Electronic Supplementary Information

bis-Zn^{II} salphen complexes bearing pyridyl functionalized ligands for efficient organic light-emitting diodes (OLEDs)

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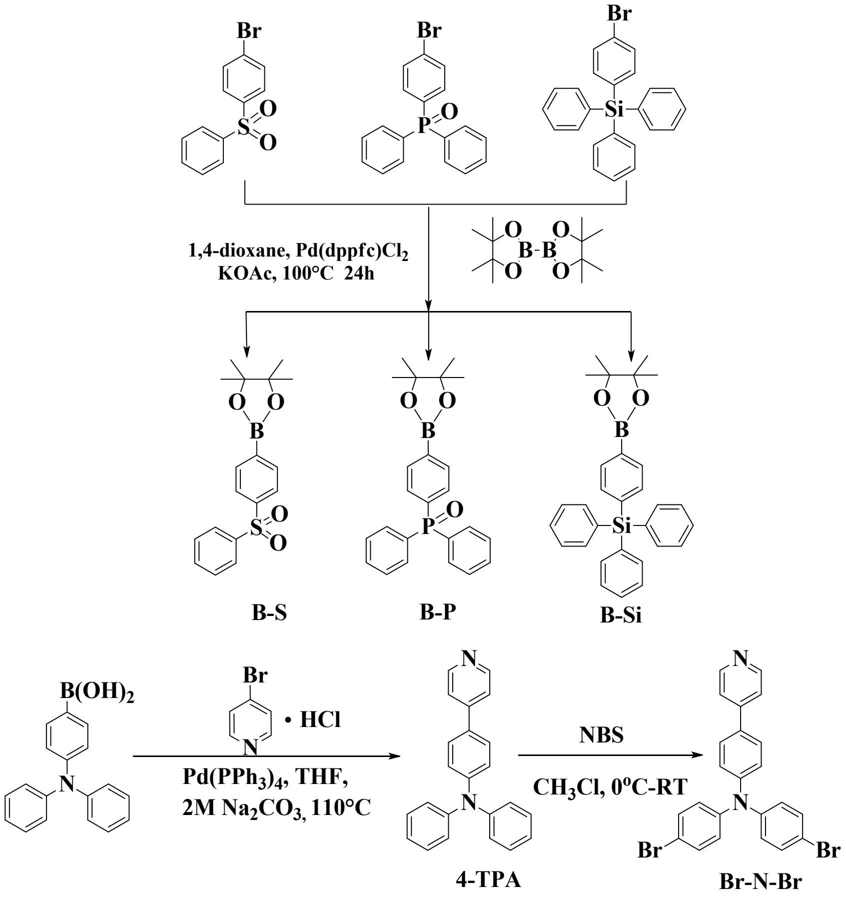
Contents

Synthesis detials for intermediate compounds.



Scheme S1 Synthetic scheme for intermediate compounds.

Preparation of *bis*-Schiff Base ligand (L-SB): To a solution of 1,2,4,5-benzenntetramine tetrahydrochloride (130 mg, 0.4577 mmol) in 20 mL anhydrous methanol was added of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (471 mg, 2.014 mmol). After 18 h continuously stirring, the yellow precipitate was collected and washed with anhydrous methanol and dried under vacuum. The yellow solid was obtained. (Yield: 92%, 423 mg); ^{1}H NMR (400 MHz, CDCl$_{3,}$□δ): 13.47 (s, 4H), 8.78 (s, 4H), 7.47 (d, J = 2.4 Hz, 4H), 7.27 (d, J = 2.4 Hz, 4H), 7.16 (s, 2H), 1.46 (s, 36H), 1.34 (s, 36H); ^{13}C

NMR (100 MHz, $CDCl_3$, δ): 164.65, 158.63, 141.57, 140.50, 137.24, 128.50, 126.91, 118.32, 111.14, 35.12, 34.19, 31.45, 29.42.

Preparation of Zn-C: To a solution of *bis*-Schiff Base compound (100 mg, 9.97 mmol) in 20 mL mixture of chloroform and methane (2 : 1) was added of $Zn(AcO)_2{\cdot}H_2O$ (67 mg, 2.989 mmol). After stirring at room temperature for 18 h, the solvent was evaporated and the red solid was dissolved in Dichloromethane, the insoluble residual was filtered off, after evaporating dichloromethane of the filtrate, the red **Zn-C** was obtained by recrystallization in Acetonitrile. (Yield: 65%, 73 mg); ^{1}H NMR (400 MHz, Acetone-$d_{6,}$ δ): 9.25 (s, 4H), 8.50 (s, 2H), 7.47 (d, J = 4 Hz, 4H), 7.19 (d, J = 2.4 Hz, 4H), 1.55 (s, 36H), 1.34 (s, 36H).

General procedures for the synthesis of borate compounds: Under a N_2 atmosphere, bis-(pinacolato)diboro (1.40 g, 5.5 mmol), the aromatic bromide prepared from literature reported[1] (5 mmol), KOAc (0.54 g, 5.5 mmol) and $Pd(dppfc)Cl_2$ (0.18 g, 5 mol-%) were heated to 100 °C in 25 mL degassed 1,4-dioxane for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane, the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residual was chromatographed using appropriate eluent to produce the title product.

B-S: 1.62 g white solid was obtained by using PE : EA = (5 : 1) as eluent (Yield: 93%);. ^{1}H NMR (400 MHz, $CDCl_{3,}$□δ): 7.94–7.92 (m, 6 H), 7.57–7.53 (m, 1 H), 7.48 (t, J = 7.2 Hz, 2 H), 1.32 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.61, 141.46, 135.46, 133.18, 129.25, 127.63, 126.61, 84.41, 24.81; FAB-MS (*m/z*): 344 $[M]^+$. Elemental analysis calcd (%) for $C_{18}H_{21}BO_4S$: C 62.80, H 6.15; found: C 62.74, H 5.98.

B-P: 1.58 g brown oil was obtained by using EA : DCM = 1: 1 as eluent (Yield: 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88–7.85 (m, 2 H), 7.68–7.60 (m, 6 H), 7.54–7.50 (m, 2 H), 7.45–7.40 (m, 4 H), 1.32 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.24, 134.52, 134.40, 134.22, 132.55, 132.07, 131.97, 131.93, 131.51, 131.16, 131.07, 128.48, 128.36, 84.12, 24.75; ^{31}P NMR (162 MHz, CDCl3): δ (ppm) 29.12; FAB-MS (*m/z*): 404 $[M]^+$. Elemental analysis calcd (%) for $C_{24}H_{26}BO_3P$: C 71.31, H 6.48; found: C 71.19, H 6.39.

B-Si: 1.81 g white solid was obtained by using EA : DCM = 1 : 1 as eluent (Yield: 78%); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.80 (d, *J* = 7.6 Hz, 2 H), 7.56 (t, *J* = 6.8 Hz, 8 H), 7.43 (t, *J* = 7.6 Hz, 3 H), 7.37 (t, *J* = 7.2 Hz, 6 H), 1.32 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.94, 136.52, 135.83, 134.19, 134.02, 129.75, 128.08, 83.98, 25.01; FAB-MS (*m/z*): 462 $[M]^+$. Elemental analysis calcd (%) for $C_{30}H_{31}BO_2Si$: C 77.91, H 6.76; found: C 77.79, H 6.68.

Preparation of 4-TPA: Under a N_2 atmosphere, 4-bromopyridine hydrochloride (0.97 g, 5.5 mmol), (4-(diphenylamino)phenyl)boronic acid (1.45 g, 5 mmol), tetrabutylammonium iodide (2.032 g, 5.5 mmol) and $Pd(PPh_3)_4$ (0.289 g, 5% mmol) were heated to 110 °C in a mixture of 10 mL 2M Na_2CO_3 and 25 mL degassed THF for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane, the organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was obtained as a crude product, which was chromatographed on a silica column using PE : EA = 2 : 1 as eluent to produce a pure product. (Yield: 62%, 998 mg); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.62 (d, *J* = 6 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 4H), 7.30 (t, *J* = 8.4 Hz, 4H), 7.15–7.13 (m, 6H), 7.8 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.16, 148.92, 147.63, 147.22, 130.91, 129.41, 127.61, 124.96, 123.58, 122.89, 120.86; FAB-MS (*m/z*): 322 $[M]^+$. Elemental analysis calcd (%) for $C_{23}H_{18}N_2$: C 85.68, H 5.63, N 8.69; found: C 85.55, H 5.59, , N 8.58.

Preparation of Br-N-Br: Under a N_2 atmosphere, **4-TPA** (0.8 g, 2.485 mmol), NBS (0.876 g, 5.093 mmol) and 3 drops AcOH was stirred in 25 mL chloroform at room temperature for 1h. After 18h continuously stirring at 50 °C, 20 ml water was added, the mixture was extracted with dichloromethane, the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The target product obtained by flash silica column using DCM : EA = 4 : 1 as eluent. (Yield: 97%, 1.157 g); ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.63 (d, *J* = 4.4 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.47 (d, *J* = 5.6 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 150.26, 147.89, 147.32, 145.96, 132.57, 132.29, 127.95, 126.08, 123.67, 120.96, 116.36; FAB-MS (*m/z*): 478 [M]$^+$. Elemental analysis calcd (%) for $C_{23}H_{16}Br_2N_2$: C 57.53, H 3.36, N 5.85; found: C 57.39, H 3.27, N 5.72

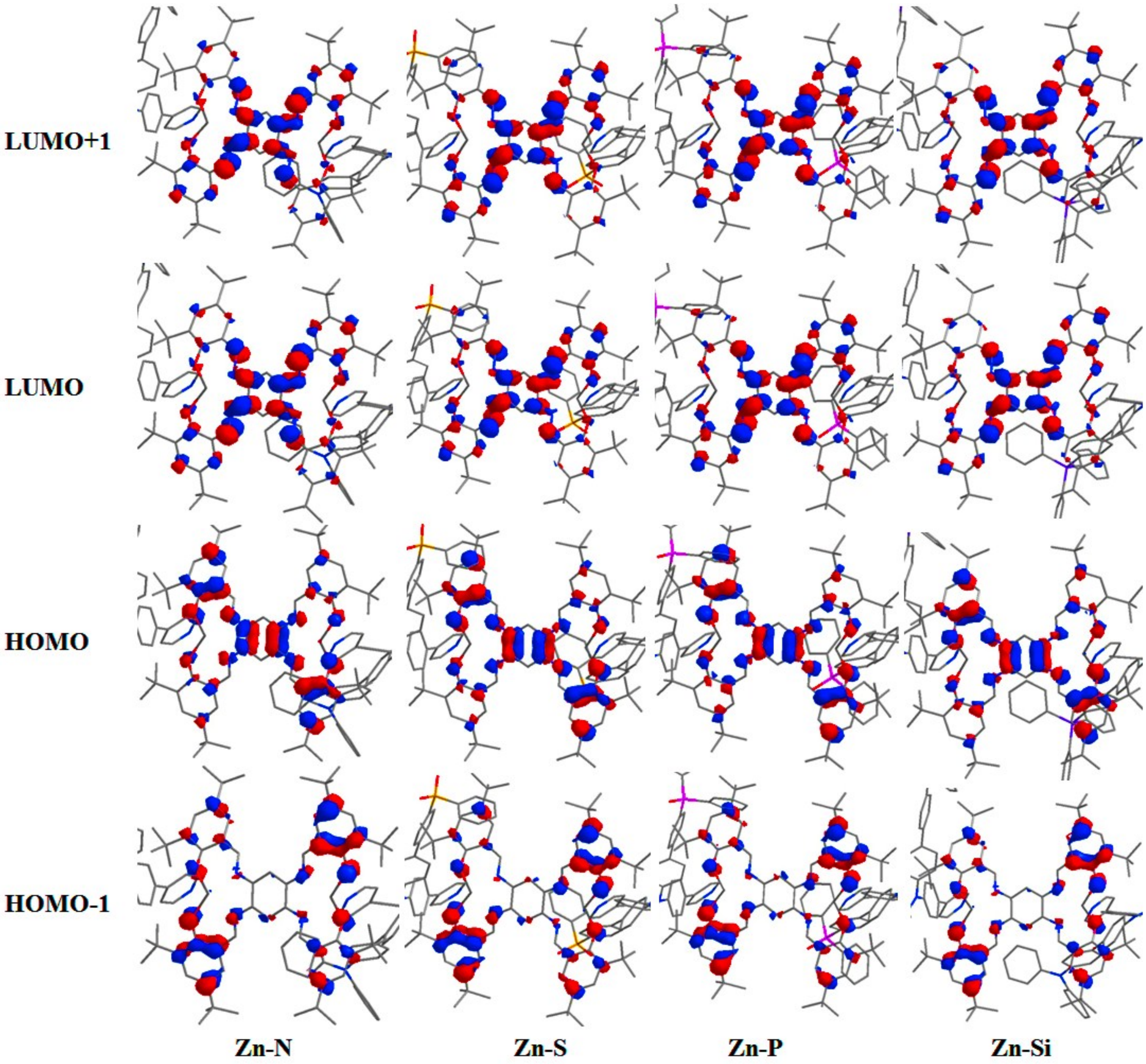


Fig. S1 Key front molecular orbital patterns of the *bis*-Zn^{II} salphen complexes with expanded view.

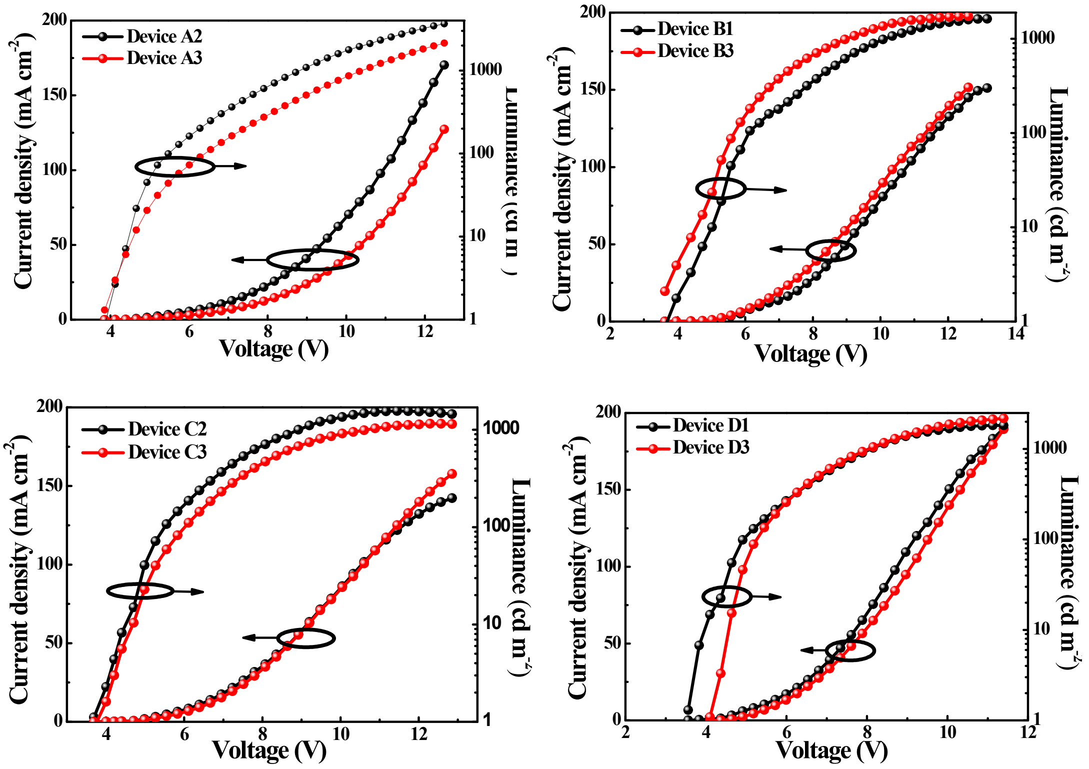


Fig. S2 Current density–voltage–luminance (*J*–*V*–*L*) curves for the OLEDs.

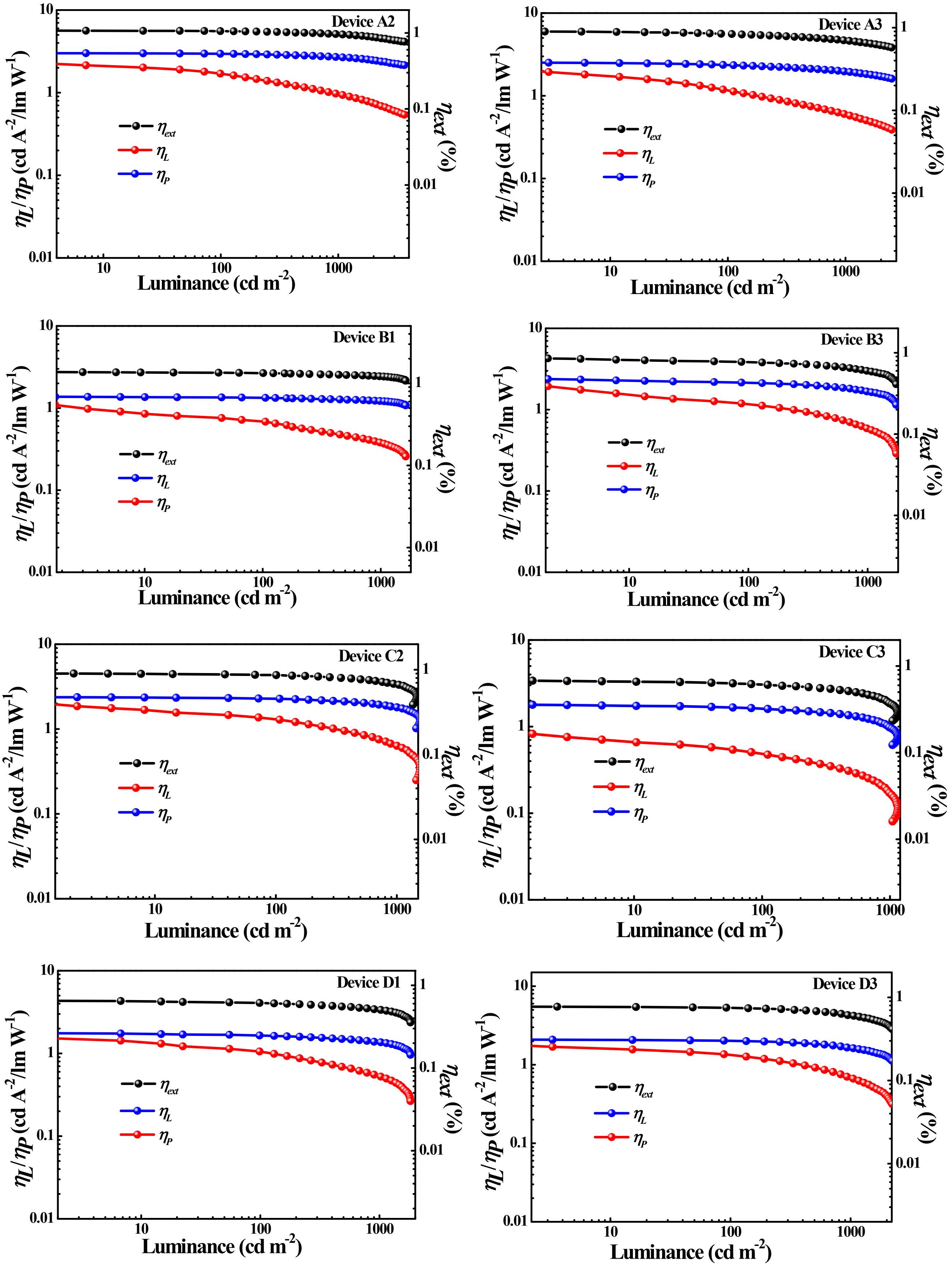


Fig. S3 EL efficiency–luminance curves for the OLEDs.

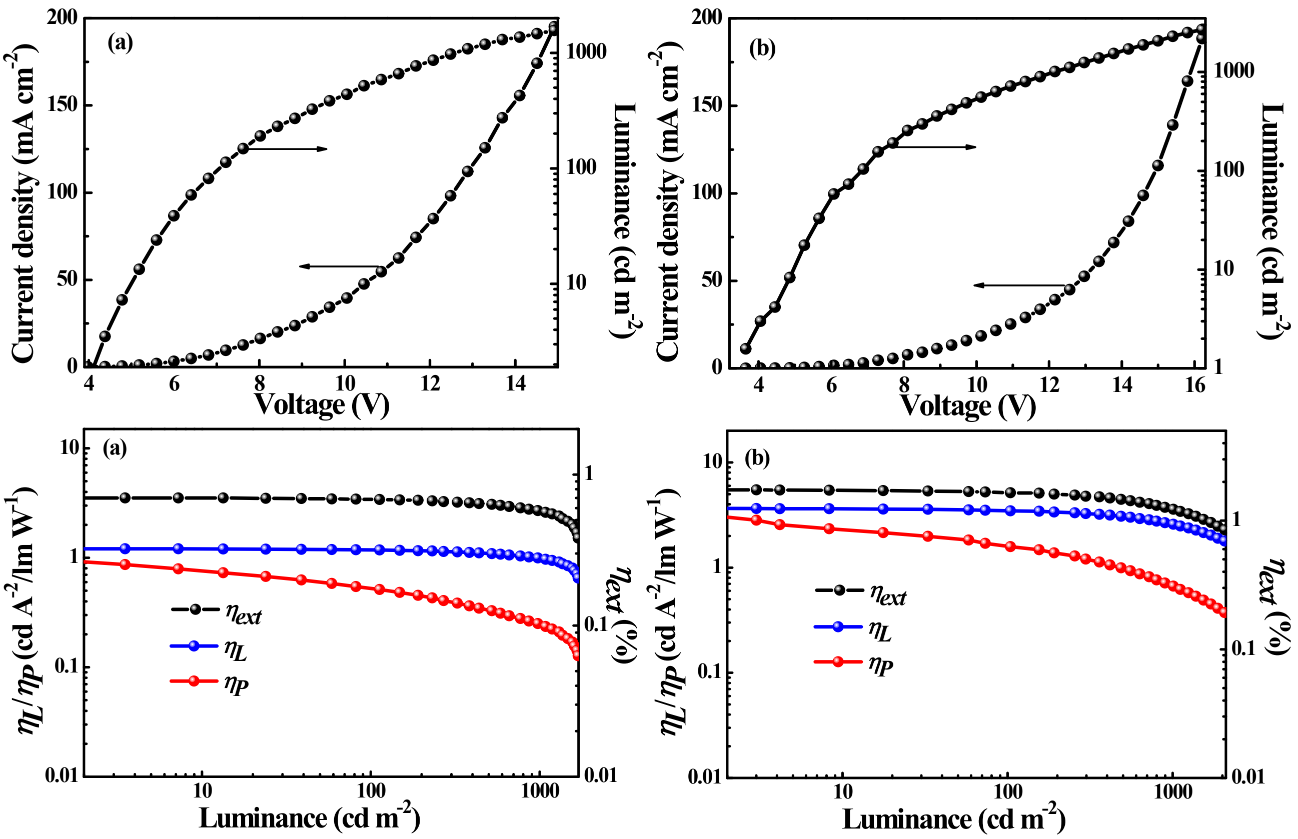


Fig. S4 Current density–voltage–luminance (*J*–*V*–*L*) curves and EL efficiency–luminance curves for OLEDs. (a) Device based on **Zn-C** with 6 wt-% doping level, (b) Device based with **Zn-N** neat film.

Reference

1. G.-J. Zhou, Q. Wang, C.-L. Ho, W.-Y. Wong, D.-G. Ma, L.-X. Wang and Z.-Y. Lin, *J. Mater. Chem.*, 2010, **20**, 7472.