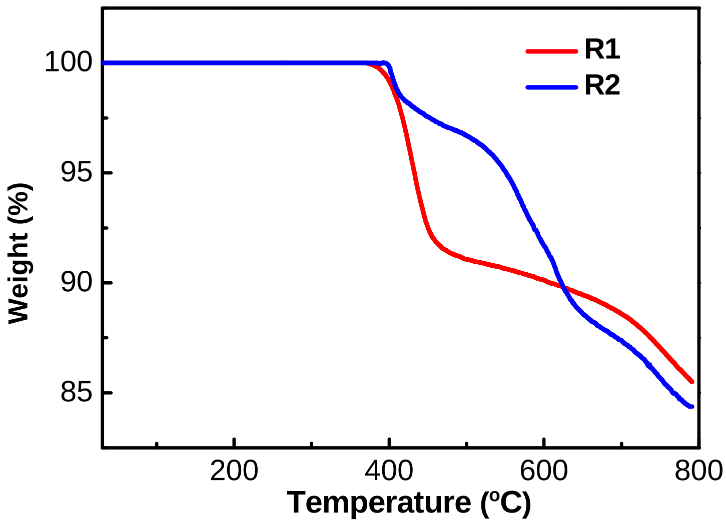

Fig. S2 TGA thermograms of **R1** and **R2**.

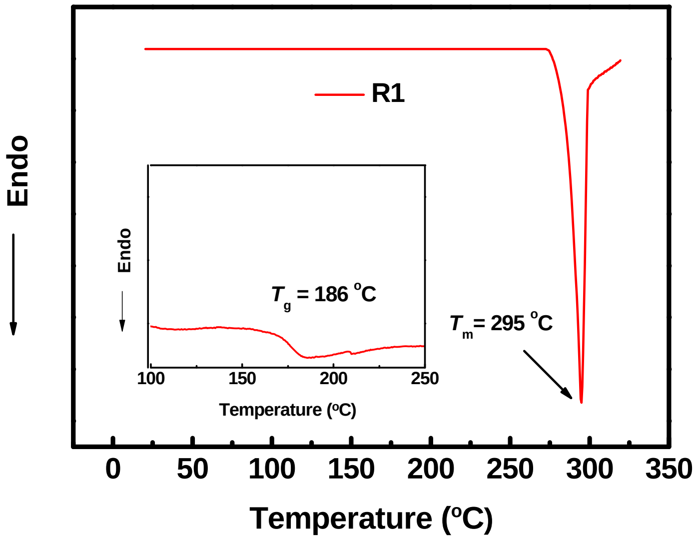

Fig. S3 DSC thermogram of **R1**.

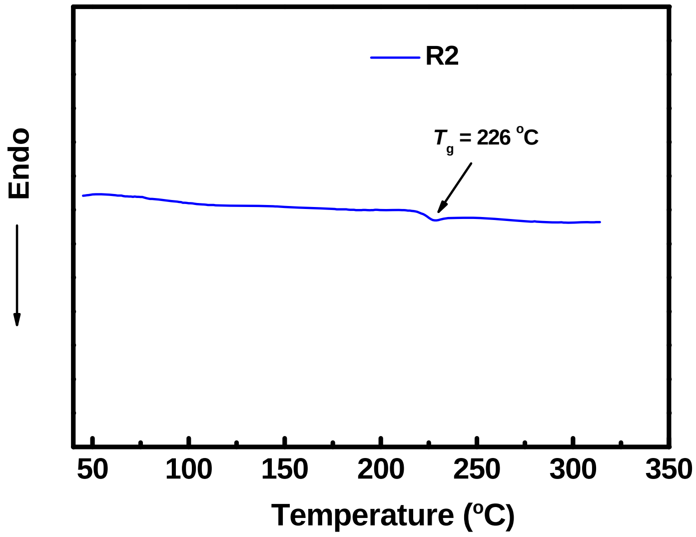

Fig. S4 DSC thermogram of **R2**.

Device Fabrication: patterned indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 15-20 ohm/square underwent a wet-cleaning course in an ultrasonic bath, beginning with acetone, followed by detergent, deionized water, and isopropanol. After oxygen-plasma treatment, a 50 nm thick anode buffer layer of PEDOT:PSS (Bayer AG) film was spin-cast on the ITO substrate and dried by baking in vacuum oven at 80 °C overnight. The emitting layer was prepared by spin-coating from xylene solution of the iridium complexes on top of the PEDOT layer, then annealed at 120 °C for 20 min. Ba (4 nm) and Al (150 nm) were evaporated with a shadow mask successively at a base pressure of $3*10^{-4}$ Pa. The thickness of the evaporated cathode was monitored by a quartz-crystal thickness/ratio monitor (Sycon model STM-100/MF). The cross-sectional area between the cathode and anode defined the pixel size of 19 mm^2. Except for the spin coating of the PEDOT layer, all the processes were carried out in the controlled atmosphere of a nitrogen dry-box (Vacuum Atmosphere Co.) containing less than 1 ppm oxygen and moisture. All measurements were carried out at room temperature under ambient conditions.

Table S1 Typical performances of devices I-IV.

Device	$V_{turn-on}$[a] [V]	L_{max}[b] [cd m^{-2}]	η_c[c] [cd A^{-1})]	η_p[d] [lm W^{-1}]	$\eta_{ext.}$[e] [%]	λ_{em} [nm]	CIE[f]
I	5.6	2468	10.6	5.9	13.8	618	(0.60,0.40)
II	8.0	1935	8.7	2.3	10.9	608	(0.59,0.40)
III	7.5	1758	9.4	3.0	11.7	612	(0.60,0.40)
IV	6.0	2116	12.2	5.1	15.3	616	(0.60, 0.39)

[a] At a brightness of 1 cd m^{-2}. [b] Maximum luminance. [c] Maximum current efficiency. [d] Maximum power efficiency. [e] Maximum external quantum efficiency. [f] CIE at 12V.

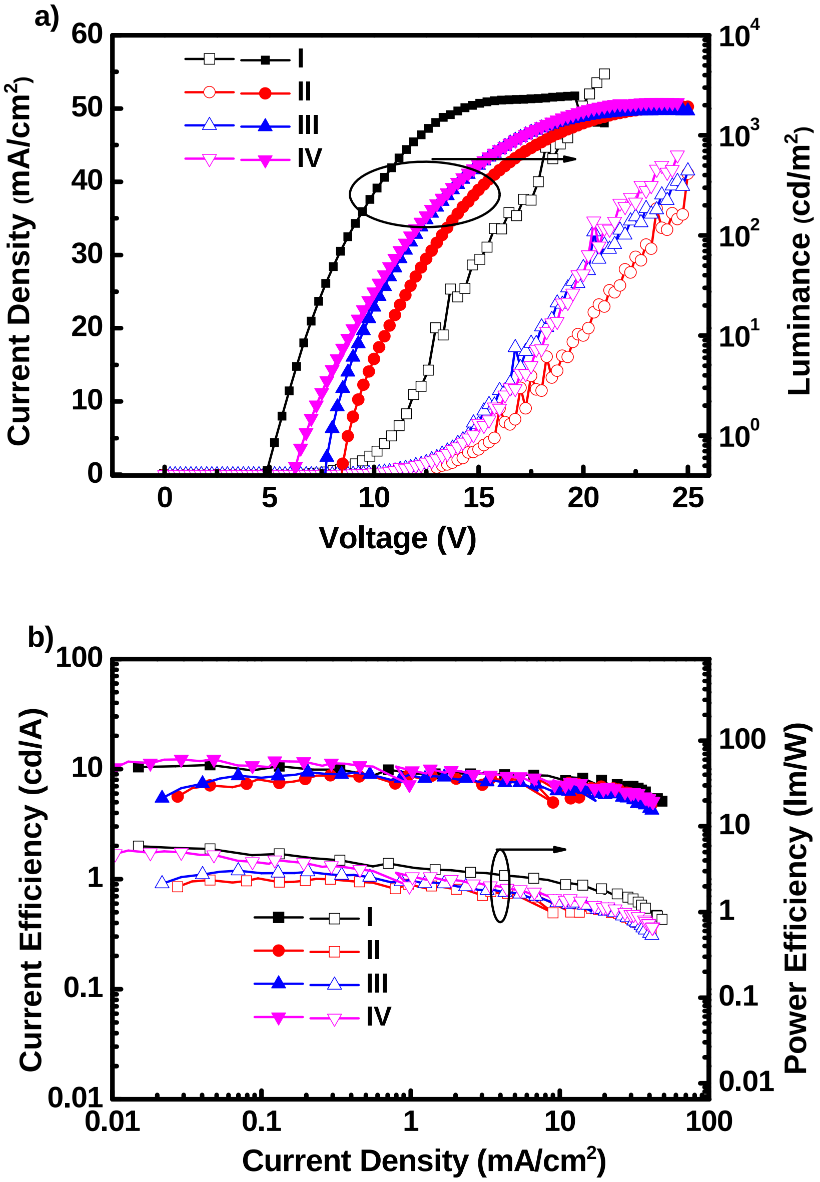

Fig. S5 a) Current density-voltage-luminance characteristics. b) Current efficiency and power efficiency versus current density curves for devices I-IV.