

Supporting Information

A Versatile Efficient One-step Approach for Carbazole/Pyridine Hybrid Molecules: Highly Efficient Host Materials for Blue Phosphorescent OLEDs

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Experimental

General Information

¹H NMR and ¹³C 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 ZAB 3F-HF mass spectrophotometer and Bruker autoflex matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF). UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min⁻¹ from -40 °C to 300 °C under argon. The glass transition temperature (T_g) was determined from the second heating scan. 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 20 °C min⁻¹ from 25 to 600 °C. Cyclic voltammetry (CV) was measured in nitrogen-purged dichloromethane for oxidation scan, with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (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.

Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

Computational details. The geometrical and electronic properties of **1-7** were performed with the Gaussian 03 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) with the 6-31G(d) atomic basis set.³² The triplet states ΔE (T_1-S_0) were calculated using time dependent density functional theory (TD-DFT) calculations with B3LYP/6-311+g(d). Molecular orbitals were visualized using Gaussview.

Device fabrication and measurement.

The hole-injection material MoO₃, hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), hole transporting and triplet exciton block layer TCTA (tris(4-(9H-carbazol-9-yl)phenyl)amine) and electron-transporting materials TmPyPb (1,3,5-tri(m-pyrid-3-ylphenyl)benzene) were commercially available. Commercial indium tin oxide (ITO) coated glass with sheet resistance of 10 Ω per square was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O₃ for 2 min. Then the sample was transferred to the deposition system. 5 nm of MoO₃ was firstly deposited to ITO substrate, followed by NPB, TCTA, emissive layer, 35 nm TmPyPb, and 2 nm CsCO₃. Finally, a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminum were sequentially deposited onto the substrate in the vacuum of 10⁻⁶ Torr to construct the device. The L-V-J of EL devices was measured with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

Synthesis

2,6-di(9H-carbazol-9-yl)pyridine (1) 2,6-CzPy.

A mixture of carbazole (0.96 g, 5.7 mmol), 2, 6- difluoropyridine (0.30 g, 2.6 mmol), and K_2CO_3 (2.2 g, 15.6 mmol) in dimethyl sulfoxide (DMSO) (10 mL) was stirred at 150°C for 12 h under an argon atmosphere. After cooling to room temperature, the mixture was poured into water, filtered, and then purified by column chromatography over silica gel with CH_2Cl_2 /petroleum ether as the eluent to afford a white solid. Yield: 95%.

1H NMR (300 MHz, $CDCl_3$): δ ppm 8.16 (d, 4H, $J=6.30$ Hz), 8.11 (d, 1H, $J=5.70$ Hz), 8.05 (d, 4H, $J=6.30$ Hz), 7.65 (d, 2H, $J=6.00$ Hz), 7.44 (t, 4H, $J=6.00$ Hz), 7.35 (t, 4H, $J=5.70$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 151.1, 139.8, 139.0, 125.8, 124.1, 120.7, 119.6, 114.4, 111.4; GC-MS (m/z): 409.25 [M^+]; Anal. Calcd. For $C_{29}H_{19}N_3$: C 85.06, H 4.68, N 10.26%; Found: C 85.38, H 4.61, N 10.26%.

3,5-di(9H-carbazol-9-yl)pyridine (2) 3,5-CzPy.

(2) was prepared according to a similar procedure to (1), using 3, 5- difluoropyridine to replace 2, 6- difluoropyridine. Yield: 87%.

1H NMR (300 MHz, $CDCl_3$): δ ppm 9.03 (s, 2H), 8.17 (t, 5H, $J=4.50$ Hz), 7.52 (t, 4H, $J=4.80$ Hz), 7.47 (d, 4H, $J=4.50$ Hz), 7.36 (t, 4H, $J=4.50$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 146.62, 140.39, 135.61, 131.98, 126.52, 124.00, 121.03, 120.69, 109.30; GC-MS (m/z): 409.11 [M^+]; Anal. Calcd. For $C_{29}H_{19}N_3$: C 85.06, H 4.68, N 10.26%; Found: C 84.74, H 4.68, N 10.18%.

2,4-di(9H-carbazol-9-yl)pyridine (3) 2,4-CzPy.

(3) was prepared according to a similar procedure to (1), using 2,4- difluoropyridine as starting material. Yield: 88%.

1H NMR (300 MHz, $CDCl_3$): δ ppm 8.97 (d, 1H, $J=5.4$ Hz), 8.15 (t, 4H, $J=7.5$ Hz), 7.95 (d, 3H, $J=7.5$ Hz), 7.68 (d, 3H, $J=8.10$ Hz), 7.49 (t, 4H, $J=8.10$ Hz), 7.36 (t, 4H, $J=7.20$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 150.55, 138.91, 126.05, 125.92, 124.10, 123.90, 120.90, 120.17, 119.80, 117.59, 114.77, 110.81, 109.39; MALDI-TOF Mass (m/z): 410.2 [$M + H$] $^+$; Anal. Calcd. For $C_{29}H_{19}N_3$: C 85.06, H 4.68, N 10.26%; Found: C 85.10, H 4.67, N 10.15%.

2,3-di(9H-carbazol-9-yl)pyridine (4) 2,3-CzPy.

(4) was prepared according to a similar procedure to **(1)**, using 2, 3- difluoropyridine replace the 2, 6- difluoropyridine. Yield: 85%.

¹H NMR (300 MHz, CDCl₃): δ ppm 8.87 (d, 1H, *J*=3.60 Hz), 8.23 (d, 1H, *J*=7.80 Hz), 7.83-7.76 (m, 4H), 7.66 (t, 1H, *J*=7.50 Hz), 7.27 (t, 2H, *J*=6.60 Hz), 7.09-6.99 (m, 10H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 148.23, 139.00, 125.72, 125.51, 123.11, 120.56, 120.42, 120.08, 119.73, 110.42, 109.13; MALDI-TOF Mass (*m/z*): 410.1 [M + H]⁺; Anal. Calcd. For C₂₉H₁₉N₃: C 85.06, H 4.68, N 10.26%; Found: C 85.16, H 4.56, N 10.00%.

9,9',9''-(pyridine-2,4,6-triyl)tris(9H-carbazole) (5) 2,4,6-CzPy.

(5) was prepared according to a similar procedure to **(1)**, using 2, 4, 6- trifluoropyridine to replace the 2, 6- difluoropyridine. Yield: 90%;

¹H NMR (300 MHz, CDCl₃): δ ppm 8.20-8.13 (m, 10H), 7.91 (s, 2H), 7.75 (d, 2H, *J*=6.30 Hz), 7.53-7.49 (m, 2H), 7.54-7.35 (m, 10H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 146.2, 140.3, 139.2, 129.1, 129.0, 128.7, 128.6, 128.2, 128.0, 127.6, 127.4; GC-MS (*m/z*): 574.31 [M + H]⁺; Anal. Calcd. For C₄₁H₂₆N₄: C 85.69, H 4.56, N 9.75 %; Found: C 85.59, H 4.65, N 9.65%.

9,9',9'',9'''-(pyridine-2,3,5,6-tetrayl)tetrakis(9H-carbazole) (6) 2,3,5,6-CzPy.

(6) was prepared according to a similar procedure to **(1)**, using 2, 3, 5, 6- tetrafluoropyridine replace the 2, 6- difluoropyridine. Yield: 90%.

¹H NMR (300 MHz, CDCl₃): δ ppm 8.76 (s, 1H), 7.88-7.80 (m, 8H), 7.52 (d, 4H *J*=6.00 Hz), 7.27 (t, 4H, *J*=3.30 Hz), 7.14-7.10 (m, 12H), 7.09-7.00 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 144.7, 139.8, 138.9, 138.7, 127.5, 126.0, 125.7, 124.2, 124.0, 121.1, 120.9, 120.3, 119.8; GC-MS (*m/z*): 739.26 [M⁺]; Anal. Calcd. For C₅₃H₃₃N₅: C 86.04, H 4.50, N 9.47 %; Found: C 86.38, H 4.43, N 9.41%.

9,9',9'',9'''-(pyridine-2,3,4,6-tetrayl)tetrakis(9H-carbazole) (7) 2,3,4,6- CzPy.

(7) was prepared according to a similar procedure to **(1)**, using 2, 3, 4, 6- tetrafluoropyridine to replace the 2, 6- difluoropyridine. Yield: 85%.

¹H NMR (300 MHz, CDCl₃): δ ppm 8.27 (s, 1H), 8.22 (d, 2H, *J*=6.00 Hz), 8.15 (d, 2H, *J*=6.00 Hz), 7.79 (dd, 4H, *J*= 6.00 Hz), 7.46-7.35 (m, 8H), 7.26 (d, 2H, *J*=6.00

Hz), 7.12-6.9 (m, 10H), 6.85-6.81 (m, 2H), 6.71-6.67 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 151.3, 149.9, 147.3, 139.1, 139.0, 138.9, 138.0, 126.8, 125.8, 125.5, 125.1, 125.0, 124.1, 124.0, 123.7, 122.2, 122.1, 121.0, 120.8, 120.3, 120.2, 120.1, 119.7, 119.5, 115.8, 112.5, 111.1, 109.8, 109.4; MALDI-TOF Mass (m/z): 738.69 [M⁺]; Anal. Calcd. For C₅₃H₃₃N₅: C 86.04, H 4.50, N 9.47 %; Found: C 85.99, H 4.60, N 9.30%.

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Table S1. Physical properties of CzPy derivatives.

Compounds	$T_g/T_m/T_d$ [°C]	$\lambda_{\text{abs}}^{[a]}$ [nm]	$\lambda_{\text{max}}^{[a]}$ [nm]	$\lambda_{\text{max}}^{[b]}$ [nm]	$E_g^{[c]}$ [eV]	HOMO/LUMO [eV] ^[d]	HOMO/LUMO [eV] ^[e]	$E_T^{[f]}$ [eV]	$E_T^{[d]}$ [eV]
(1) 2,6-CzPy	75/222/329	289, 337	377	379	3.54	-5.63/-2.08	-5.43/-1.07	3.00	3.00
(2) 3,5-CzPy	74/209/310	290, 336	392	377	3.56	-5.72/-2.16	-5.57/-1.23	3.00	3.00
(3) 2,4-CzPy	70/218/337	290, 333	387	364	3.61	-5.69/-2.08	-5.50/-1.15	2.95	3.16
(4) 2,3-CzPy	78/256/286	290, 331	401	391	3.59	-5.66/-2.07	-5.40/-1.18	2.95	3.16
(5) 2,4,6-CzPy	124/312/412	288, 334	387	376	3.46	-5.67/-2.21	-5.51/-1.27	2.99	2.99
(6) 2,3,5,6-CzPy	150/330/434	287, 334	429	424	3.19	-5.67/-2.48	-5.43/-1.50	2.81	3.00
(7) 2,3,4,6-CzPy	- /384/419	287, 333	417	413	3.24	-5.67/-2.43	-5.41/-1.50	2.99	2.99

[a] Measured in CHCl₃ solution at room temperature. [b] Measured in film state at room temperature. [c] Bandgap was calculated from the absorption edge of UV-Vis spectra. [d] HOMO was measured by CV, LUMO was calculated from the difference of HOMO and bandgap. [e] Values from DFT calculations. [f] Triplet energy was calculated from low temperature (77 K) phosphorescence spectra.

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Scheme S1 General synthetic routes for Cu-catalyzed Ullman reactions for CzPy compounds.

Figure S1. TGA curves for **1-7**.

Figure S2. DSC curves for **1-6**.

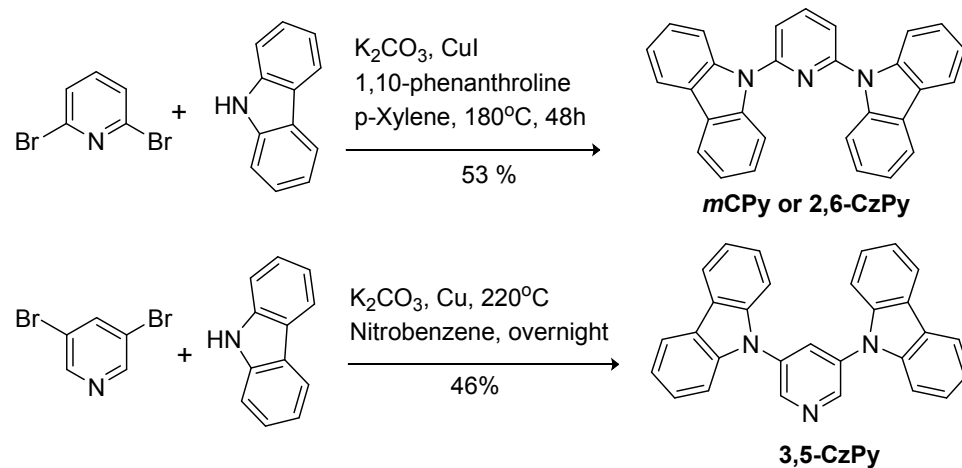
Figure S3. (a) Normalized PL spectra of the CHCl₃ solutions samples of **(1) - (7)** at 300K. (b) Normalized PL spectra of the solid films **1-7** at room temperature.

Figure S4. The cyclic voltammograms of **(1) - (7)** in DCM/0.1 M Bu₄NPF₆ at scanning rate 100 mV s⁻¹.

Figure S5. Contours of the spin density distributions of T₁ states of **1-7**.

Figure S6. HOMO/LUMO energy distributions of **1-7** by DFT calculation.

Figure S7. (a) Current Efficiency *versus* Luminance (*L*) curves, (b) Power Efficiency *versus* Luminance (*L*) curves and (c) EL spectra recorded at 8 V of Device A-G.



Scheme S1 General synthetic routes for Cu-catalyzed Ullman reactions for CzPy compounds.

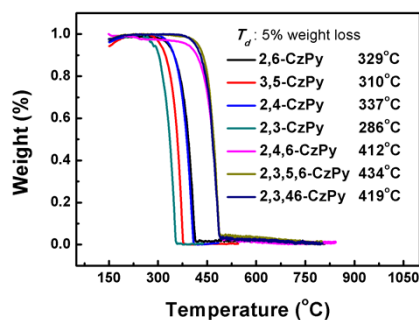


Figure S1. TGA curves for 1-7.

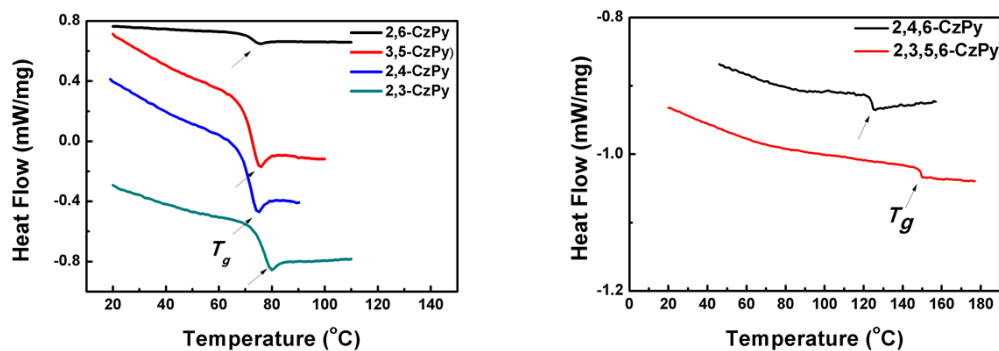


Figure S2. DSC curves for 1-6.

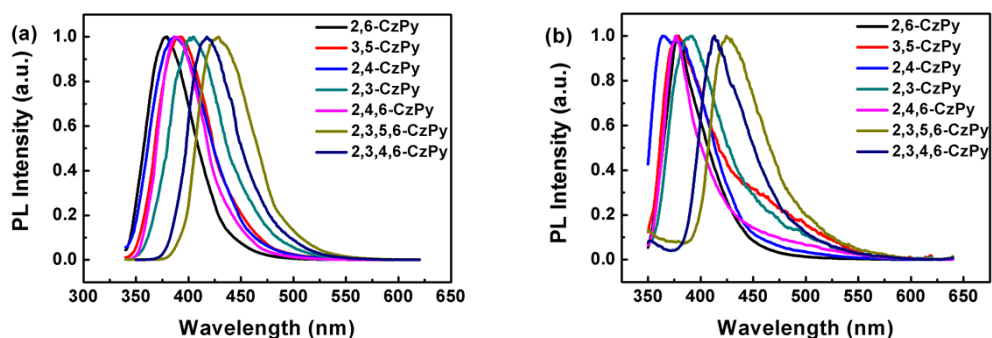


Figure S3. (a) Normalized PL spectra of the CHCl_3 solutions samples of (1) - (7) at 300K. (b) Normalized PL spectra of the solid films 1-7 at room temperature.

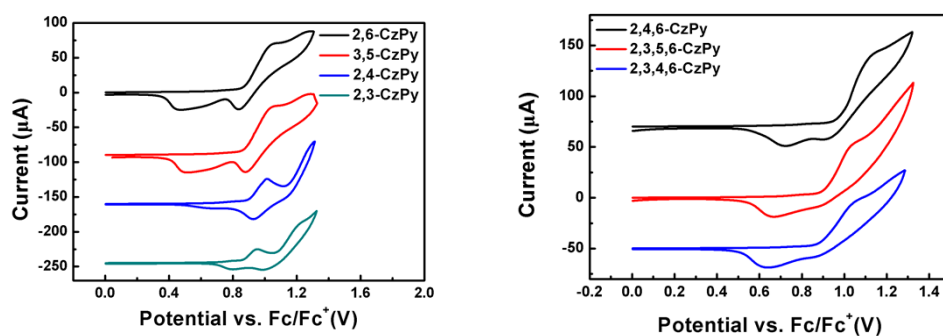


Figure S4. The cyclic voltammograms of (1) - (7) in DCM/0.1 M Bu_4NPF_6 at scanning rate 100 mV s^{-1} .

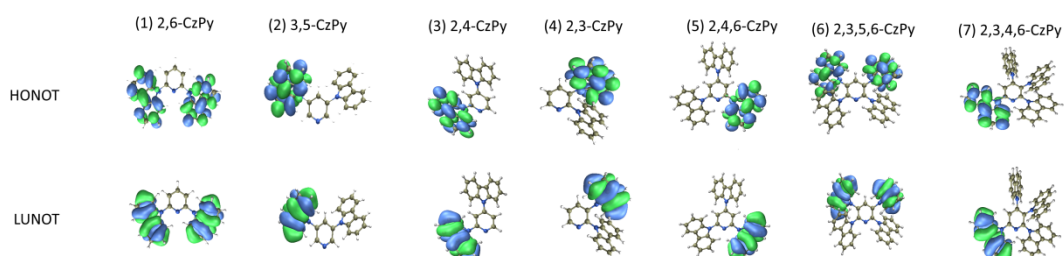


Figure S5. Contours of the spin density distributions of T_1 states of 1-7.

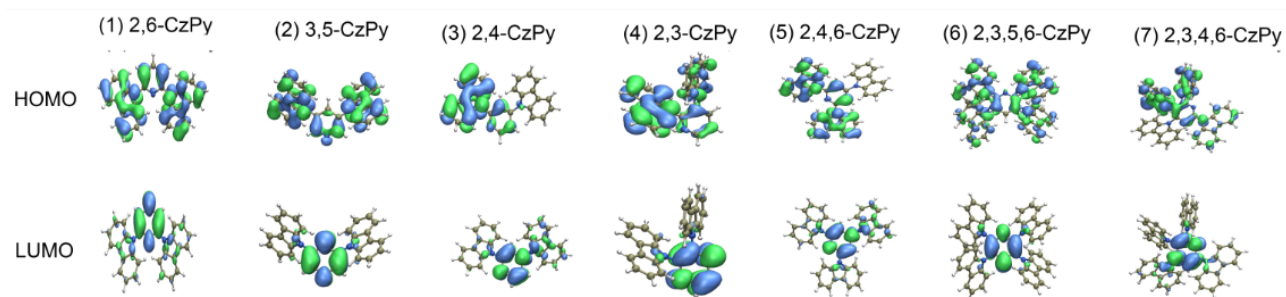


Figure S6. HOMO/LUMO energy distributions of **1-7** by DFT calculation.

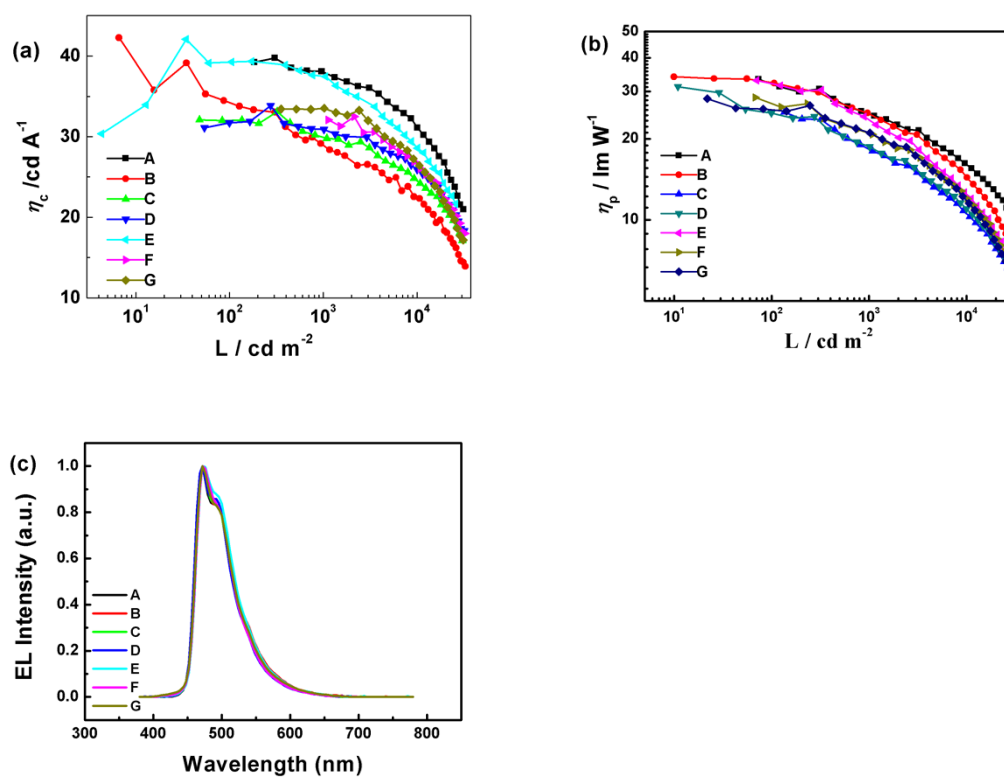


Figure S7. (a) Current Efficiency *versus* Luminance (L) curves, (b) Power Efficiency *versus* Luminance (L) curves and (c) EL spectra recorded at 8 V of Device A-G.