

Supporting Information

for

Multifunctional metallophosphors with anti triplet-triplet annihilation properties for solution-processable electroluminescent devices

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Experimental Section

Synthesis of organic ligands:

9,9-Bis(4-diphenylaminophenyl)-2-bromofluorene

A mixture of 2-bromofluorenone⁹ (0.20 g, 0.77 mmol) and triphenylamine (2.64 g, 10.78 mmol) in methanesulfonic acid (74 mg, 0.77 mmol) was heated at 140 °C under an inert atmosphere overnight. The cooled reaction mixture was dissolved in CH₂Cl₂ (100 mL), washed with Na₂CO₃ solution, dried over anhydrous MgSO₄ and finally concentrated. Chromatography of the mixture on silica gel, first eluting with hexane/CH₂Cl₂ (20:1, v/v) to remove the excess triphenylamine, followed by hexane/CH₂Cl₂ (2:1, v/v) to isolate the product as a white solid (0.39 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.62 (d, *J* = 7.6 Hz, 1H, Ar), 7.52 (d, *J* = 8.0 Hz, 1H, Ar), 7.47 (t, *J* = 1.4 Hz, 1H, Ar), 7.41–7.38 (m, 1H, Ar), 7.34–7.32 (m, 1H, Ar), 7.29–7.20 (m, 2H, Ar), 7.16–7.12 (m, 8H, Ar), 7.00–6.89 (m, 16H, Ar), 6.84–6.82 (m, 4H, Ar). FAB-MS (*m/z*): 732 [M]⁺. Anal. Calcd for C₄₉H₃₅N₂Br: C, 80.43; H, 4.82; N, 3.83. Found: C, 80.12; H, 4.78; N, 3.60.

9,9-Bis(4-diphenylaminophenyl)-2-pyridinylfluorene (HL1)

9,9-Bis(4-diphenylaminophenyl)-2-bromofluorene (1.83 g, 2.50 mmol) and 2-(tributylstannyl)pyridine (1.01 g, 2.75 mmol) were mixed in dry toluene (50 mL) and Pd(PPh₃)₄ (0.29 g, 0.25 mmol) was then added to the solution. The resulting mixture was stirred at 110 °C overnight. After cooling to room temperature, the reaction mixture was poured into a separating funnel and CH₂Cl₂ (150 mL) was added followed by washing with water (3 × 100 mL). The organic phase was dried over MgSO₄ and concentrated. The residue was purified by column chromatography eluting with CH₂Cl₂/hexane (1:1, v/v). The title product was obtained as a white solid (1.19 g, 65%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70–8.69 (m, 1H, Ar), 8.07 (s, 1H, Ar), 8.05 (d, *J* = 8.0 Hz, 1H, Ar), 7.86 (d, *J* = 7.6 Hz, 1H,

Ar), 7.80 (d, $J = 7.6$ Hz, 1H, Ar), 7.74–7.71 (m, 2H, Ar), 7.46 (d, $J = 7.6$ Hz, 1H, Ar), 7.40 (t, $J = 7.4$ Hz, 1H, Ar), 7.32 (t, $J = 7.4$ Hz, 1H, Ar), 7.24–7.20 (m, 9H, Ar), 7.14 (d, $J = 8.4$ Hz, 4H, Ar), 7.09–7.07 (m, 8H, Ar), 7.01–6.93 (m, 8H, Ar). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 157.48, 152.16, 152.09, 149.57, 147.59, 146.14, 140.95, 139.41, 138.80, 136.67, 129.11, 128.89, 127.87, 127.42, 126.54, 126.26, 124.61, 124.33, 123.06, 122.68, 121.95, 120.71, 120.39 (Ar), 64.59 (quat. C). FAB-MS (m/z): 729 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{54}\text{H}_{39}\text{N}_3$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.76; H, 5.21; N, 5.58.

9,9-Bis(4-diphenylaminophenyl)-2-isoquinolinylfluorene (HL2)

Under a N_2 atmosphere, 9-bis(4-diphenylaminophenyl)-2-bromofluorene (1.20 g, 1.64 mmol) in dry THF (30 mL) was cooled to -78 °C and then $n\text{BuLi}$ (1.6 M in hexane) (1.2 mL) was added. The reaction mixture was stirred at the same temperature for 30 min and trimethylborate (0.21 g, 0.23 mL) was introduced to the reaction mixture with a syringe. Then the reaction mixture was warmed to room temperature slowly and dilute HCl (30 mL) was added. The mixture was stirred vigorously for 10 min and poured into a separating funnel. It was extracted with CH_2Cl_2 (3×60 mL). The combined organic phase was washed with water (3×100 mL) and dried over MgSO_4 . After concentration, the residue was purified by column chromatography on silica gel eluting first with CH_2Cl_2 to remove the impurity and then diethyl ether to elute the product. The organic boronic acid derivative was obtained as a white solid (0.80 g, 70%). Then 1-chloroisoquinoline (0.10 g, 0.61 mmol) and the as-prepared organic boronic acid (0.50 g, 0.72 mmol) were combined in a mixture of toluene (20 mL), THF (10 mL) and 2 M Na_2CO_3 (20 mL) under an inert atmosphere. The catalyst $\text{Pd}(\text{PPh}_3)_4$ (0.07 g, 0.06 mmol) was then added to the solution. The resulting reaction mixture was stirred at 110 °C for 24 h. Then water (100 mL) was added to the cooled reaction mixture which was extracted with CH_2Cl_2 (3×60 mL). The organic solution was washed with water (3×100 mL) and dried over MgSO_4 . The solvent was

removed under reduced pressure and the residue was purified on a silica gel column with CH₂Cl₂/hexane (3:1, v/v) to give the title product as a pale yellow solid (0.40 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.62 (d, *J* = 6.0 Hz, 1H, Ar), 7.99–7.96 (m, 2H, Ar), 7.90–7.86 (m, 2H, Ar), 7.83–7.80 (m, 2H, Ar), 7.70–7.65 (m, 2H, Ar), 7.50 (d, *J* = 7.6 Hz, 1H, Ar), 7.46–7.41 (m, 2H, Ar), 7.38–7.34 (m, 1H, Ar), 7.25–7.20 (m, 8H, Ar), 7.19–7.15 (m, 4H, Ar), 7.09–7.06 (m, 8H, Ar), 7.01–6.94 (m, 8H, Ar). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.58, 151.81, 151.33, 147.61, 146.20, 142.12, 140.45, 139.57, 139.53, 138.54, 136.90, 129.91, 129.39, 129.11, 128.89, 128.08, 127.92, 127.53, 127.47, 127.06, 127.00, 126.66, 126.30, 124.17, 123.32, 122.63, 120.50, 120.44, 119.86 (Ar), 64.58 (quat. C). FAB-MS (*m/z*): 779 [M]⁺. Anal. Calcd for C₅₈H₄₁N₃: C, 89.31; H, 5.30; N, 5.39. Found: C, 89.18; H, 5.33; N, 5.45.

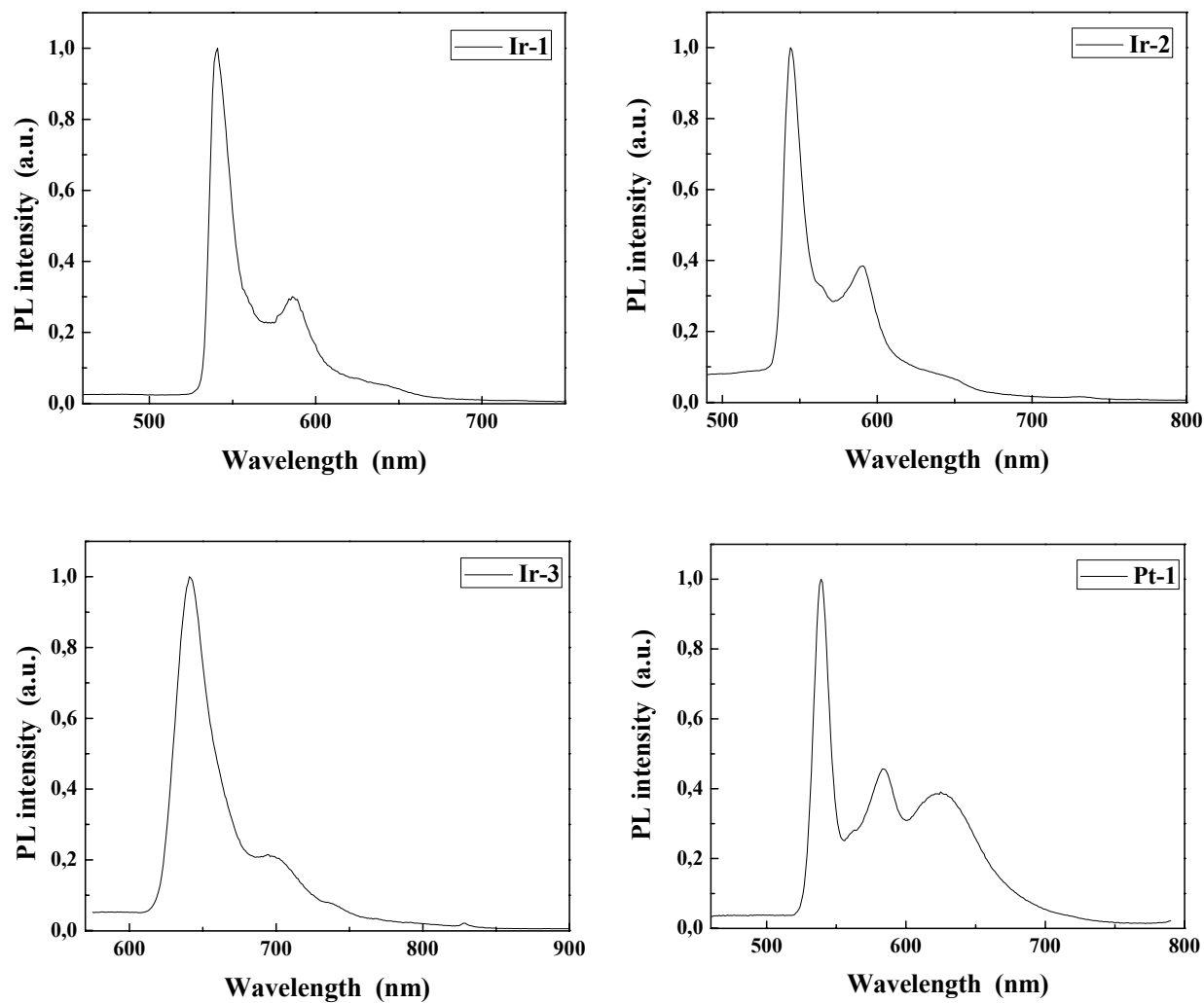


Fig. S1 PL spectra for the triplet emitters in CH₂Cl₂ glass at 77 K.

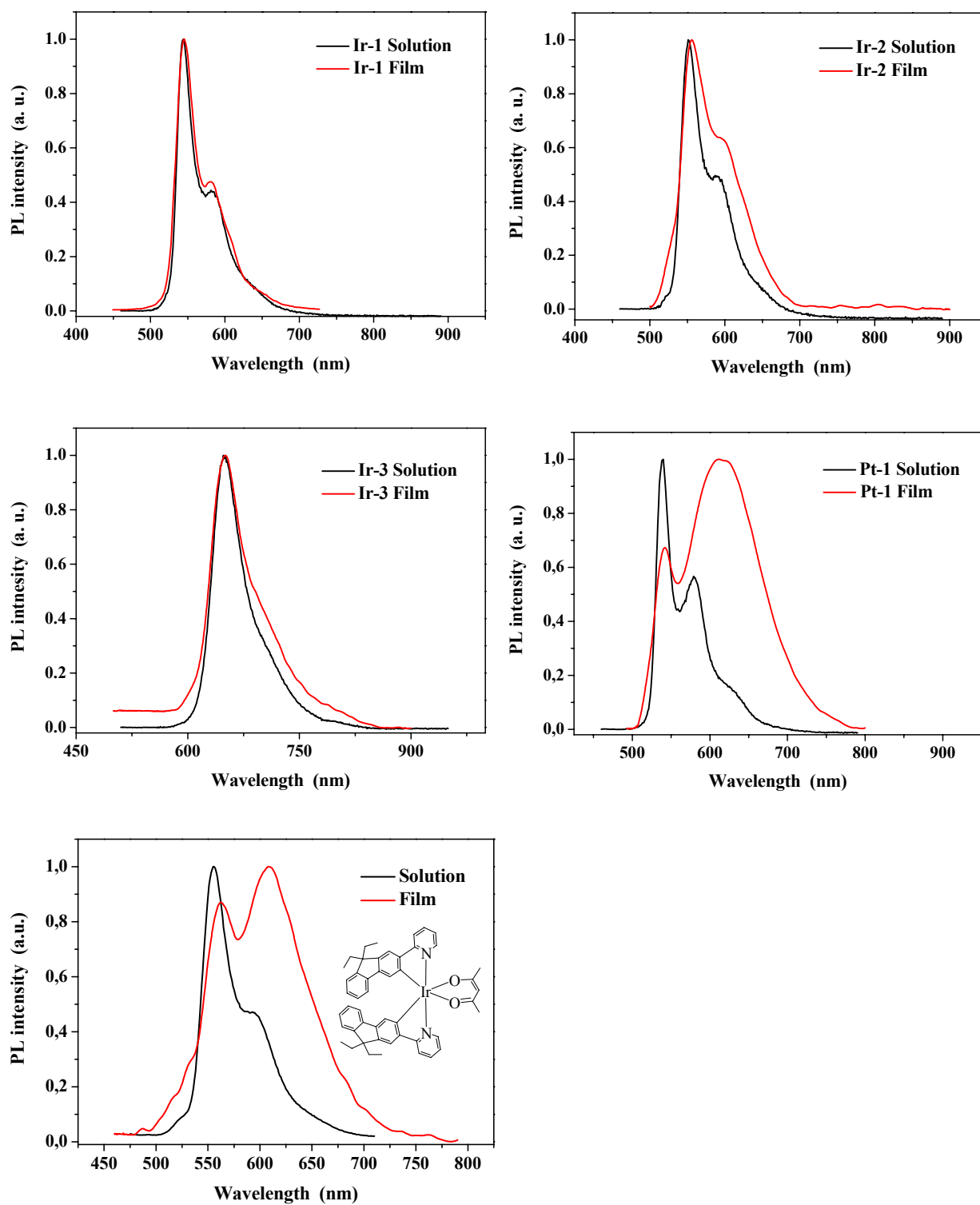
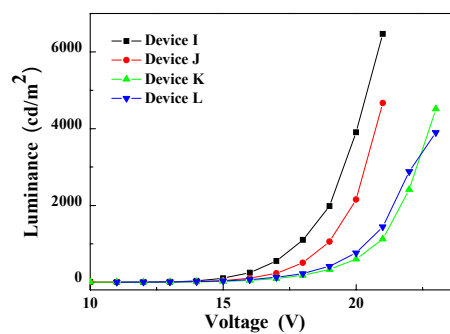
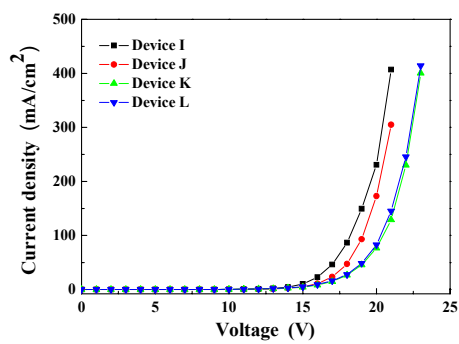
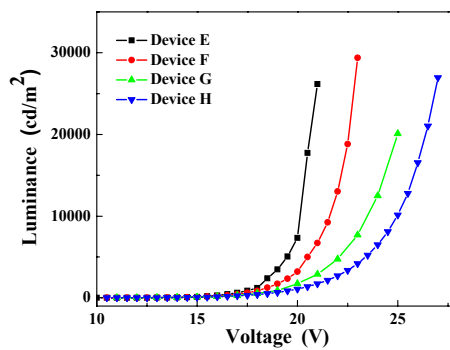
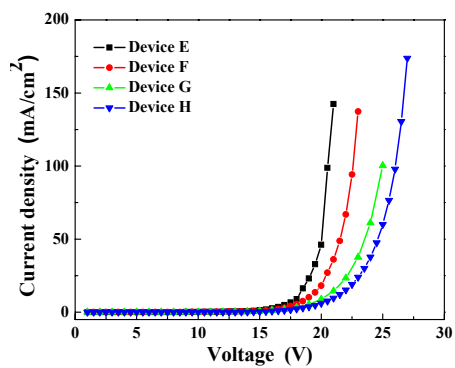
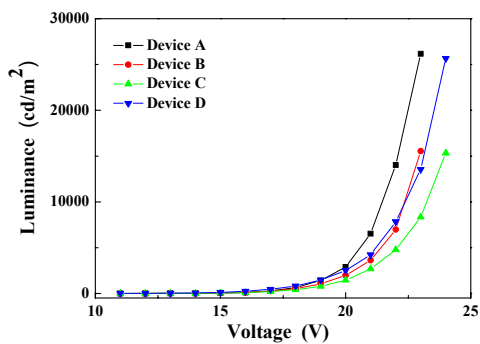
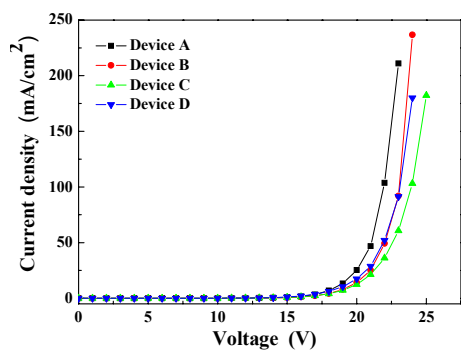


Fig. S2 PL spectra for the triplet emitters in CH_2Cl_2 solution and neat film at 293 K.



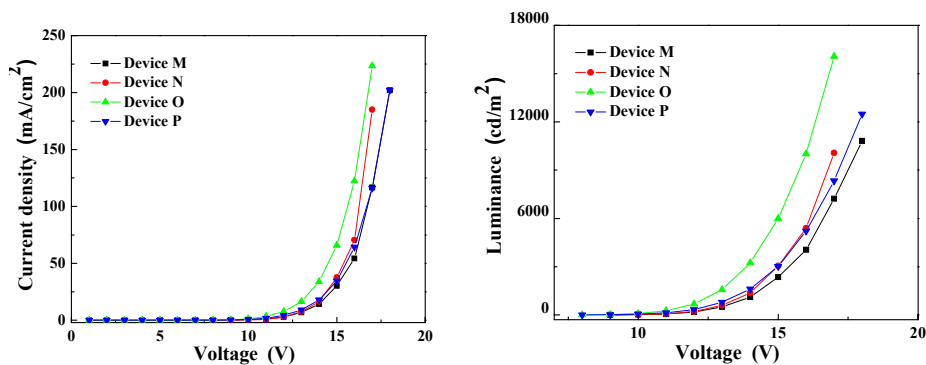


Fig. S3 The current density–voltage–luminance (J – V – L) characteristics of all of the OLED devices with different doping levels.

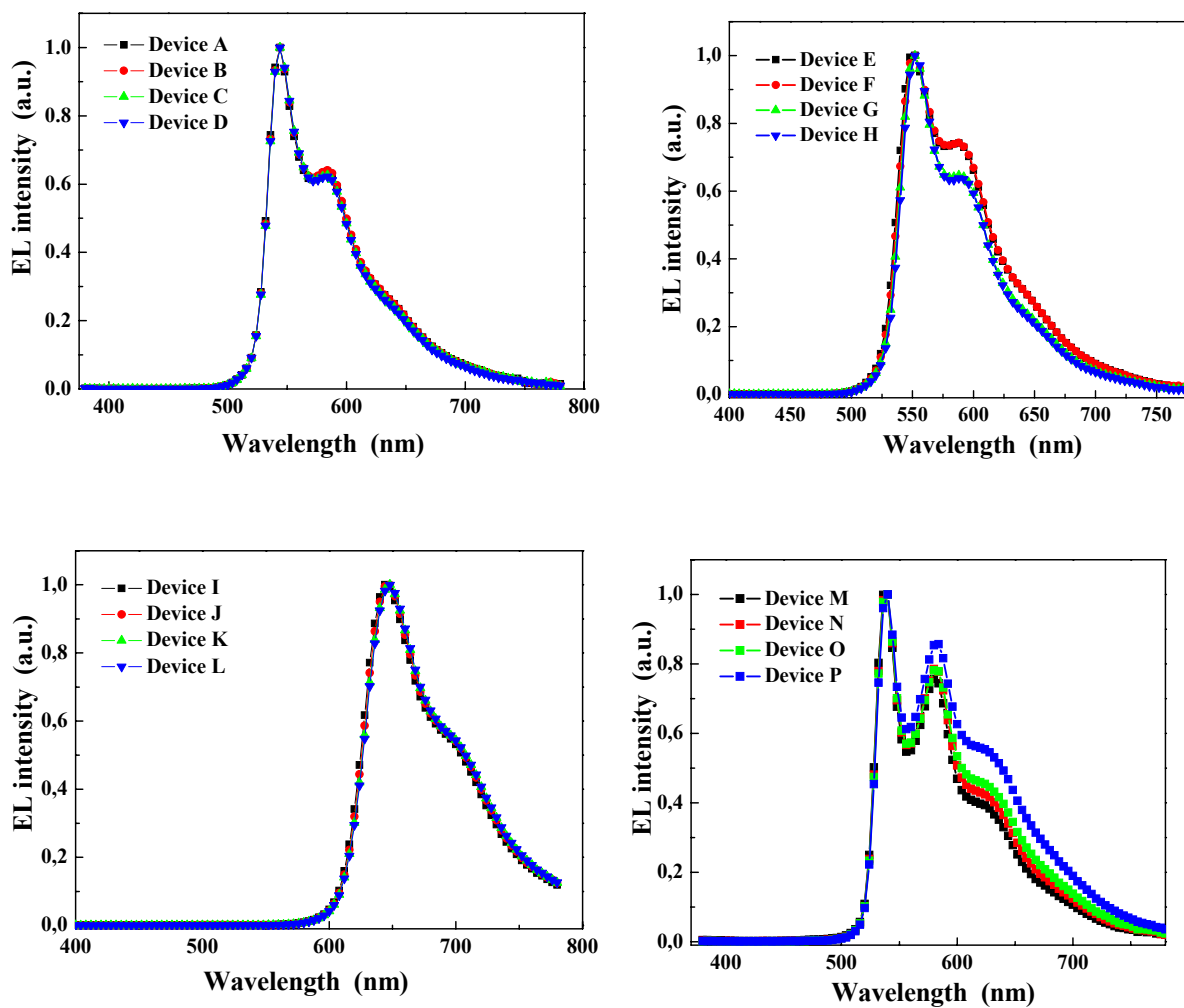
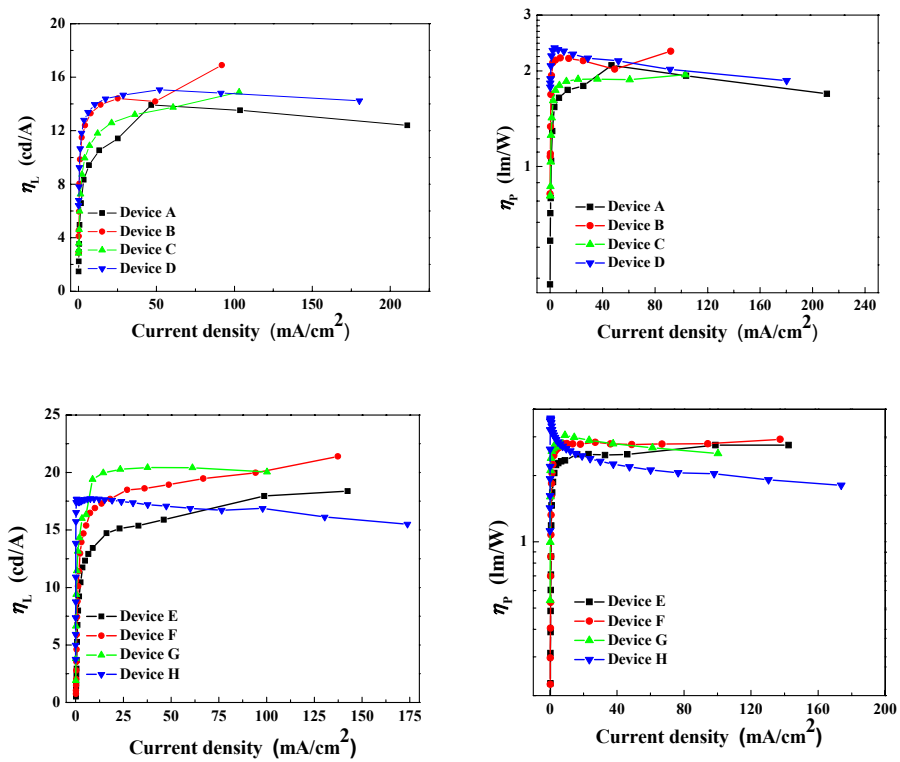


Fig. S4 EL spectra for all of the OLED devices with different doping levels.



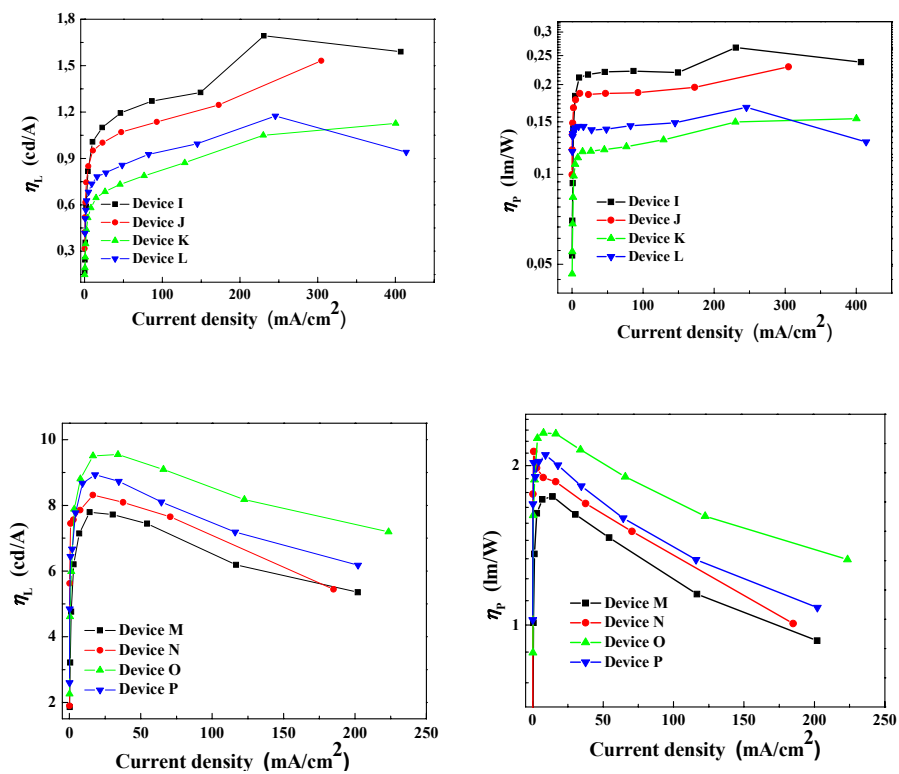


Fig. S5 Luminance and power efficiencies as a function of current density for all of the OLED devices with different doping levels.

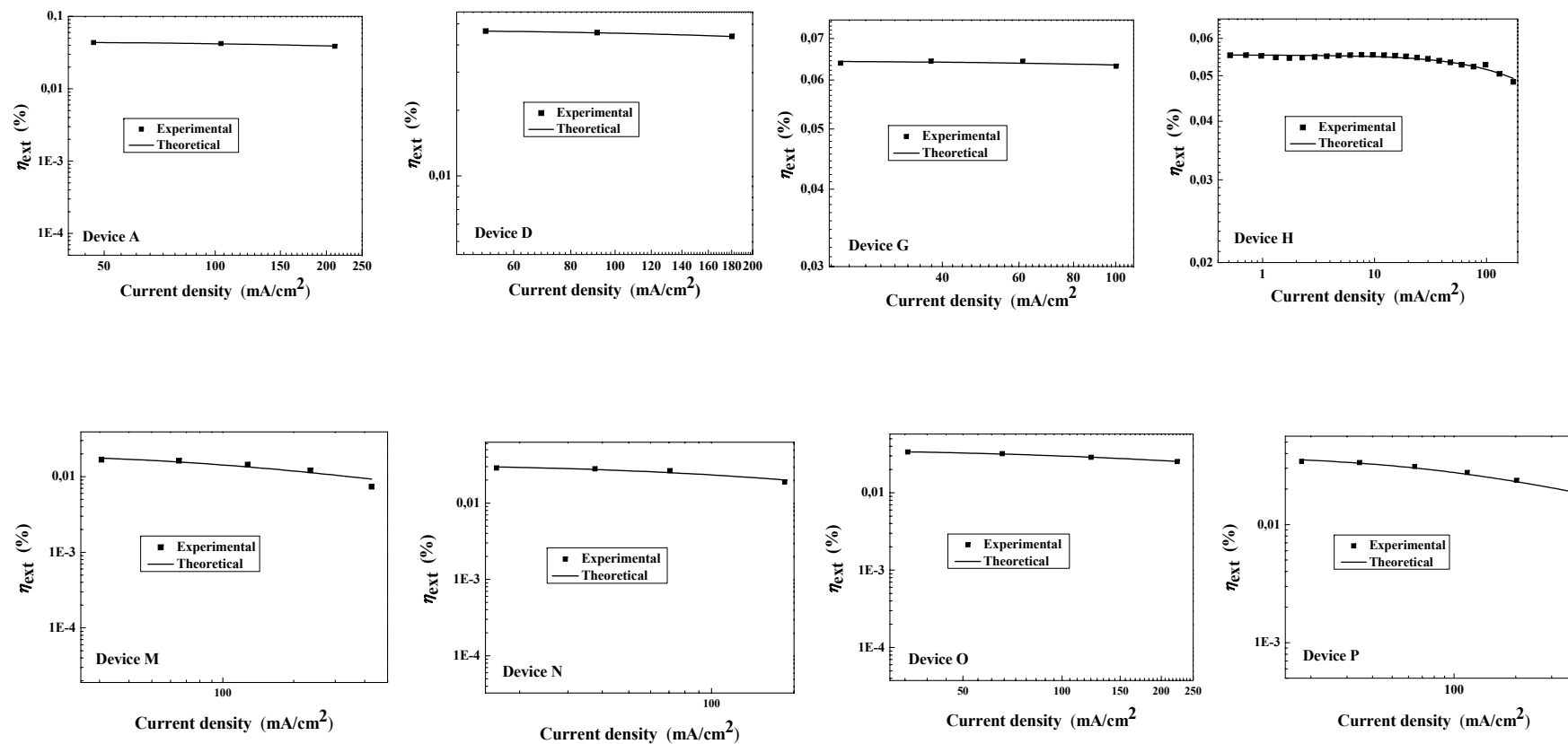


Fig. S6 Experimental η_{ext} versus current density data fitted by a theoretical equation involving T-T annihilation.

Table S1 Performance of the electrophosphorescent OLEDs **A–P**.

| Device | Phosphor dopant | $V_{\text{turn-on}}$ /V | Luminance L /cd m ⁻² | η_{ext} /% | η_{L} /cd A ⁻¹ | η_{p} /lm W ⁻¹ | λ_{max} /nm ^d |
|----------|------------------------|----------------------------|--------------------------------------|---------------------------|--|--|--|
| A | Ir-1 (3 wt.-%) | 11.0 | 26160 (23) ^a | 4.34 (21) | 13.93 (21) | 2.08 (21) | 544 |
| | | | 2237 ^b | 3.44 | 11.02 | 1.77 | (0.45, 0.54) |
| | | | 13499 ^c | 4.22 | 13.55 | 2.31 | |
| B | Ir-1 (6 wt.-%) | 11.0 | 15540 (23) | 5.26 (23) | 16.90 (23) | 2.31 (23) | 544 |
| | | | 2835 | 4.42 | 14.19 | 2.17 | (0.45, 0.54) |
| | | | 15540 | 5.26 | 16.90 | 1.93 | |
| C | Ir-1 (9 wt.-%) | 11.0 | 15330 (24) | 4.60 (24) | 14.88 (24) | 1.95 (24) | 544 |
| | | | 2511 | 3.86 | 12.47 | 1.88 | (0.45, 0.54) |
| | | | 14864 | 4.57 | 14.79 | 1.94 | |
| D | Ir-1 (12 wt.-%) | 11.0 | 25660 (24) | 4.63 (22) | 15.07 (22) | 2.36 (17) | 544 |
| | | | 2913 | 4.44 | 14.45 | 2.25 | (0.45, 0.54) |
| | | | 14712 | 4.54 | 14.76 | 2.01 | |
| E | Ir-2 (3 wt.-%) | 10.0 | 26180 (21) | 6.02 (21) | 18.38 (21) | 2.75 (21) | 552 |
| | | | 2991 | 4.90 | 14.94 | 2.50 | (0.48, 0.52) |
| | | | 18074 | 5.89 | 17.96 | 2.75 | |
| F | Ir-2 (6 wt.-%) | 10.5 | 29380 (23) | 7.04 (23) | 21.40 (23) | 2.92 (23) | 552 |
| | | | 3624 | 5.88 | 17.86 | 2.79 | (0.48, 0.52) |
| | | | 20317 | 6.64 | 20.16 | 2.81 | |
| G | Ir-2 (9 wt.-%) | 10.6 | 20100 (25) | 6.43 (23) | 20.42 (23) | 3.05 (23) | 552 |
| | | | 4073 | 6.35 | 20.15 | 2.93 | (0.47, 0.52) |
| | | | 20023 | 6.32 | 20.06 | 2.52 | |
| H | Ir-2 (12 wt.-%) | 10.6 | 26960 (27) | 5.54 (16) | 17.72 (16) | 3.64 (15) | 552 |
| | | | 3505 | 5.49 | 17.56 | 2.44 | (0.47, 0.52) |
| | | | 16806 | 5.26 | 16.82 | 2.03 | |
| I | Ir-3 (3 wt.-%) | 11.0 | 6471 (21) | 4.23 (20) | 1.69 (20) | 0.27 (20) | 648 |
| | | | 220 | 2.70 | 1.08 | 0.21 | (0.70, 0.30) |
| | | | 1288 | 3.21 | 1.28 | 0.22 | |
| J | Ir-3 (6 wt.-%) | 11.0 | 4669 (21) | 4.00 (21) | 1.53 (21) | 0.23 (21) | 648 |
| | | | 197 | 2.58 | 0.99 | 0.19 | (0.70, 0.30) |
| | | | 1147 | 2.99 | 1.15 | 0.19 | |
| K | Ir-3 (9 wt.-%) | 11.0 | 4512 (23) | 3.03 (23) | 1.13 (23) | 0.15 (23) | 648 |
| | | | 132 | 1.79 | 0.66 | 0.12 | (0.70, 0.30) |
| | | | 842 | 2.23 | 1.83 | 0.13 | |
| L | Ir-3 (12 wt.-%) | 11.0 | 3898 (23) | 3.20 (22) | 1.17 (22) | 0.17 (22) | 648 |
| | | | 158 | 2.16 | 0.79 | 0.14 | (0.70, 0.29) |
| | | | 959 | 2.58 | 0.95 | 0.15 | |
| M | Pt-1 (3 wt.-%) | 8.0 | 10810 (18) | 1.68 (14) | 7.79 (14) | 1.75 (14) | 540 |
| | | | 1552 | 1.62 | 7.76 | 1.70 | (0.46, 0.53) |
| | | | 6354 | 1.52 | 6.52 | 1.22 | |
| N | Pt-1 (6 wt.-%) | 9.0 | 10070 (18) | 2.88 (14) | 8.31 (11) | 2.13 (14) | 540 |
| | | | 1652 | 2.87 | 8.27 | 1.83 | (0.46, 0.53) |
| | | | 6632 | 2.45 | 7.08 | 1.35 | |
| O | Pt-1 (10 wt.-%) | 8.0 | 16070 (17) | 3.36 (14) | 9.55 (11) | 2.31 (14) | 540 |
| | | | 1907 | 3.35 | 9.51 | 2.27 | (0.47, 0.52) |
| | | | 8369 | 3.01 | 8.54 | 1.72 | |
| P | Pt-1 (15 wt.-%) | 8.0 | 12490 (18) | 3.42 (14) | 8.93 (13) | 2.10 (14) | 540 |
| | | | 1776 | 3.41 | 8.91 | 1.98 | (0.48, 0.51) |
| | | | 7404 | 2.86 | 7.47 | 1.42 | |

^a Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. ^b Values collected at 20 mA cm⁻². ^c Values collected at 100 mA cm⁻². ^d CIE coordinates [x, y] in parentheses.