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Electronic Supporting Information

High colour rendering index and colour stable hybrid white efficient OLEDs with a double emitting layer structure using single phosphorescence dopant of heteroleptic platinum complexes.

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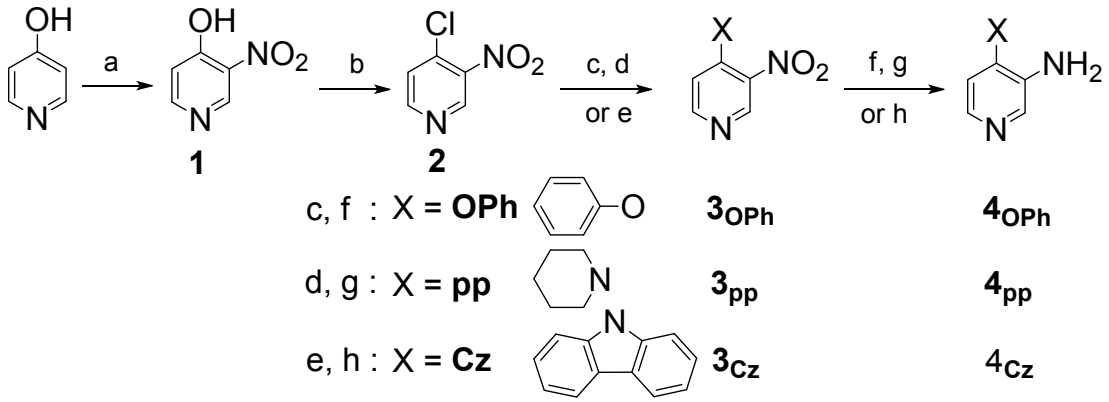
Synthesis procedure

Synthesis of pyridylamine derivatives



4-Hydroxy-3-nitropyridine (1).[1] A round-bottomed flask was charged with H_2SO_4 (120 mL) and cooled to 0 °C. 4-Hydroxypyridine (20.0 g, 0.21 mol) was added in portions followed by slow addition of KNO_3 (42.5 g, 0.42 mol) via a solid addition funnel. The resulting mixture was heated to 100 °C for 1 h and then cooled to 0 °C and poured onto ice water (100 mL). The mixture was neutralized (pH 6.5) with 5M NaOH at 0 °C. The precipitate was filtered and dried in vacuo to provide **1** (27.1 g, 92%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (s, 1H), 7.82 (d, 1H, J = 7.4 Hz), 6.47(d, 1H, J =

7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.30, 139.86, 138.38, 138.11, 122.35. EI-MS : calcd. 140.0, m/z = 140.0 (M^+).

4-Chloro-3-nitropyridine (2).[2] To a suspension of 4-Hydroxy-3-nitropyridine (**1**) (25 g, 0.18 mol) in toluene (375 mL) was added phosphorous oxychloride (82.1 g, 0.54 mol) at 0 °C. The resulting mixture was warmed to room temperature, then heated to reflux (110 °C) for 16 hours. After cooling to rt, the solvent was removed in vacuo and the residue was poured on ice, then basified with K_2CO_3 to pH ≈ 10. The mixture was extracted with ethyl acetate (200 mL x 2 times) and the organic phase was washed twice with water, followed by once with brine before concentrating to a brown oil which solidified on standing (25.4 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1 H), 8.67 (d, 1H, *J* = 5.2 Hz), 7.53 (d, 1H, *J* = 5.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.27, 146.30, 144.42, 137.60, 126.50. EI-MS : calcd. 158.0, m/z = 158.0 (M^+).

3-Nitro-4-phenoxypyridine (3_{OPh}).[3] A stirred mixture of 4-chloro-3-nitropyridine (**2**) (10 g, 63.3 mmol), K_2CO_3 (15.5 g, 112.1 mmol) and phenol (8.0 g, 85.1 mmol) in DMF (100 mL) was heated to 70°C for 2 h then stirred overnight at ambient temperature. The reaction mixture was quenched with water (300 mL) and extracted with ethyl acetate (2 × 250 mL). The organic phase was washed with saturated aqueous K_2CO_3, water and brine, then dried over anhydrous magnesium sulfate. The solvent was removed to leave a red oil (13.0 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): 9.10 (s, 1H), 8.52 (d, 1H, *J* = 5.7 Hz) 7.49 (t, 2H, *J* = 8.0 Hz), 7.34 (t, 1H, *J* = 7.4 Hz), 7.15 (d, 2H, *J* = 7.8 Hz), 6.76 (d, 1H, *J* = 6.0 Hz). ^{13}C NMR (100 MHz, CDCl3) δ: 158.19, 154.55, 152.77, 147.44, 136.86, 130.62, 126.70, 120.89, 111.89. FAB-MS : calcd. 216.1, m/z = 217.1 ($M+H^+$).

3-nitro-4-(piperidin-1-yl)pyridine (3_{pp}).[4] A solution of 4-chloro-3nitropyridine (**2**) (5.0 g, 31.6 mmol) and piperidine (5.4 g, 63.5 mmol) in ethanol (100 mL) was stirred at rt for 48 hours, Ethanol was then removed in vacuo. The residue was partitioned between ethyl acetate (300 mL) and Na_2CO_3 (aq) (75 mL). The organic phase was washed further with water and brine, then dried over magnesium sulfate and the volatiles were removed in vacuo yielding product (6.1 g, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.29 (d, 1H, *J* = 6.0 Hz), 6.83 (d, 1H, *J* = 6.0 Hz), 3.18 (m, 4H), 1.72 (m, 6H). ^{13}C NMR (100 MHz, CDCl3) δ: 152.29, 149.94, 148.35, 136.14, 112.72, 50.85, 25.29, 23.66. EI-MS : calcd. 207.1, m/z = 207.1 (M^+).

9-(3-nitropyridin-4-yl)-9H-carbazole (3_{Cz}).[5] A mixture of 4-chloro-3nitropyridine (**2**) (10 g, 63.3 mmol) and carbazole (15.8 g, 94.6 mmol) was dissolved

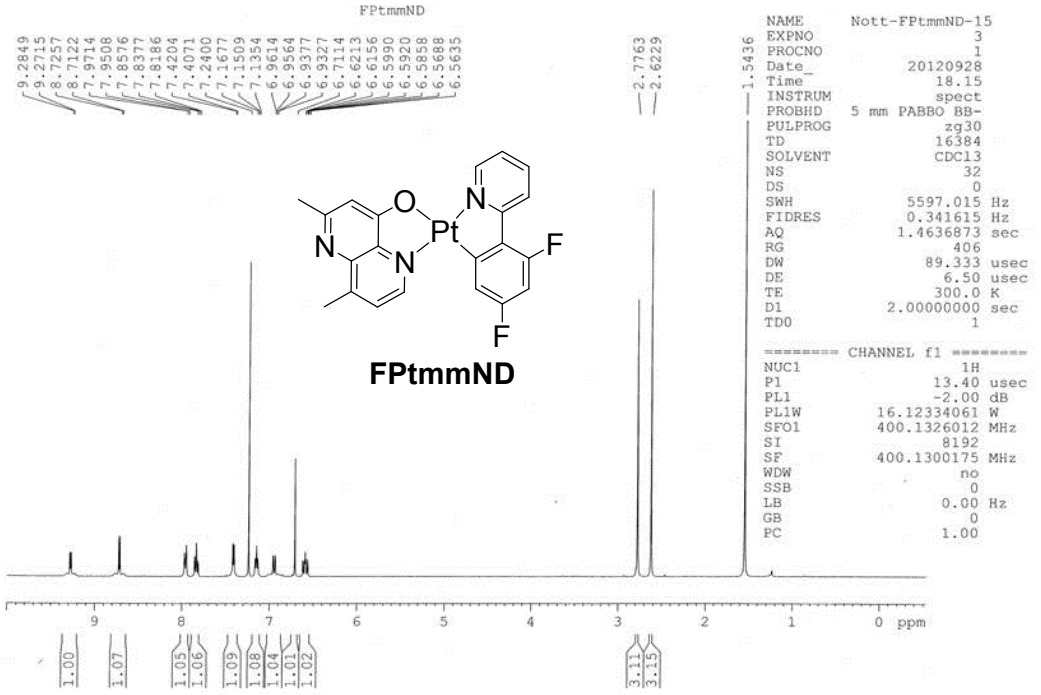
in MeCN (200 mL), and Cs_2CO_3 (26.8 g, 82.3 mmol) was added to the solution with stirring. The suspension was stirred for 30 h at 80 °C, the solution was concentrated under reduced pressure. The resultant residue was subjected to column chromatography (silica gel, Hexane/EtOAc 1:1(v/v)) to give product (11. 3 g, 62%). ^{1}H NMR (400 MHz, CDCl3) : δ 9.41 (s, 1H), 9.01 (d, 1H, *J* = 5.2 Hz), 8.13 (d, 2H, 7.6 Hz), 7.75 (d, 1H, *J*= 5.2 Hz), 7.43 (t, 2H, *J* = 7.6 Hz), 7.36 (t, 2H, *J* = 7.6 Hz)7.21 (d, 2H, *J*= 7.6 Hz). ^{13}C NMR (100 MHz, CDCl3) δ: 155.07, 148.08, 142.25, 139.41, 126.96, 124.86, 124.02, 122.15, 121.08, 109.19. EI-MS: calcd. 289.10, m/z = 289.10(M+).

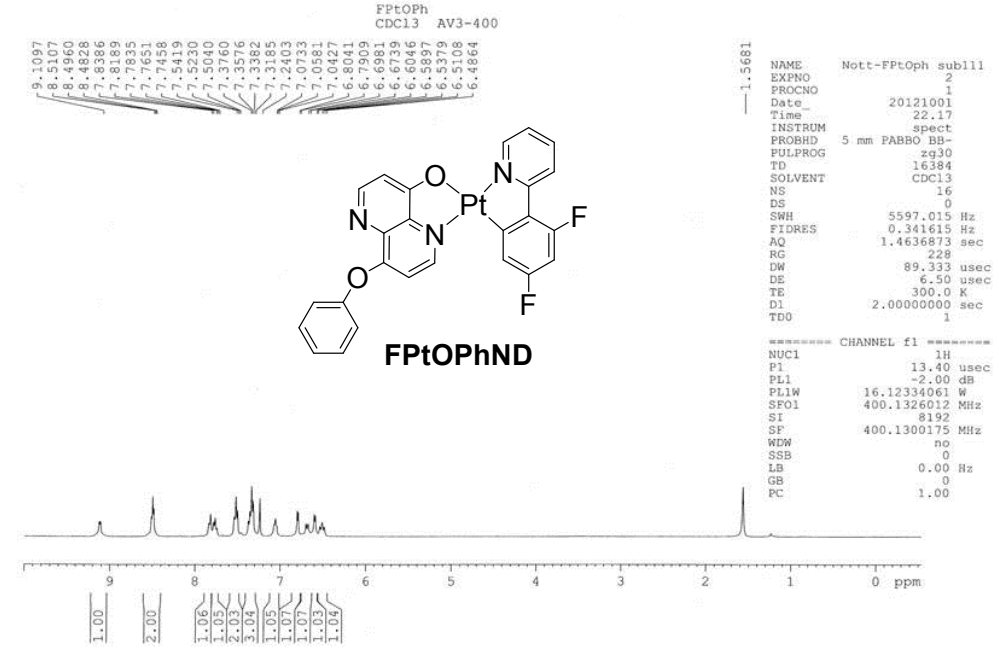
4-phenoxypyridin-3-amine (4_{OPh}). A mixture of 3-Nitro-4-phenoxypyridine (**2a**) (5.0 g, 23.1 mmol), $SnCl{\cdot}2H_2O$ (35.7 g, 158.2 mmol) and 6N HCl (30 mL) was dissolved in MeOH, and stirred at 65 °C for 16 h. After evaporation of MeOH, the residue was basified with 5 N NaOH to pH ≥ 10 and extracted with EtOAc (300 mL x 2 times). Combined organic extracts were washed with water and brine, then dried over anhydrous $MgSO_4$. The solvent was removed to leave a colourless oil which was dried under high vacuum (3.7 g, 85%). ^{1}H NMR (400 MHz, CDCl3): δ 8.12 (s, 1H), 7.88 (d, 1H, *J* = 5.4 Hz), 7.40 (t, 2H, *J* = 7.9 Hz), 7.21 (t, 1H, *J* = 7.4 Hz), 7.07 (d, 2H, *J* = 8.0 Hz), 6.56 (d, 1H, *J* = 5.4 Hz), 3.86 (br, 2H). ^{13}C NMR (100 MHz, CDCl3) δ: 154.61, 151.04, 141.10, 138.25, 133.94, 130.08, 124.84, 119.85, 110.99. MALDI-TOF-MS: calcd. 186.1, m/z = 187.1 ($M+H^+$).

4-(piperidin-1-yl)pyridin-3-amine (4_{pp}). A solution of 3-nitro-4-(piperidin-1-yl)pyridine (**2b**) (5.0 g, 24.1 mmol) and 10% Pd/C (0.26 g, 2.4 mmol) in THF (50 mL) was stirred under H_2 atmosphere at rt for 48. The reaction mixture was filtered and then concentrated under reduced pressure to provide the product (3.6 g, 85%). ^{1}H NMR (400 MHz, CDCl3): δ 7.95 (s, 1H), 7.91 (d, 1H, *J* = 4.9 Hz), 6.73 (t, 2H, *J* = 5.0 Hz), 3.70 (br, 2H), 2.86 (br, 4H), 1.67 (m, 4H), 1.56 (m, 2H). ^{13}C NMR (100 MHz, CDCl3) δ: 146.72, 140.99, 136.97, 113.48, 50.76, 26.18, 24.12. MALDI-TOF-MS: calcd. 177.1, m/z = 178.1 ($M+H^+$).

4-(9*H*-carbazol-9-yl)pyridin-3-amine (4_{Cz}). The mixture of 9-(3-nitropyridin-4-yl)-9H-carbazole (**2c**) (5.0 g, 17.3 mmol), 10% Pd/C (0.5 g, 4.7 mmol) and 5 mL of hydrazine in mixed solvent of THF/EtOH 1:1(v/v) (58 mL) was stirred at 70 °C for 12 h under nitrogen atmosphere. The Pd/C was separated by filtration. The reaction mixture was then concentrated under reduced pressure to afford the product (4.1 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.42 (s, 1H), 8.19 (d, 1H, *J* = 5.2 Hz), 8.16 (d, 2H, *J* = 8.0 Hz), 7.44(t, 3H, *J* = 7.6 Hz), 7.32 (t, 3H, *J* = 7.6 Hz), 7.24 (d, 1H, *J* = 5.2 Hz), 7.19 (d, 2H, *J* = 8.0 Hz), 3.72 (br, 2H). ^{13}C NMR (100 MHz, CDCl3) δ: 140.36,

139.81, 139.52, 129.04, 126.30, 123.80, 123.14, 120.58, 120.53, 110.11. FAB-MS: calcd. 259.11, m/z= 260.12 ($M+H^+$).





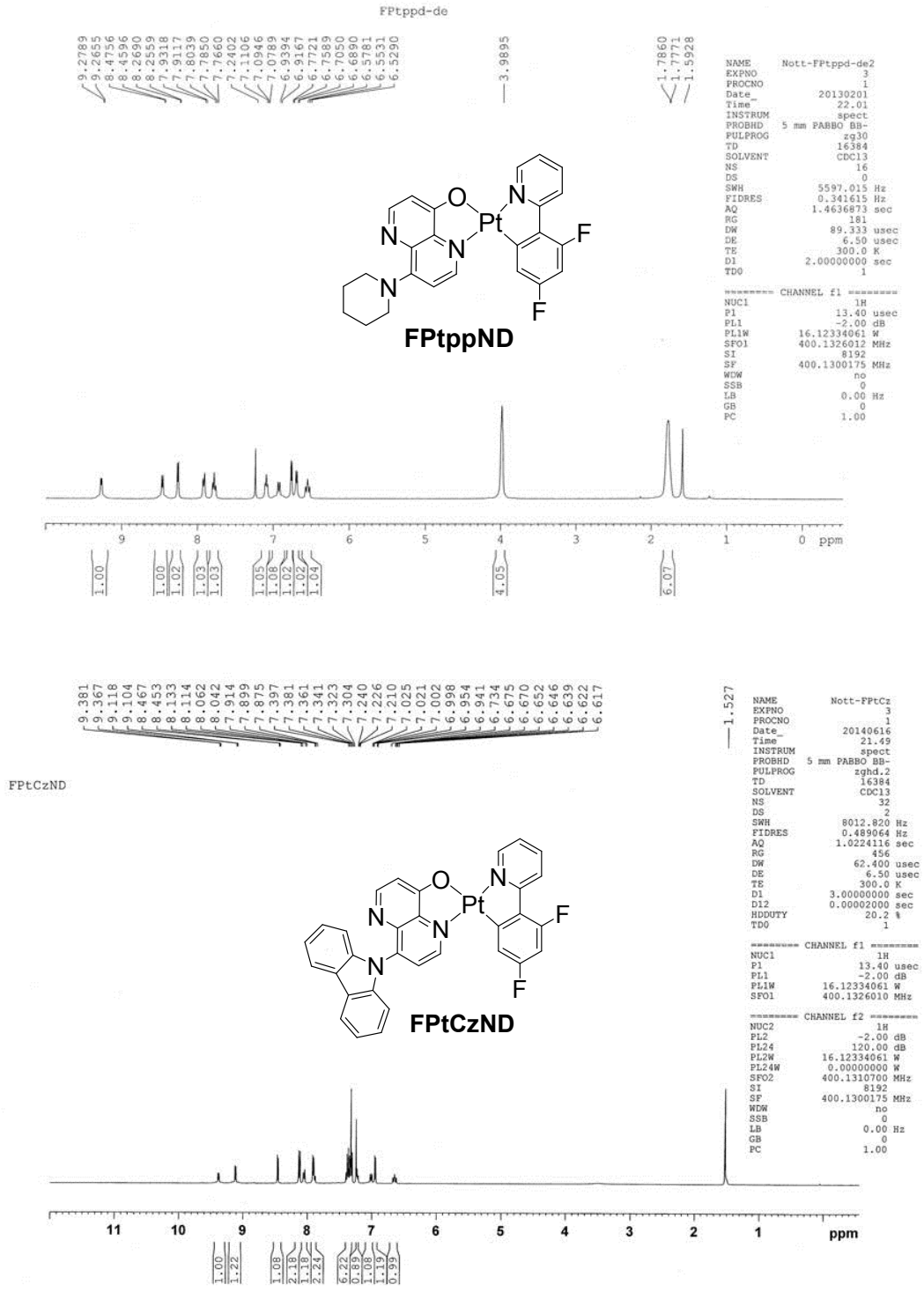


Figure S1 ^{1}H NMR spectrum of **FPtXND**.

Electroluminescence data

CBP hosted single EML devices (Device A and B)

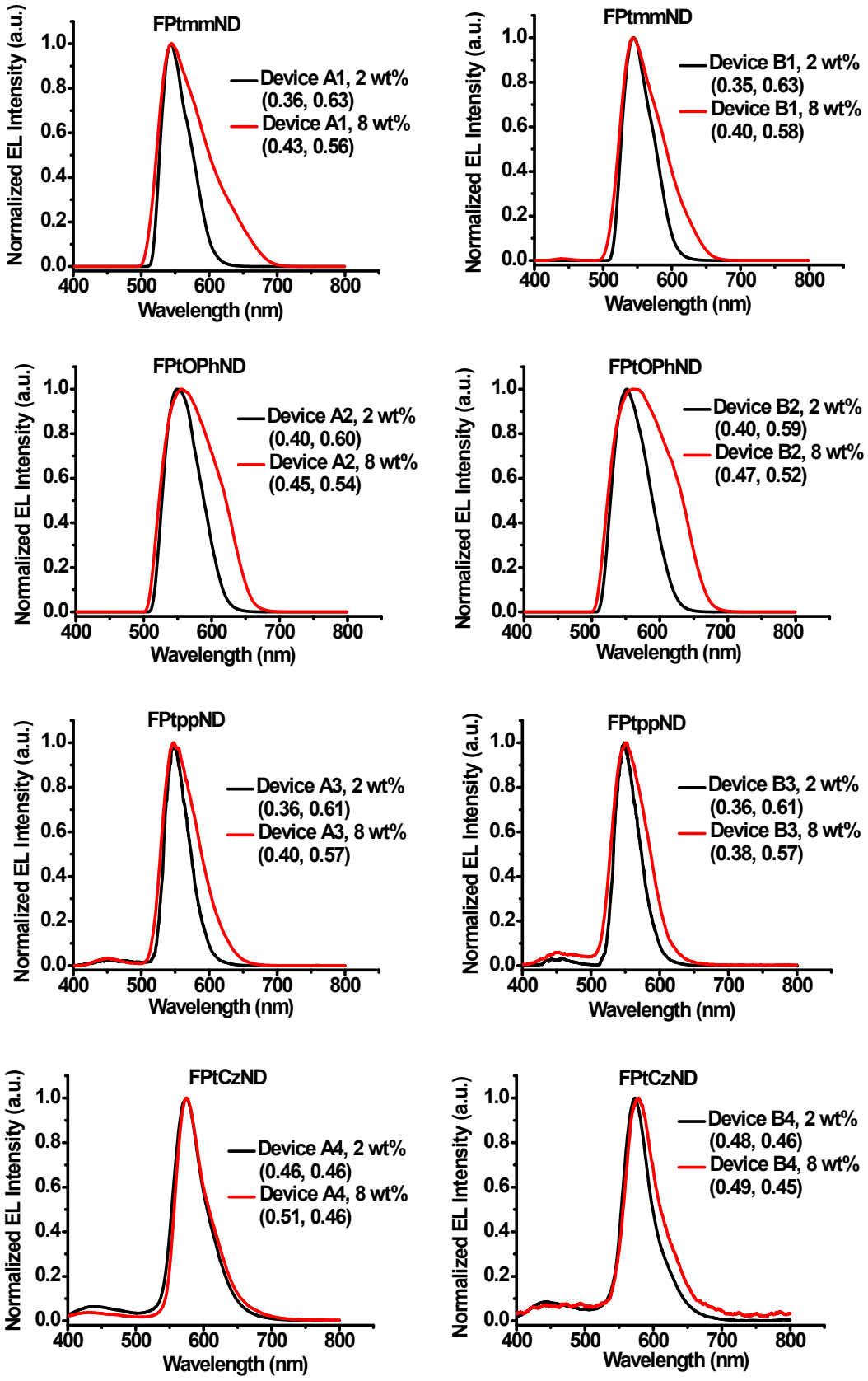


Figure S2 EL spectra of Device A and B with 2 and 8 wt% dopant concentration.

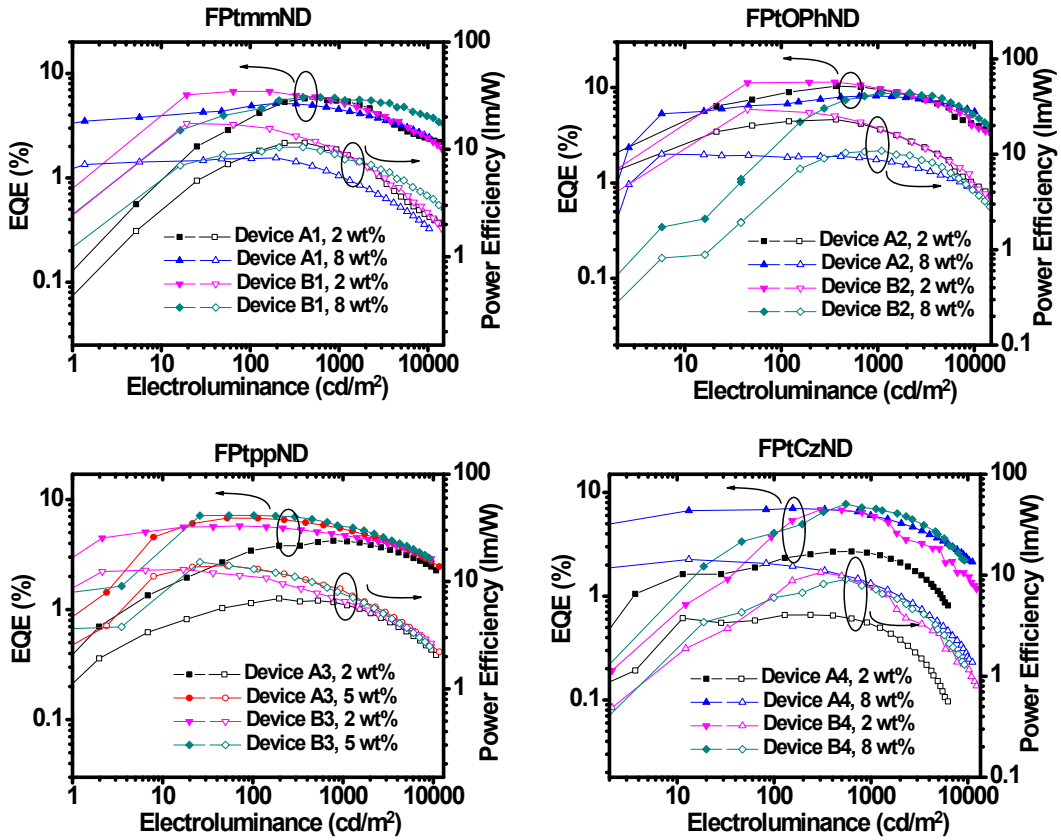
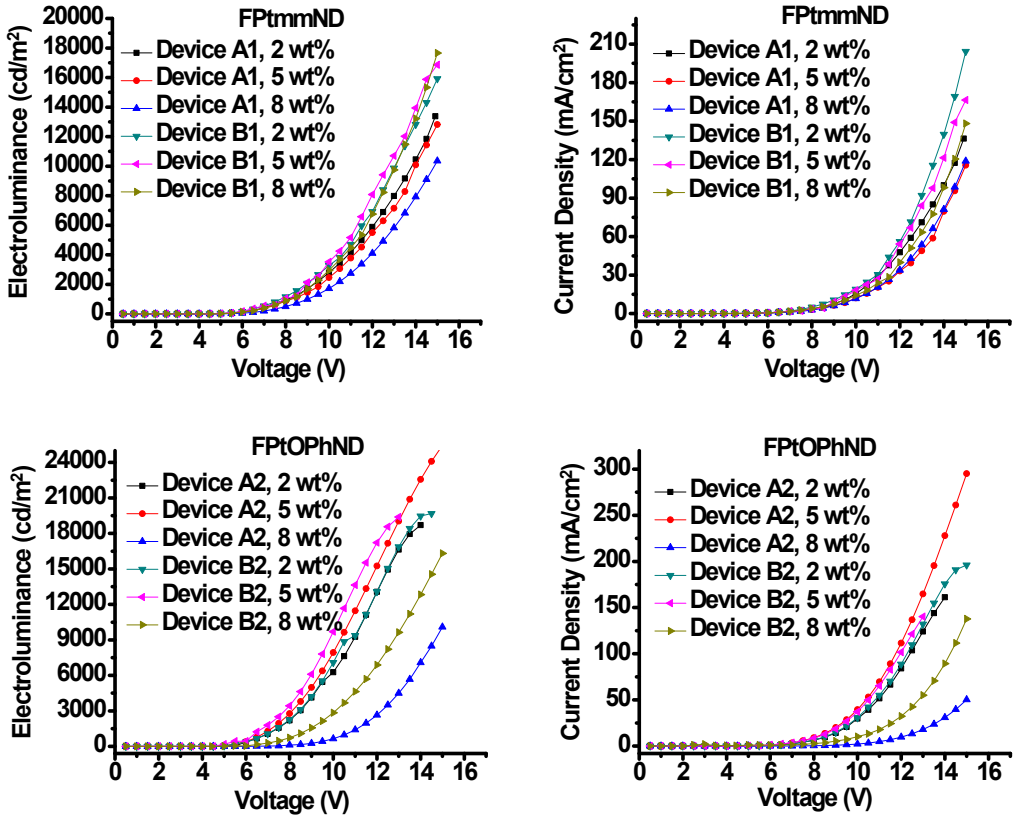


Figure S3 External quantum efficiency (EQE) and power efficiency as a function of electroluminance of Device A and B.



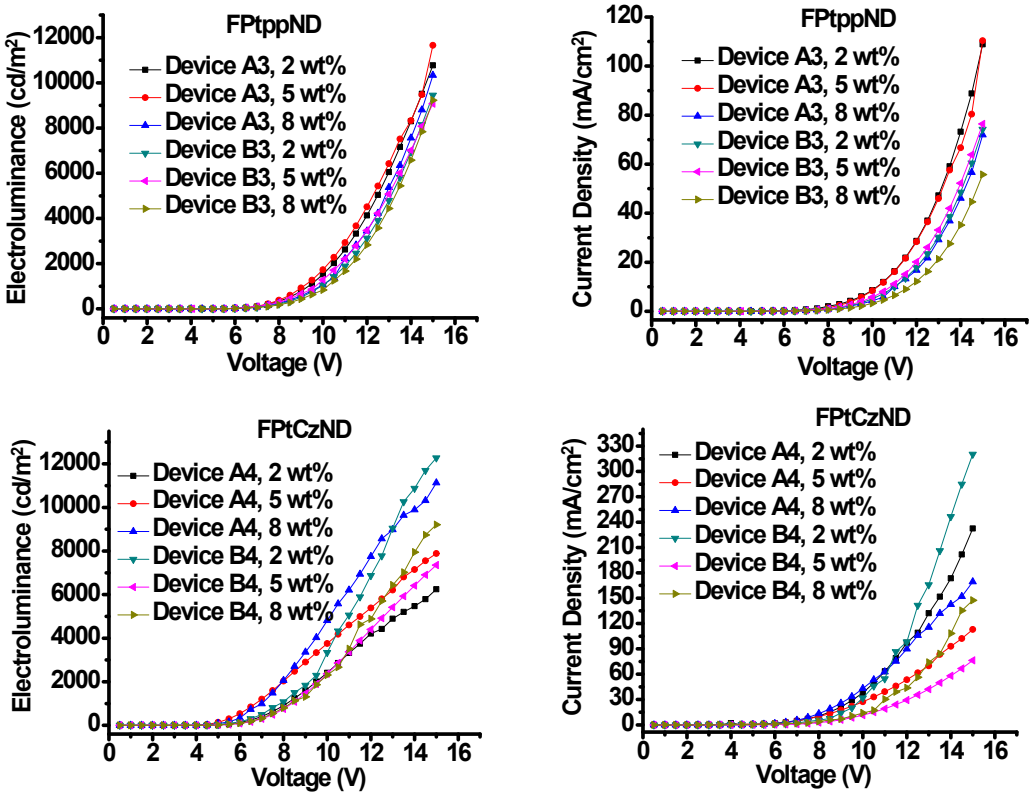
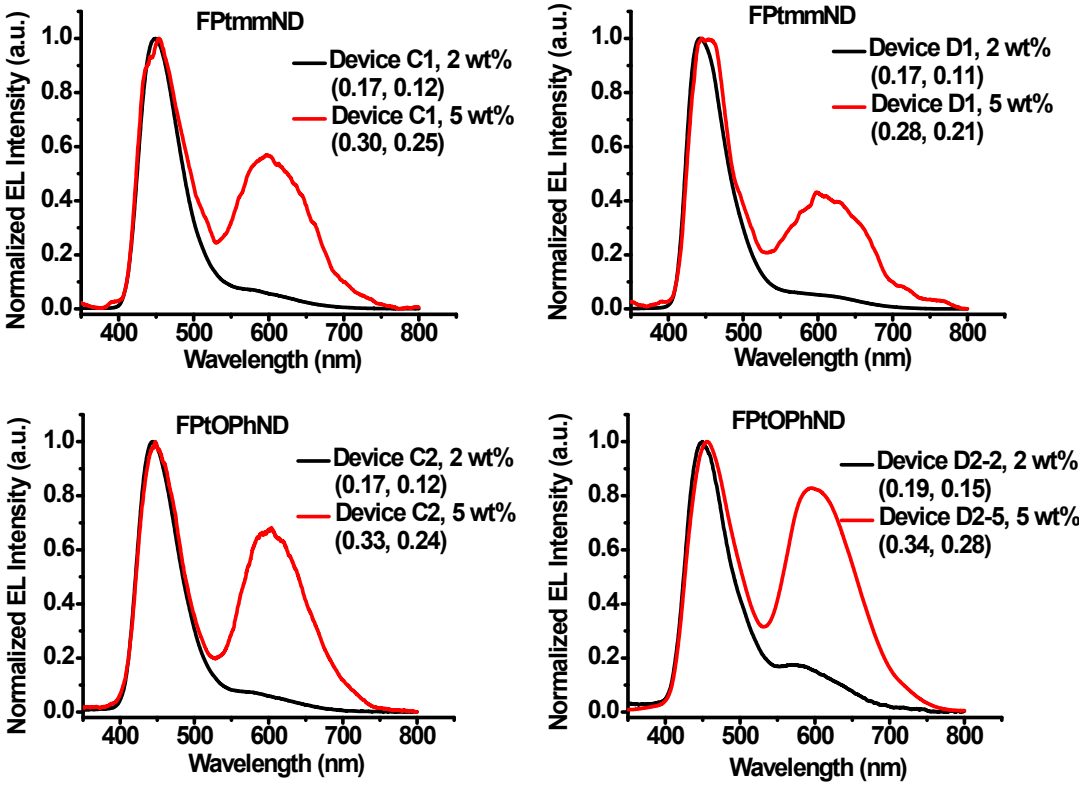


Figure S4 Luminance-voltage characteristics and current density-voltage characteristics of Device A and B.

4P-NPD hosted single EML devices (Device C and D)



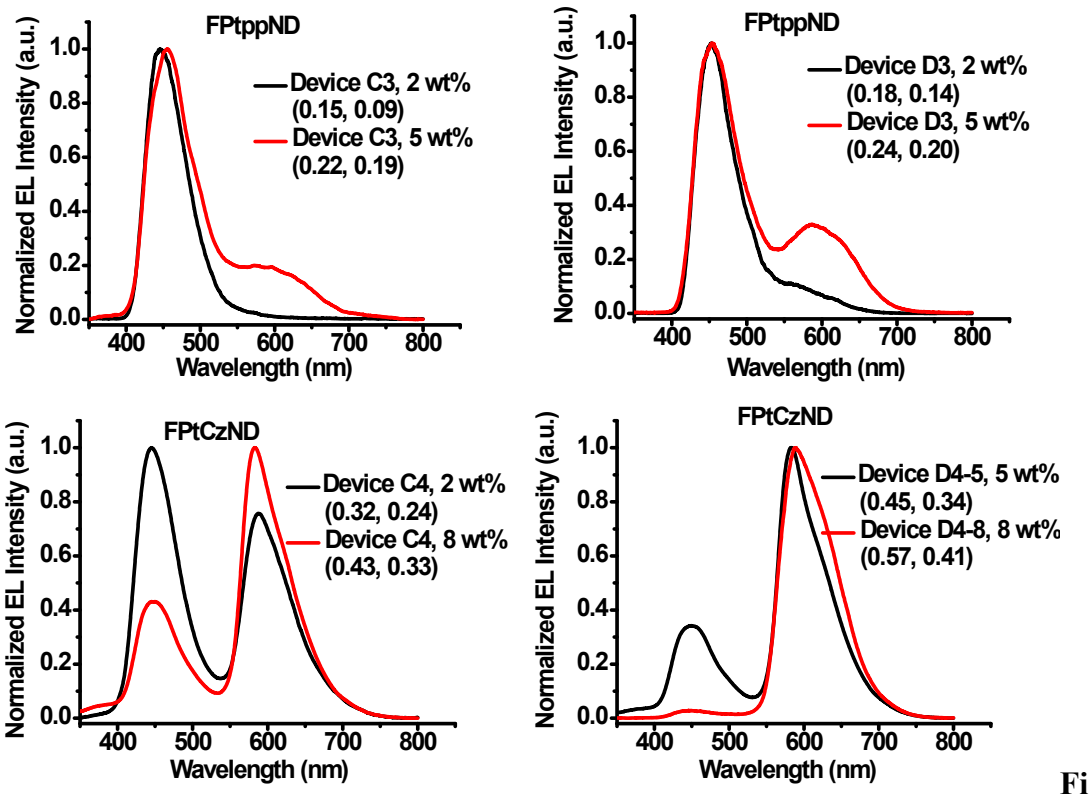


Figure S5 EL spectra of Device C and D with varied **FPtXND** dopant concentration.

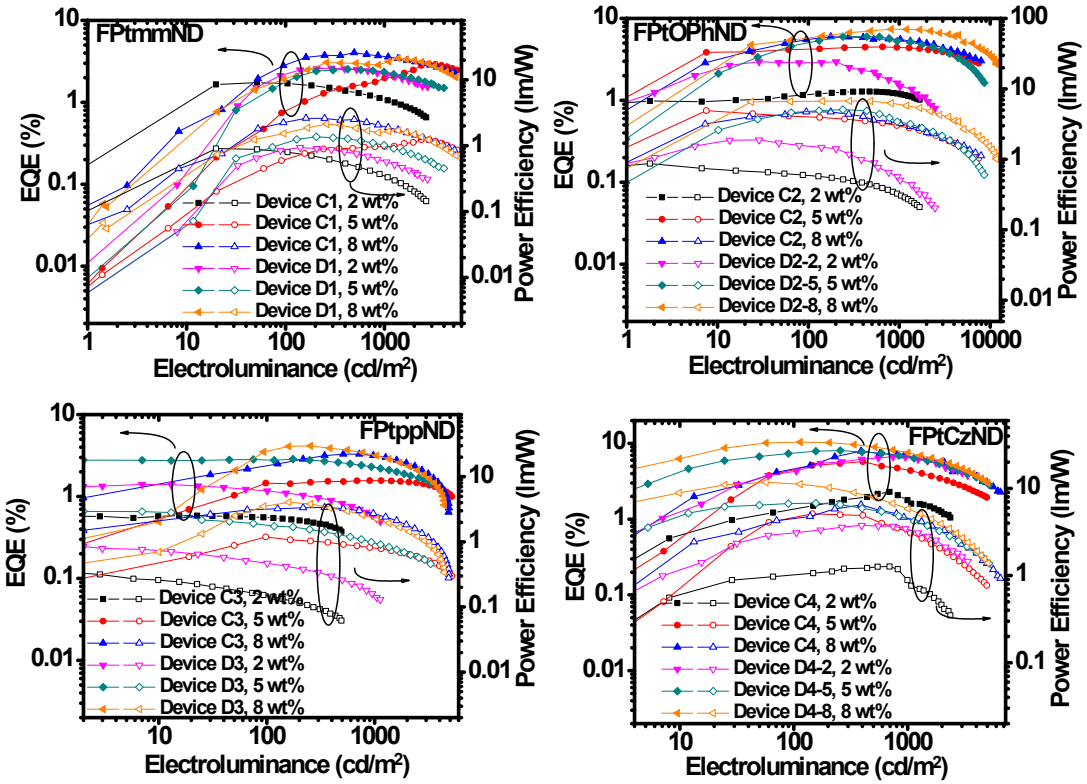


Figure S6 External quantum efficiency (EQE) and power efficiency as a function of electroluminance of Device C and D.

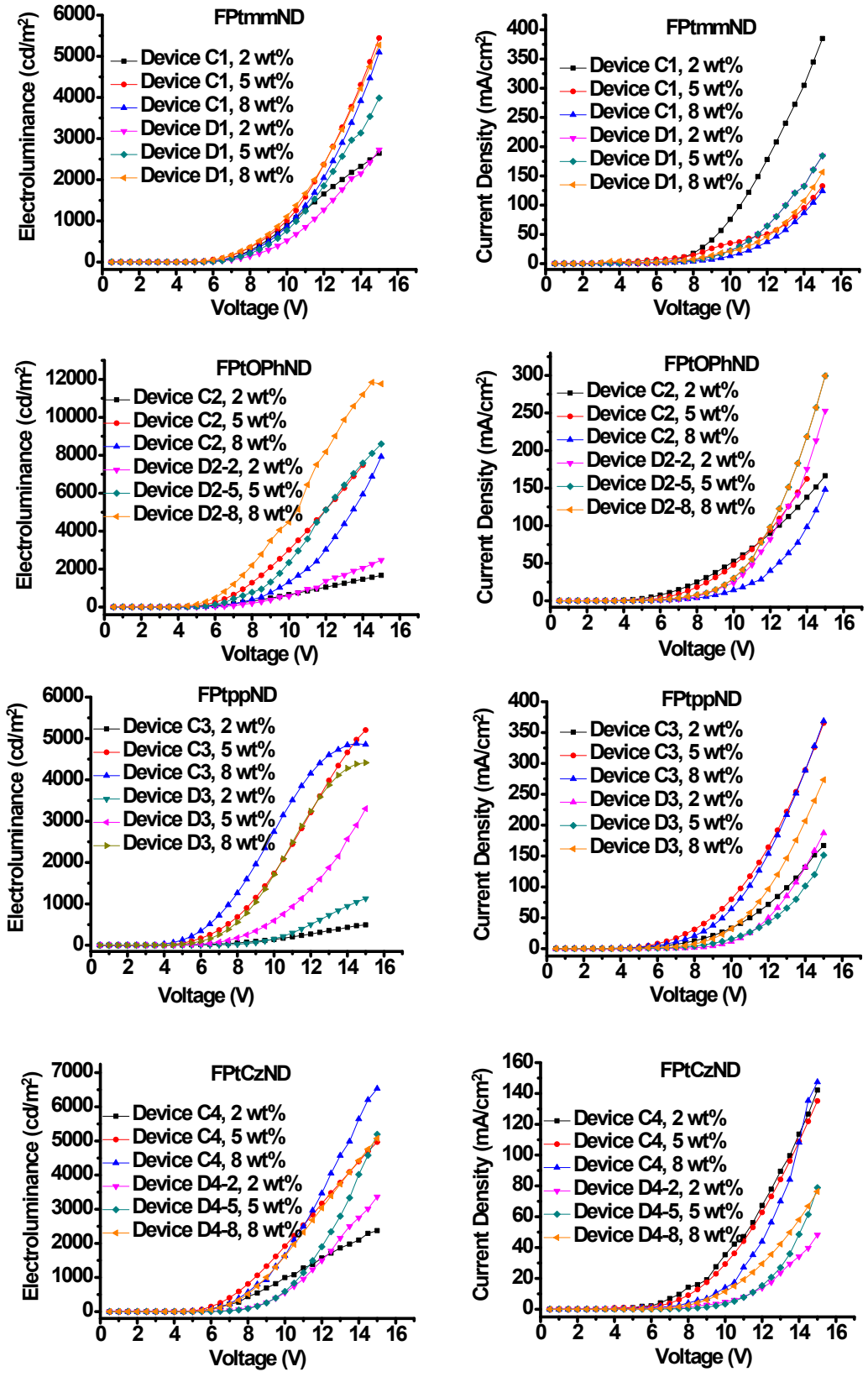


Figure S7 Luminance-voltage characteristics and current density-voltage characteristics of Device C and D.

References

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