

## Electronic supplementary information

for

### **Asymmetric *tris*-Heteroleptic Iridium(III) Complexes Containing Three Different 2-Phenylpyridine-Type Ligands: A New Strategy for Improving Electroluminescent Ability of Phosphorescent Emitters†**

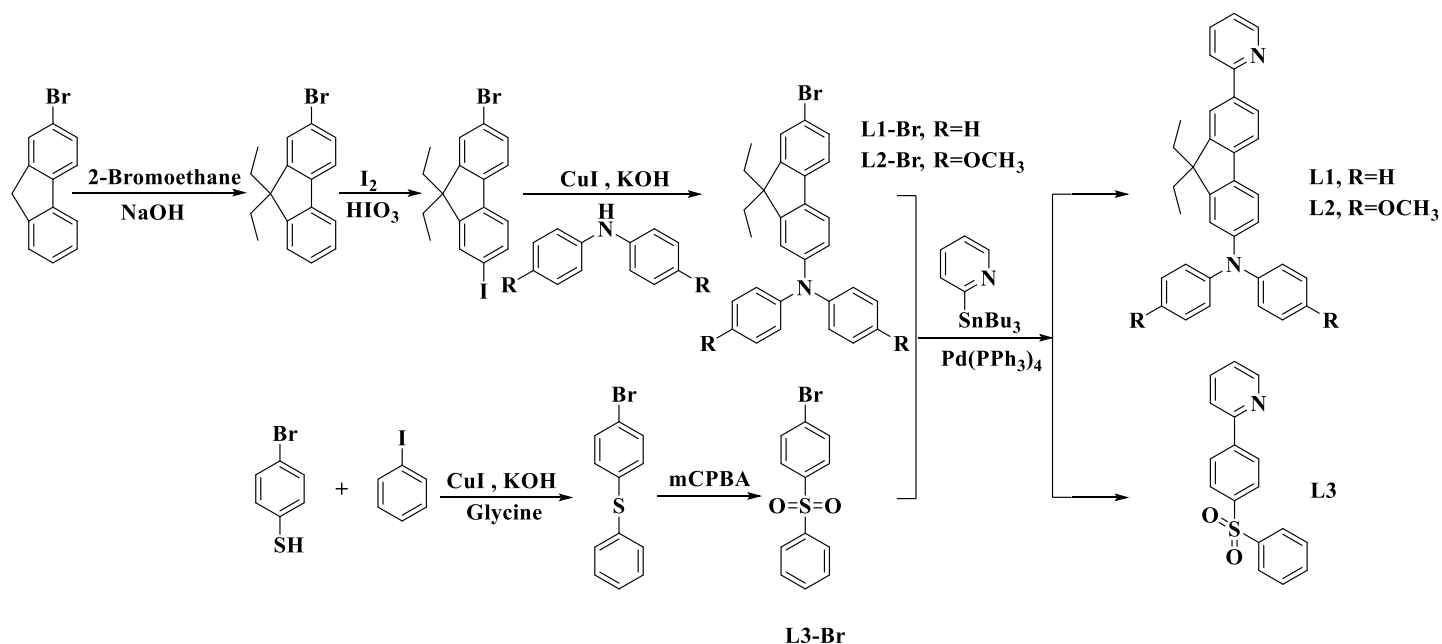
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## Experimental



**Scheme S1** Synthetic scheme for the organic ligands.

### 2-bromo-9,9-diethylfluorene.

To a stirred solution of 2-bromofluorene (5.00 g, 20.40 mmol) in 50 ml DMSO, NaOH (2.44 g, 61.00 mmol) was added. After 5 min of stirring, bromoethane (14.00 g, 44.00 mmol) was added slowly. The reaction mixture were stirred continuously for 24 h at 90 °C. Then the reaction mixture was poured into cold water (100 mL), and extracted with dichloromethane (3×30 mL). The organic phase was washed with water, and dried over MgSO<sub>4</sub> before the solvent was evaporated. Then the mixture was purified by column chromatograph with hexane. The product was obtained as a white solid (5.40 g, Yield: 88%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.69–7.65 (m, 1H), 7.57–7.55 (m, 1H), 7.47–7.44 (m, 2H), 7.34–7.29 (m, 3H), 2.06–1.96 (m, 4H), 0.32 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) 152.13, 149.45, 140.52, 140.41, 129.91, 127.45, 126.98, 126.19, 122.89, 120.96, 119.69, 99.96, 56.40, 32.67, 8.41.

### 2-Bromo-9,9-diethyl-7-iodofluorene.

A mixture of 2-bromo-9,9-diethylfluorene (4.5 g, 15.00 mmol), iodine (1.52 g, 6.00 mmol), iodic acid (0.6 g, 3.41 mmol), concentrated sulfuric acid (0.8 mL), acetic acid (40 mL), water (4 mL) and carbon tetrachloride (5 mL) was maintained at 80-85 °C for 2.5 h with mechanical stirring. The product slurry was cooled to room temperature and filtered, and the solids was washed with acetic acid-water (1:1) and water. The product was obtained as light yellow solid after dried (5.71 g, Yield: 92%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.68–7.64 (m, 1H), 7.57–7.54 (m, 1H), 7.47–7.40 (m, 3H), 7.35–7.30 (m, 1H), 2.04–1.96 (m, 4H), 0.31 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) 151.84, 151.49, 140.04, 139.50, 136.10, 132.12, 130.09, 126.16, 121.38, 121.10, 92.89.

#### **L1-Br.**

Under N<sub>2</sub> atmosphere, the mixture of 2-bromo-9,9-diethyl-7-iodofluorene (4.50 g, 10.50 mmol), diphenylamine (1.96 g, 11.60 mmol), phenanthroline (0.34 mg, 1.86 mmol), CuI (0.22 mg, 1.18 mmol) and p-xylene (30 mL) was heated to 100 °C for 15 min. Then KOH (4.48 g, 0.08 mol) were added. The reaction mixture was stirred vigorously and refluxed for 2 days. After the solution was cooled to room temperature, glacial acetic acid (10 g) was added. The mixture was dissolved in toluene (100 mL) and washed with water (100 mL). Then the organic layer was washed with conc. Na<sub>2</sub>CO<sub>3</sub> (100 mL) and water (100 mL) and dried over MgSO<sub>4</sub>. The solvent was removed and the crude product was purified by column chromatography with hexane. The product was obtained as white solid (3.12 g, Yield: 64%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.52 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.43–7.40 (m, 3H), 7.25–7.23 (m, 4H), 7.11 (d, J = 7.6 Hz, 4H), 7.07–7.01 (m, 3H), 1.94–1.84 (m, 4H), 0.35 (t, J = 7.4Hz, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) 152.01, 151.10, 147.97, 147.50, 140.43, 135.63, 130.22, 129.50, 129.32, 129.10, 126.13, 124.23, 124.05, 123.79, 123.73, 123.63, 122.90, 122.72, 122.45, 120.51, 120.43, 120.20, 119.11, 56.41, 32.63, 8.60.

## L1

Under N<sub>2</sub> atmosphere, **L1-Br** (2.8 g, 5.98 mmol) and 2-tributylstannanyl-pyridine (2.42 g, 6.58 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.35 g, 0.30 mmol) were added to 30 mL dry toluene. The reaction mixture was stirred at 110 °C for 24 h. After it was cooled to room temperature, the reaction mixture was poured into separation funnel. Dichloromethane (50 mL) was added and washed with water (3×100 mL). The organic phase was dried over MgSO<sub>4</sub>. Then solvent was removed and the crude product was purified by column chromatography with dichloromethane-hexane (1:1) as eluent. The product was obtained as yellow solid (1.67 g, Yield: 60%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 8.70 (d, J = 4.6 Hz, 1H), 7.98–7.58 (m, 6H), 7.27–6.97 (m, 13H), 2.07–1.91 (m, 4H), 0.38 (t, J = 7.3 Hz, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) 157.64, 151.71, 150.31, 149.44, 147.81, 147.30, 142.18, 137.31, 136.49, 135.98, 129.05, 125.81, 123.76, 123.44, 122.42, 121.60, 121.01, 120.54, 120.38, 119.15, 119.13, 56.27, 32.72, 8.71.

## L2-Br.

The synthetic method was similar to **L1-Br**. **L2-Br** was obtained as yellow solid (0.17 g, Yield: 60%) using 2-tributylstannanyl-pyridine (2.42 g, 6.58 mmol) as raw material. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 7.44 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 9.6 Hz, 2H), 7.05 (d, J = 8.8 Hz, 4H), 6.93 (s, 1H), 6.88 (m, 1H), 6.82 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H), 1.94–1.79 (m, 4H), 0.34 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) 155.45, 151.75, 150.68, 148.49, 141.20, 140.48, 133.43, 129.75, 125.93, 125.88, 120.50, 120.03, 119.94, 119.45, 115.99, 114.50, 56.30, 32.63, 8.64.

## L2

The synthetic method was similar to **L1**. **L2** was obtained as orange solid (0.67 g, Yield: 56%) using bis(4-methoxyphenyl)amine (1.20 g, 2.27mmol) as raw material. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ

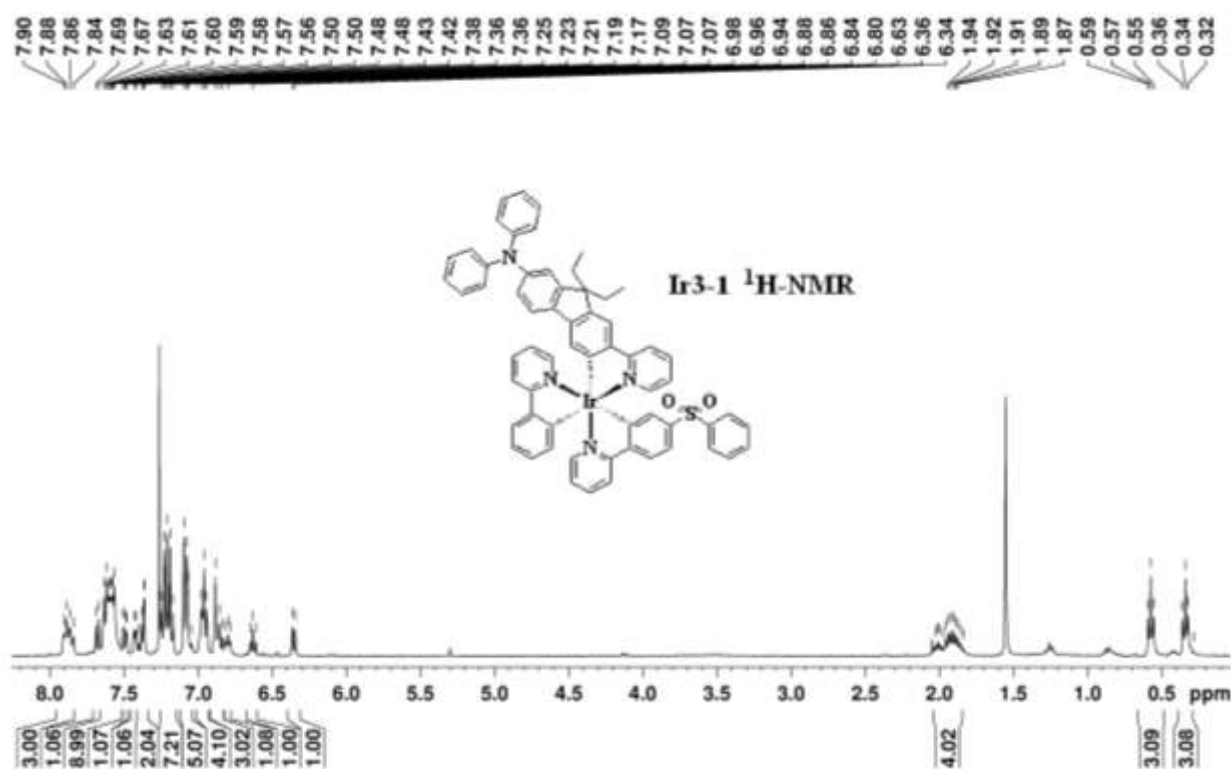
(ppm) 8.71 (d,  $J = 4.4$  Hz, 1H), 7.95–7.92 (m, 2H), 7.80–7.72 (m, 2H), 7.66 (d,  $J = 8.0$  Hz, 1H), 7.53 (d,  $J = 8.0$  Hz, 1H), 7.22–7.19 (m, 1H), 7.07 (d,  $J = 8.8$  Hz, 4H), 6.99 (s, 1H), 6.92–6.90 (m, 1H), 6.85–6.81 (m, 4H), 3.81(s, 6H), 2.07–1.87 (m, 4H), 0.37 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 157.76, 155.32, 151.63, 150.10, 149.43, 148.38, 142.52, 141.28, 136.86, 136.49, 134.18, 125.88, 125.77, 121.54, 120.95, 120.56, 120.33, 120.29, 118.80, 116.19, 114.53, 56.72, 55.47, 32.74, 8.68.

### **L3-Br**

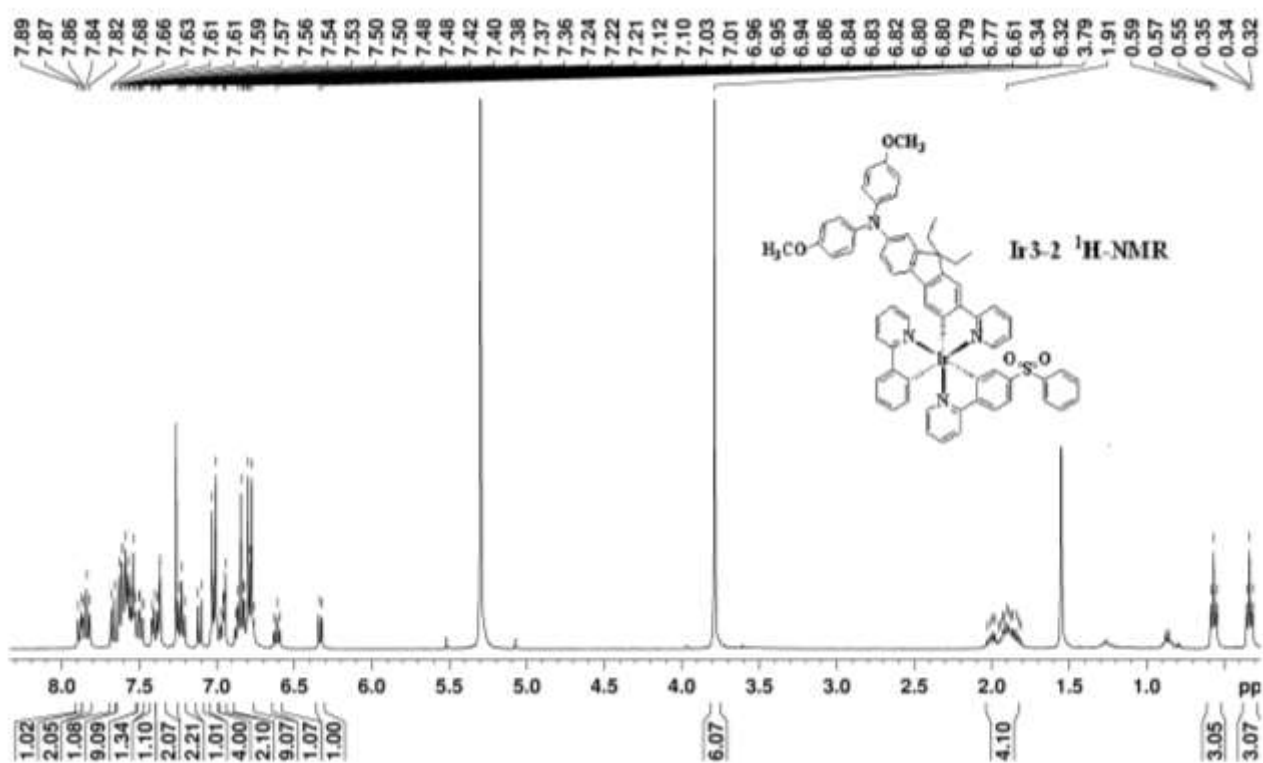
4-Bromothiophenol (1.00g, 5.29mmol) and iodobenzene (1.19g, 5.82mmol) were mixed in dioxane under a  $\text{N}_2$  atmosphere. Then, KOH (0.59g, 10.60mmol), CuI (0.10g, 0.53mmol) and glycine (0.08g, 1.06mmol) were added into the reaction mixture. The mixture was heated to 110 °C for 16 h. After cooling to room temperature, water was added and the mixture was extracted three times with  $\text{CH}_2\text{Cl}_2$ . The organic layer was collected and dried over  $\text{MgSO}_4$ . After the solvent was removed, the residue was dissolved in  $\text{CHCl}_3$  and *m*-chloroperoxybenzoic acid (mCPBA, 1.47g, 8.52mmol) was added slowly at 0 °C. After the addition, the reaction mixture was warmed to room temperature. slowly and stirred for 2 days to ensure completion of the reaction. Chloroform (50 mL) was added and the mixture was washed with 2 M sodium thiosulfate solution (3\*100 mL) and water (3\*100 mL). The organic phase was separated and dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent. The product was obtained as white crystals (0.94 g, 80%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.93–7.91 (m, 2H), 7.80–7.78 (m, 2H), 7.63–7.48 (m, 5H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 140.98, 140.53, 133.40, 132.50, 129.34, 129.09, 128.36, 127.54.

### **L3**

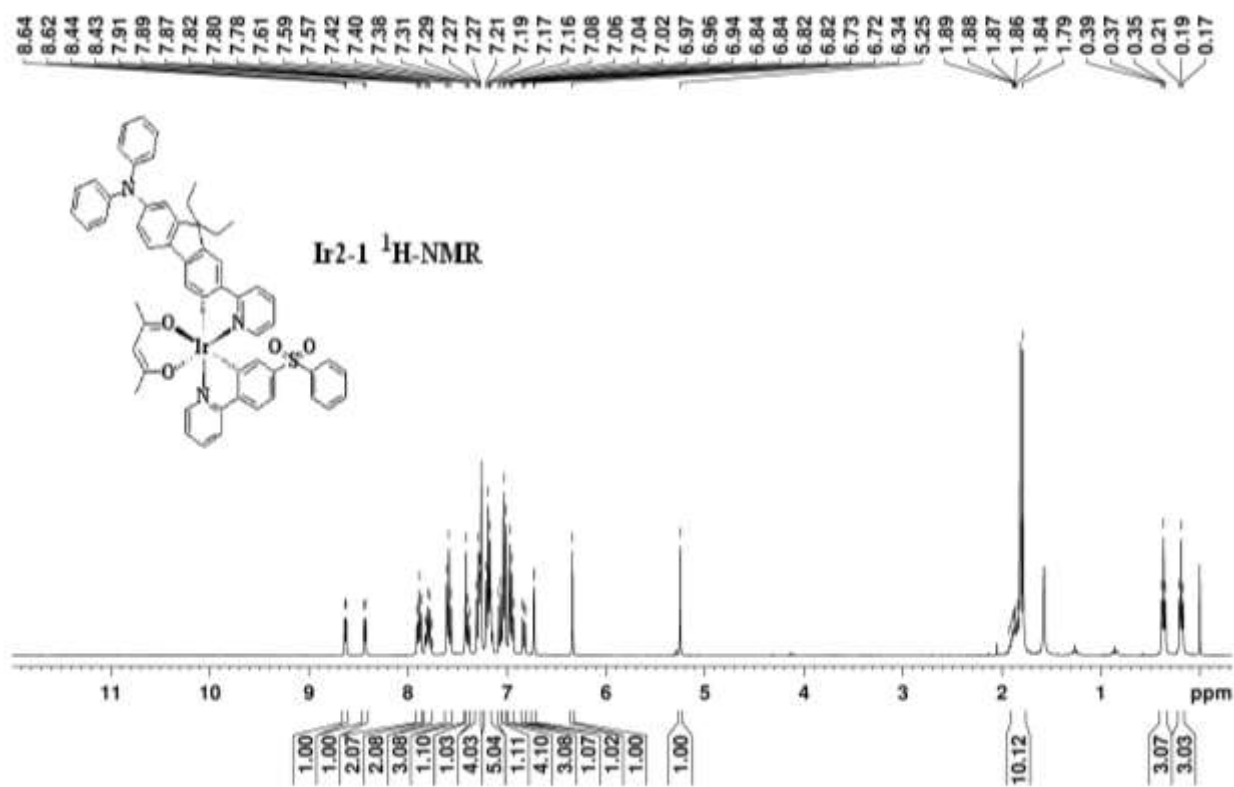
Under N<sub>2</sub> atmosphere, **L3-Br** (0.59 g, 1.98mmol ) and 2-(tributylstannyl) pyridine (0.80g, 2.17mmol) were mixed in dry toluene (50 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.114g, 0.10mmol) was added. The resulting mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a separating funnel and CH<sub>2</sub>Cl<sub>2</sub> (50mL) was added followed by washing with water (3\*100 mL). The organic phase was dried over MgSO<sub>4</sub>. The solvent was then removed and the residue was purified by column chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/ ethyl acetate (15:1, v/v). The product was obtained as a white solid (0.33 g, 65%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 8.71 (d, J = 4.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.98–7.96 (m, 2H), 7.81–7.74 (m, 2H), 7.59–7.49 (m, 3H), 7.32–7.29 (m, 1H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) 155.28, 149.99, 143.97, 141.55, 141.49, 137.02, 133.21, 129.28, 128.14, 127.71, 127.61, 123.26, 121.05.



(a)

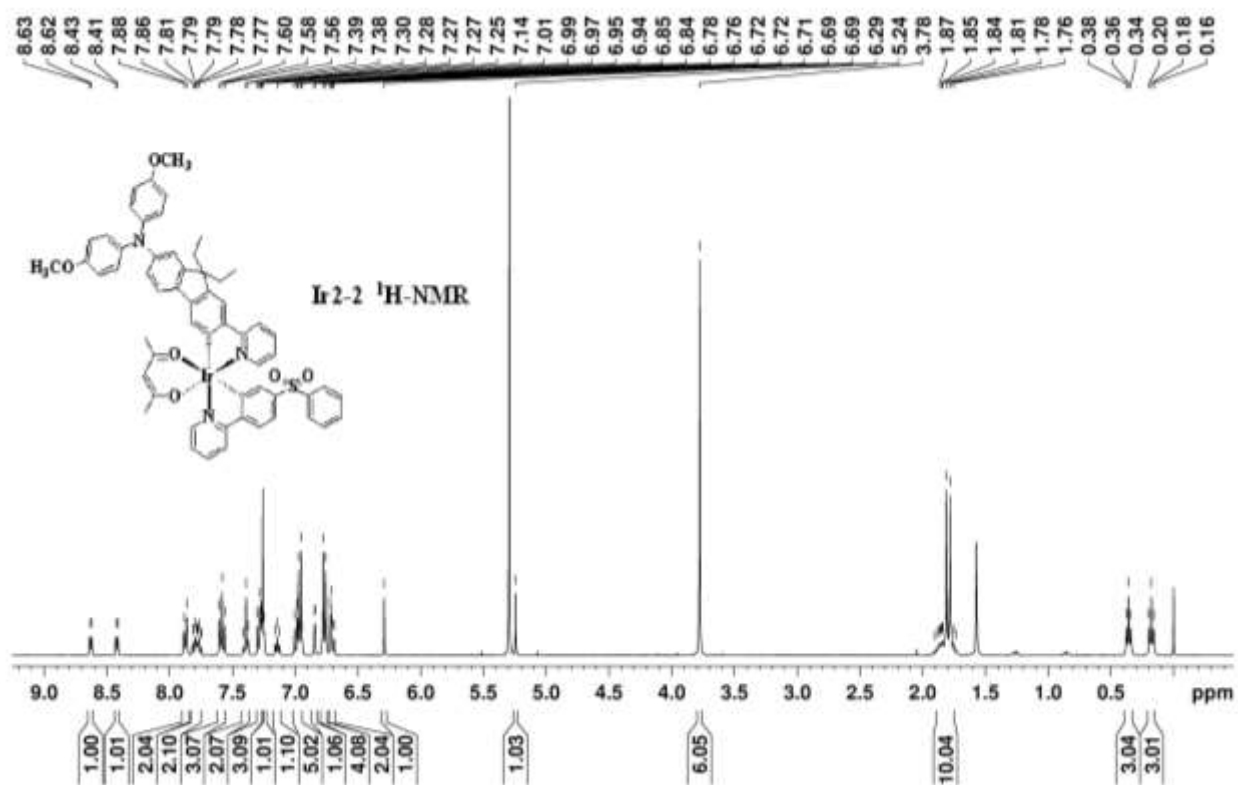


(b)

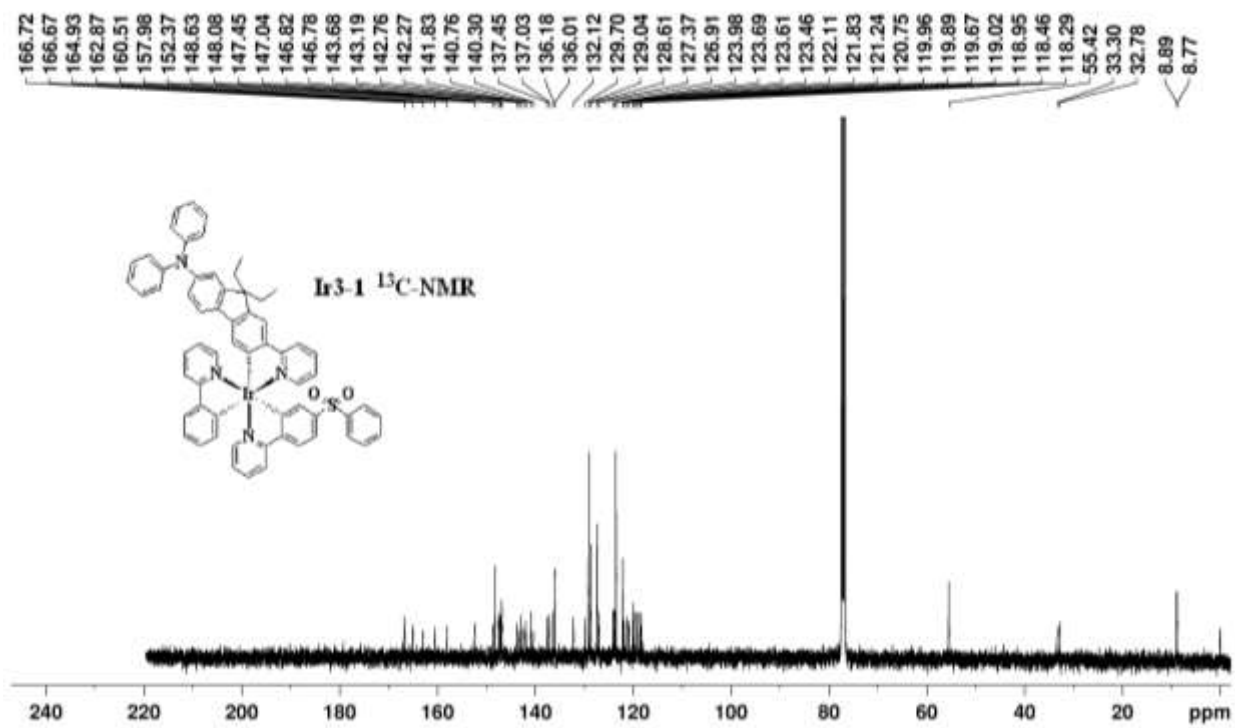


(c)

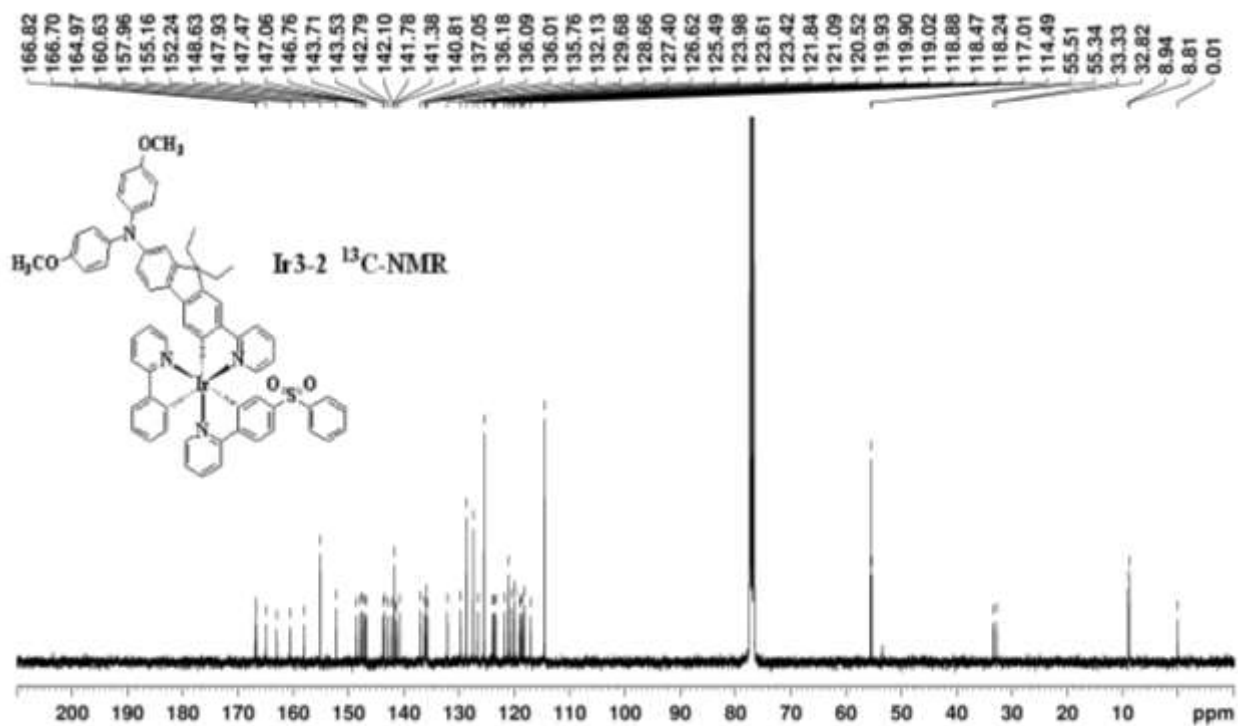




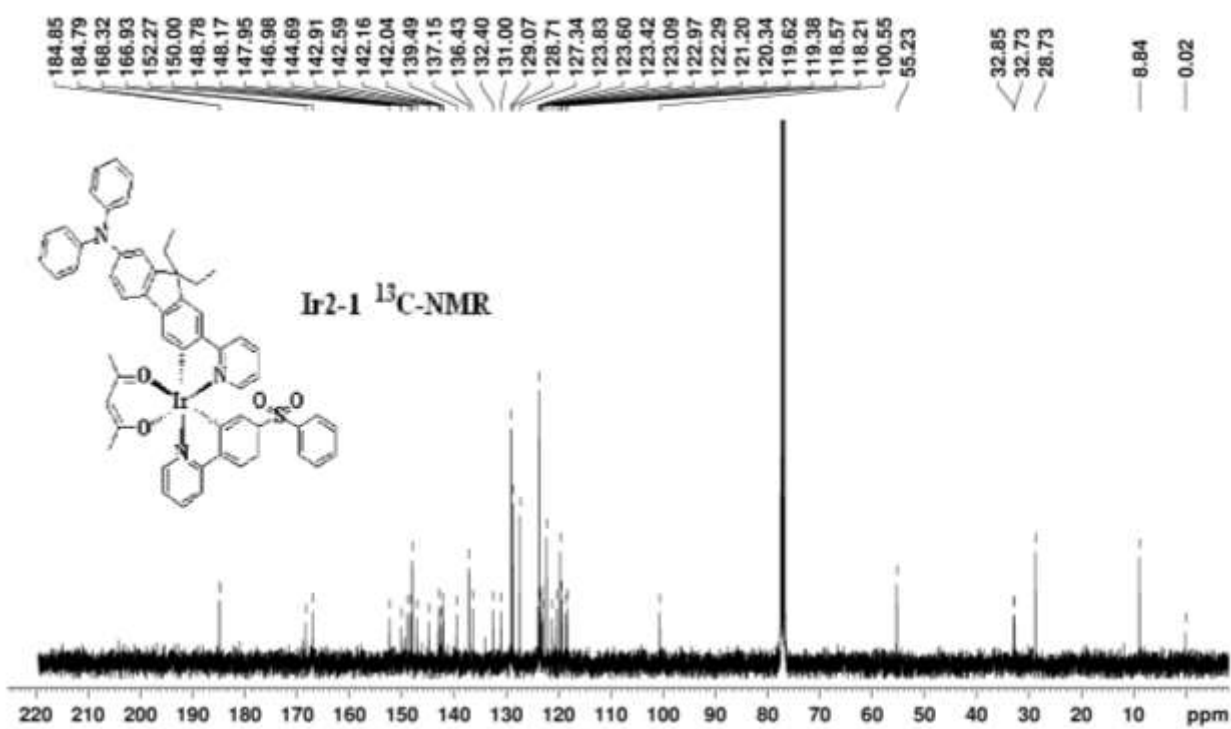
(d)



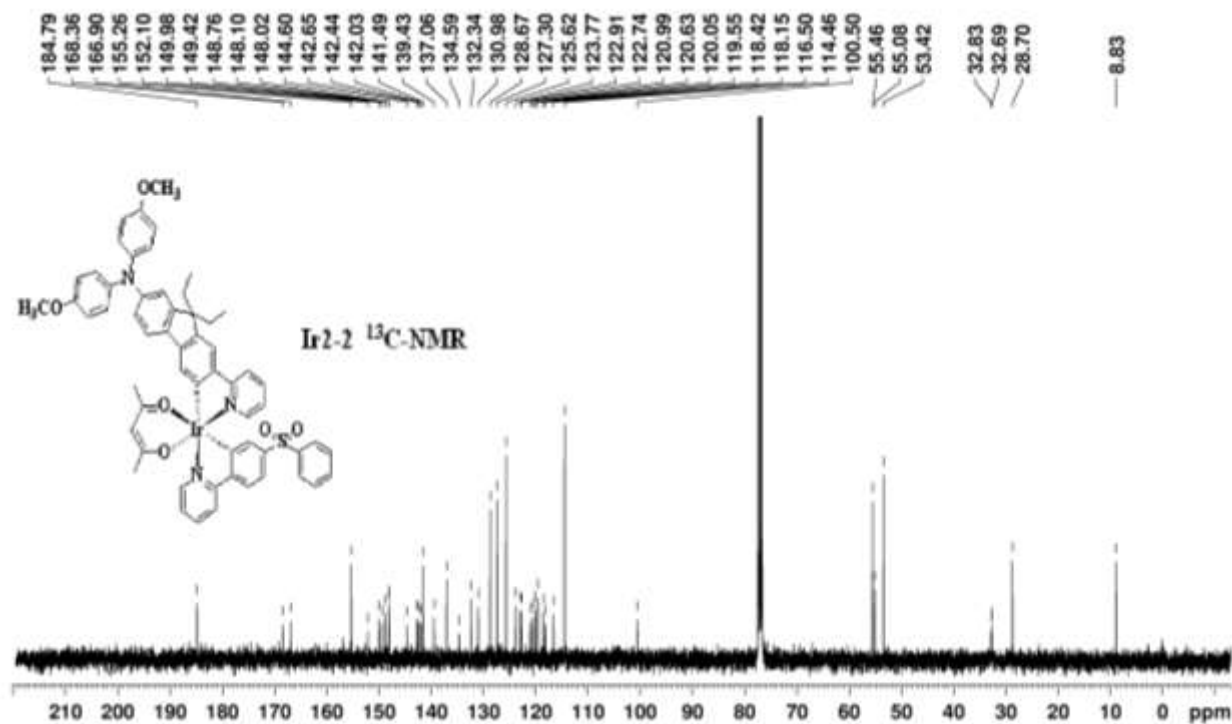
(e)



(f)



(g)



(h)

Fig. S1 The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra of Ir3-1, Ir3-2, Ir2-1 and Ir2-2.

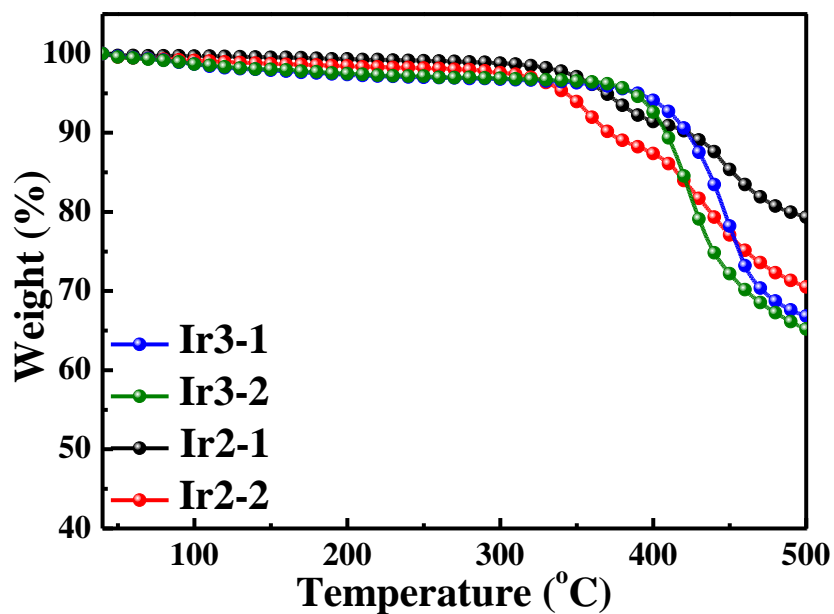
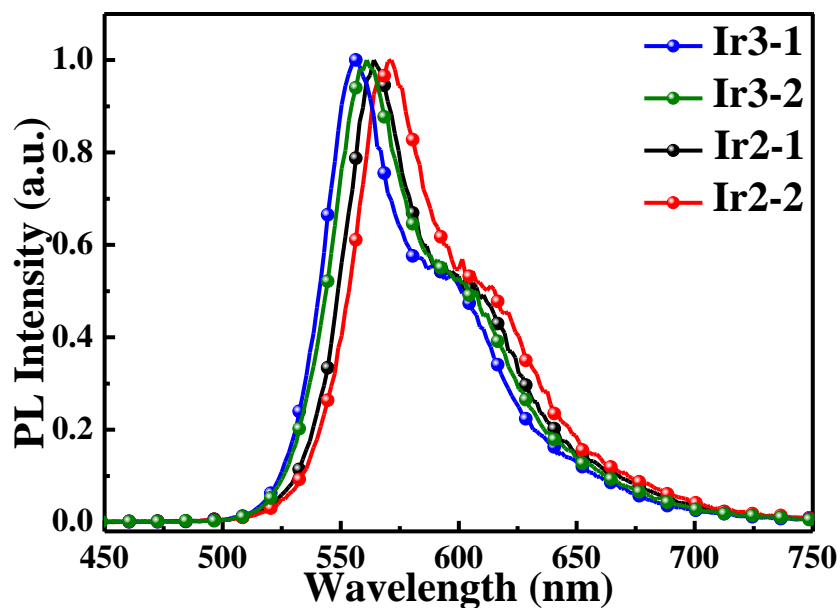
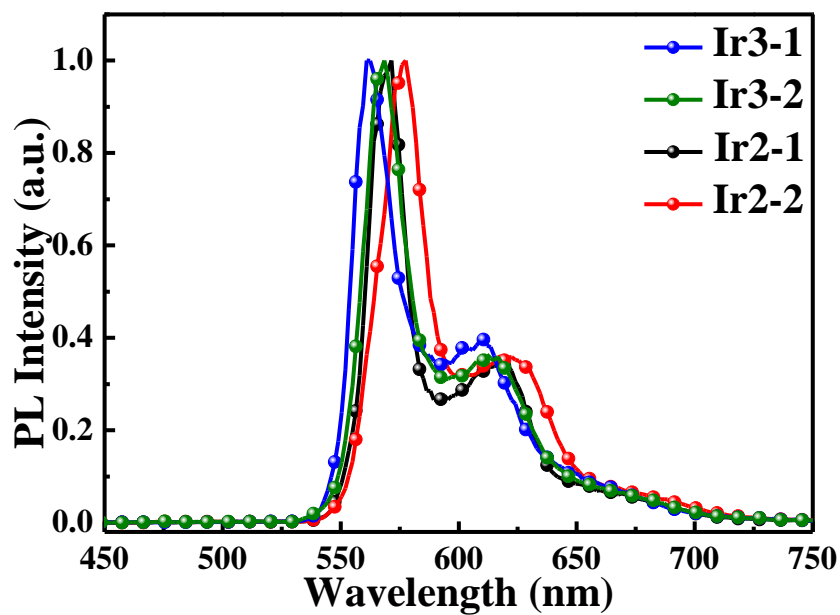


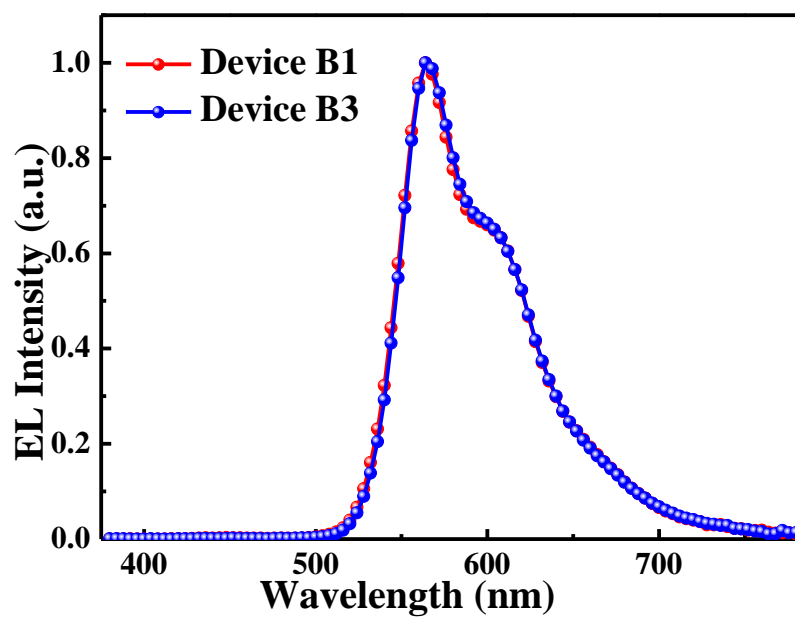
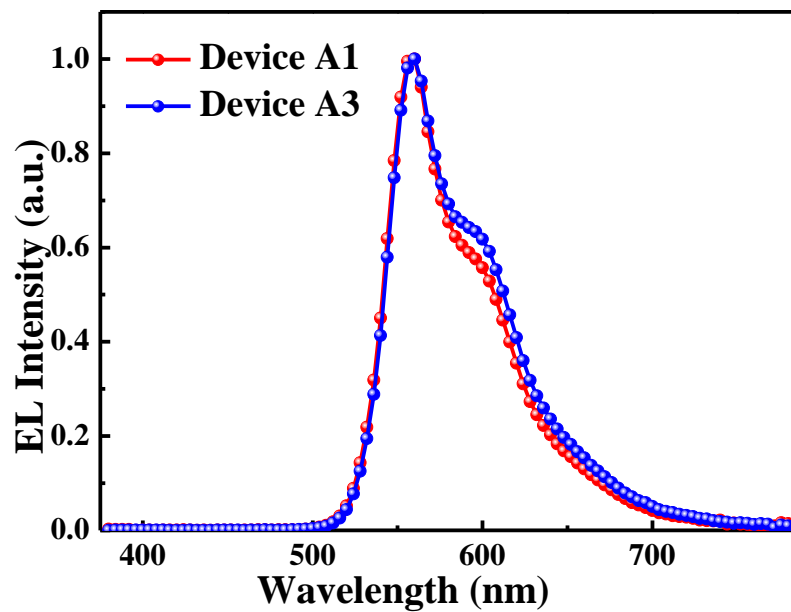
Fig. S2 TGA curves for the phosphorescent Ir(III) complexes.

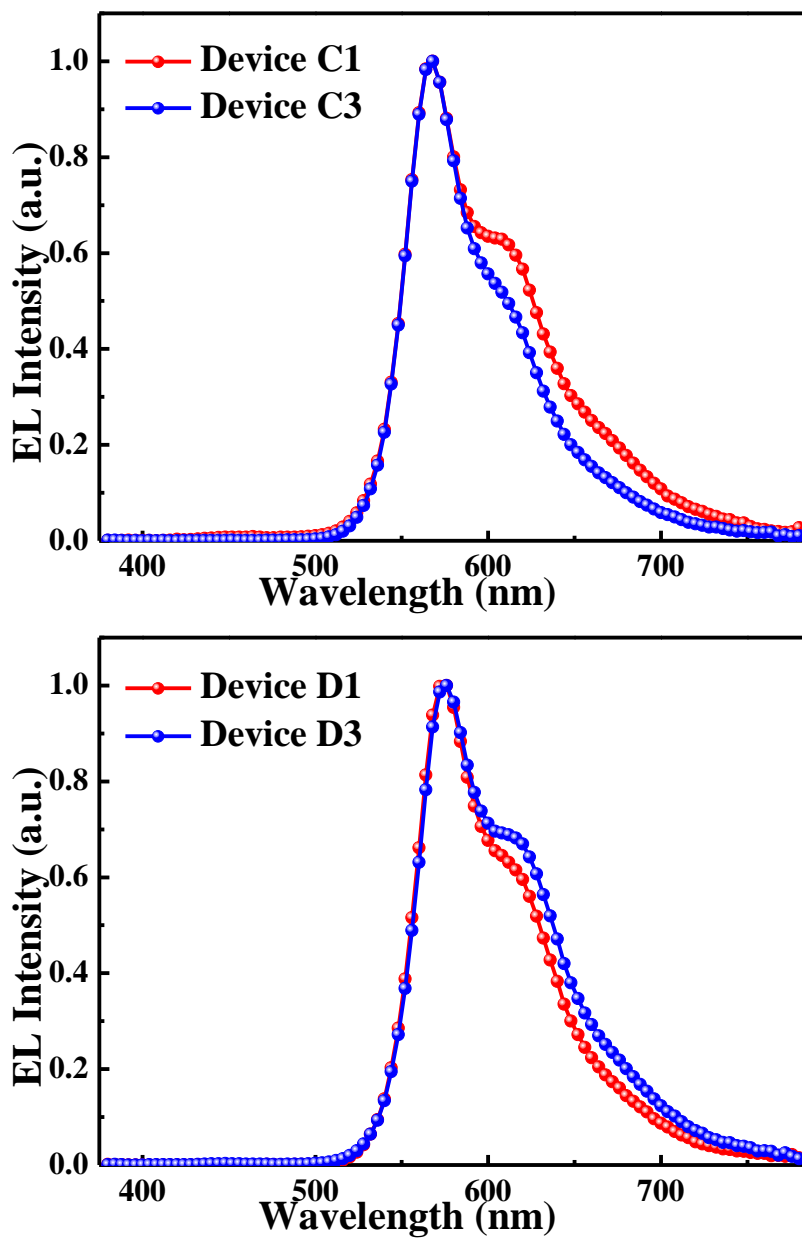


**Fig. S3** PL spectra for the phosphorescent Ir(III) complexes measured in PMMA film (6% wt doping level) at 298 K.

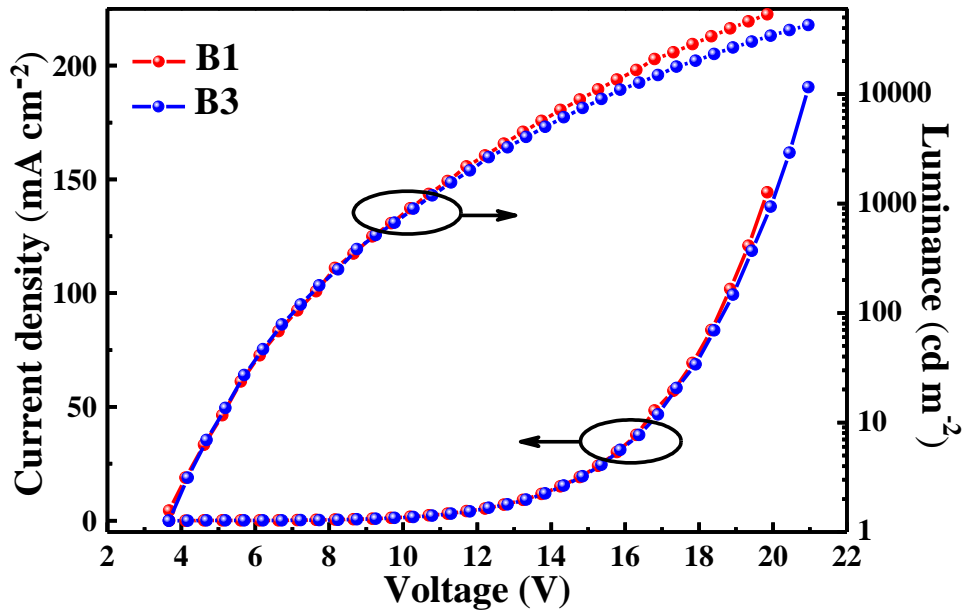
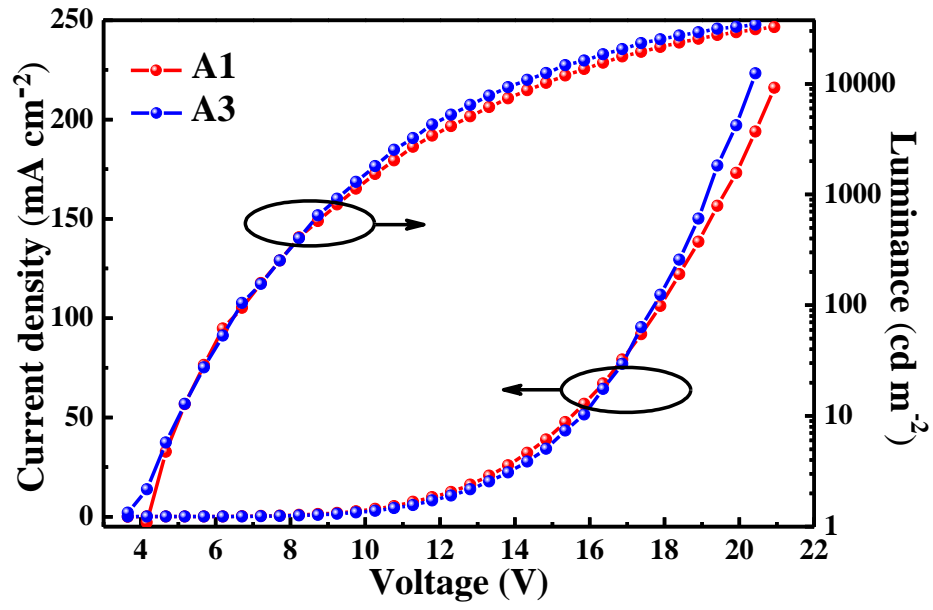


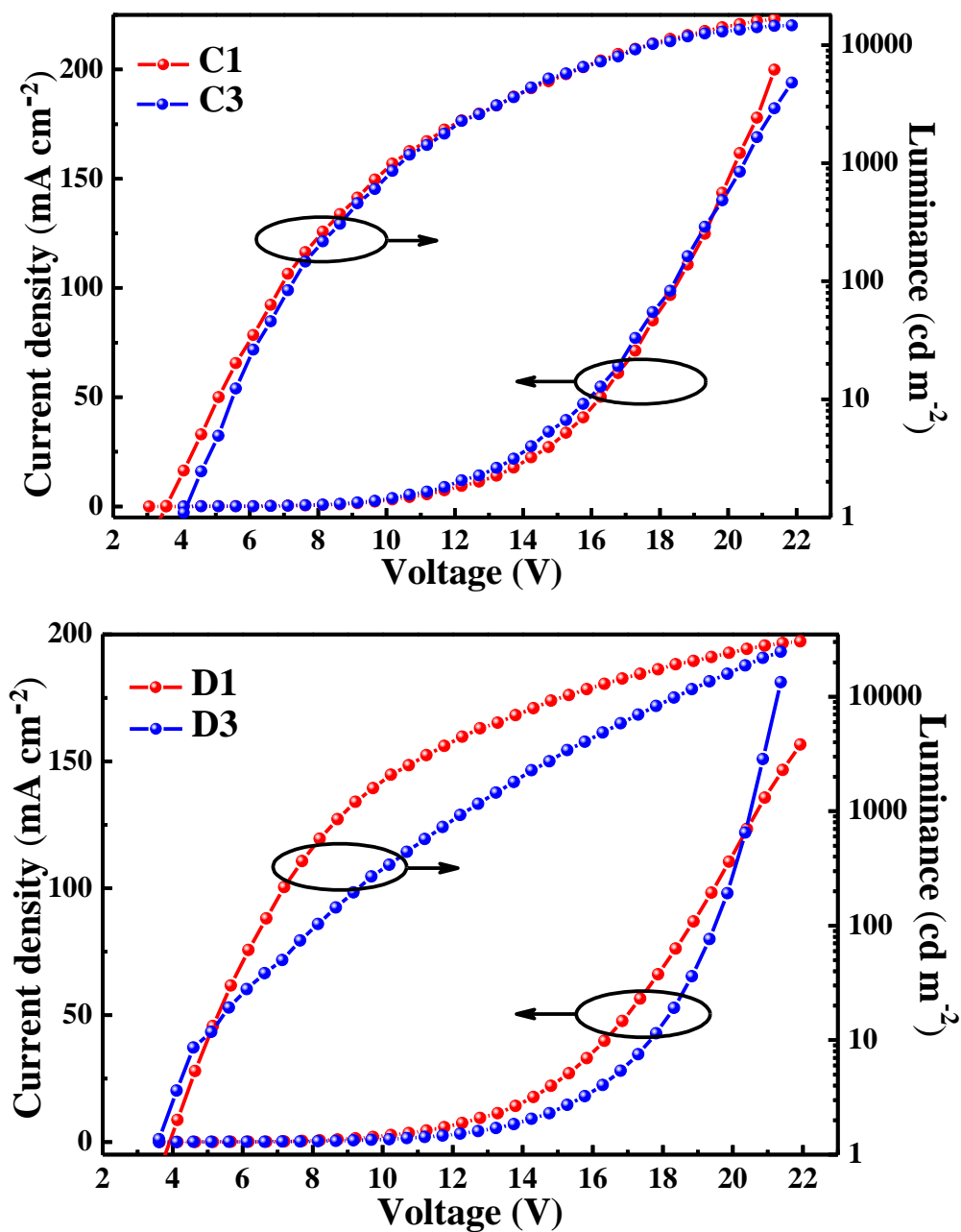
**Fig. S4** PL spectra for the phosphorescent Ir(III) complexes measured in CH<sub>2</sub>Cl<sub>2</sub> solution at 77 K.





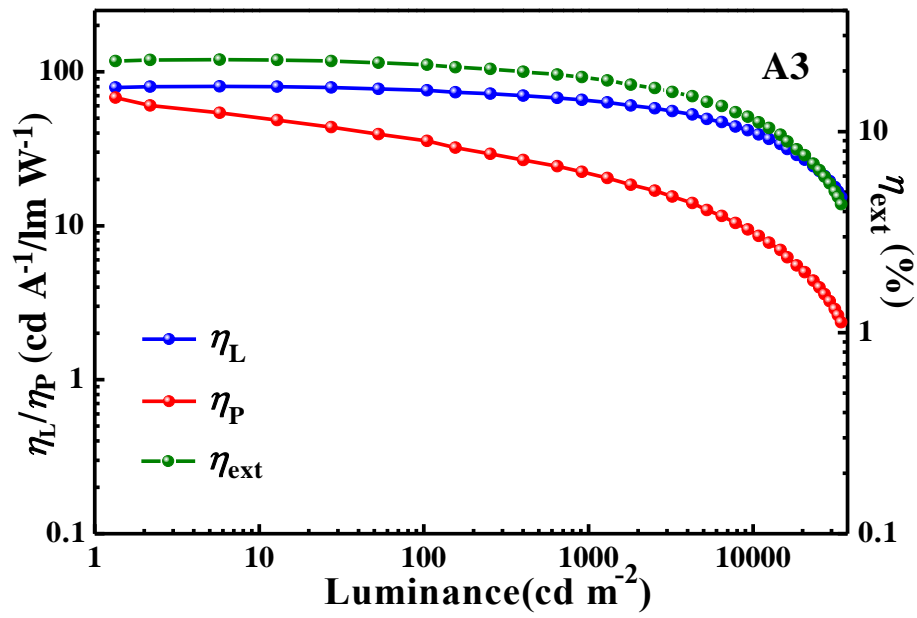
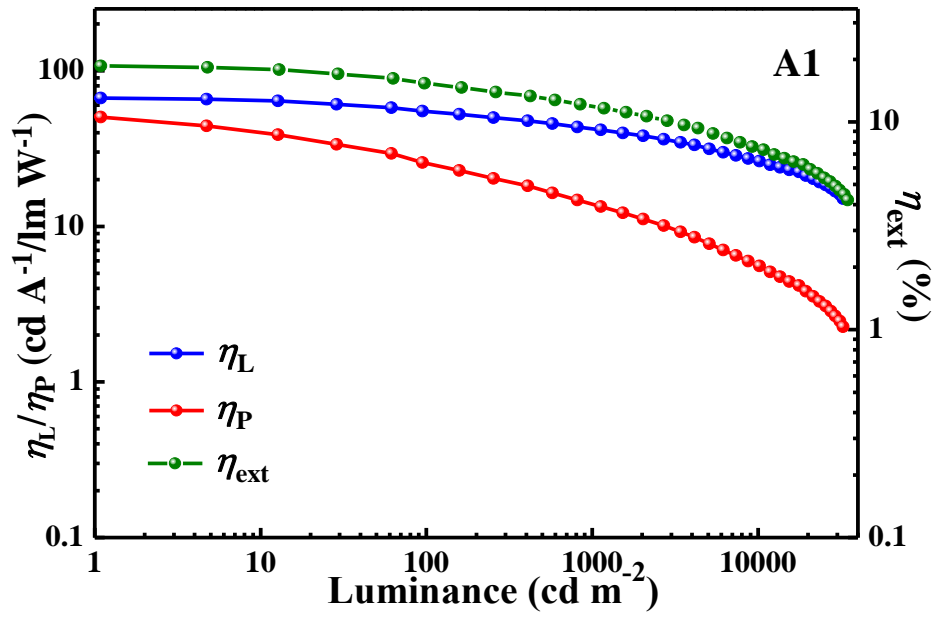
**Fig. S5** EL spectra for the OLEDs except the optimized ones at *ca.* 10 V.

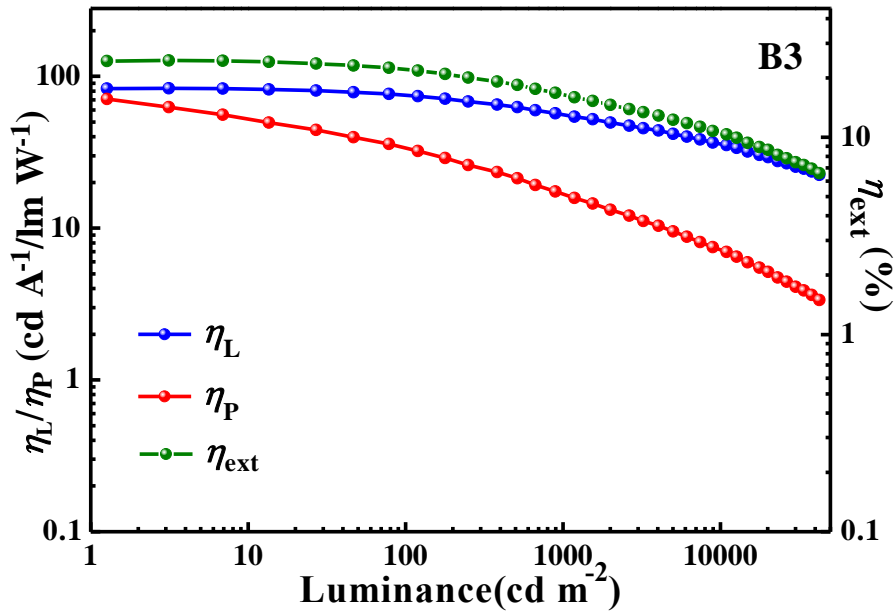
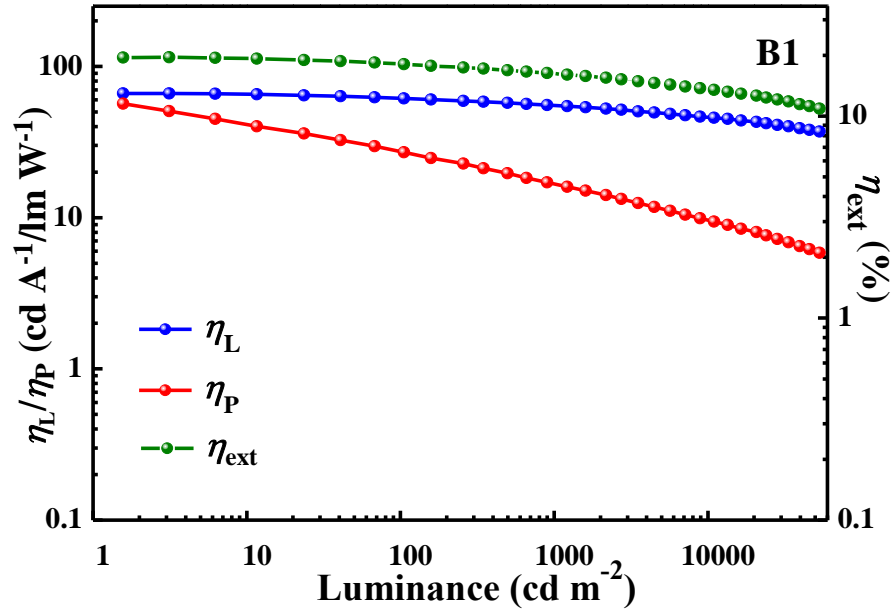


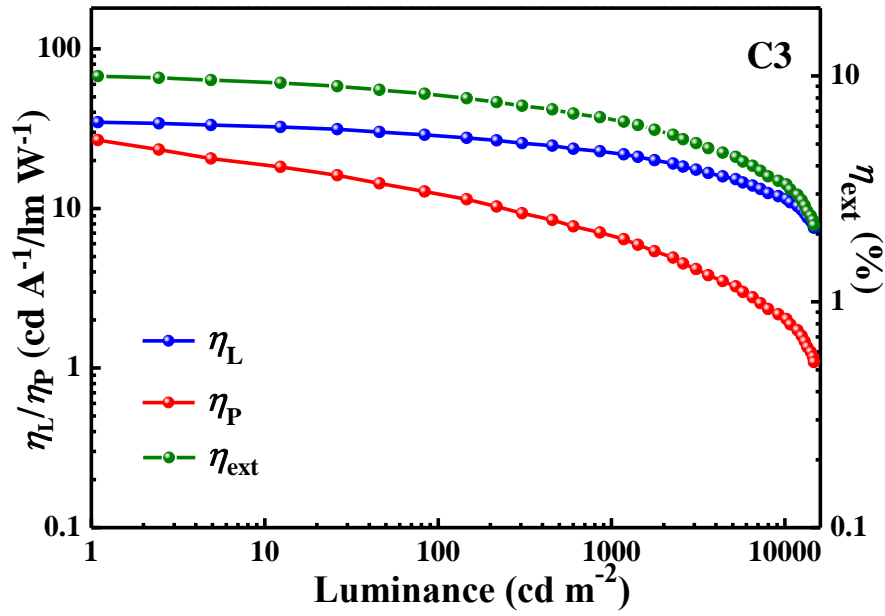
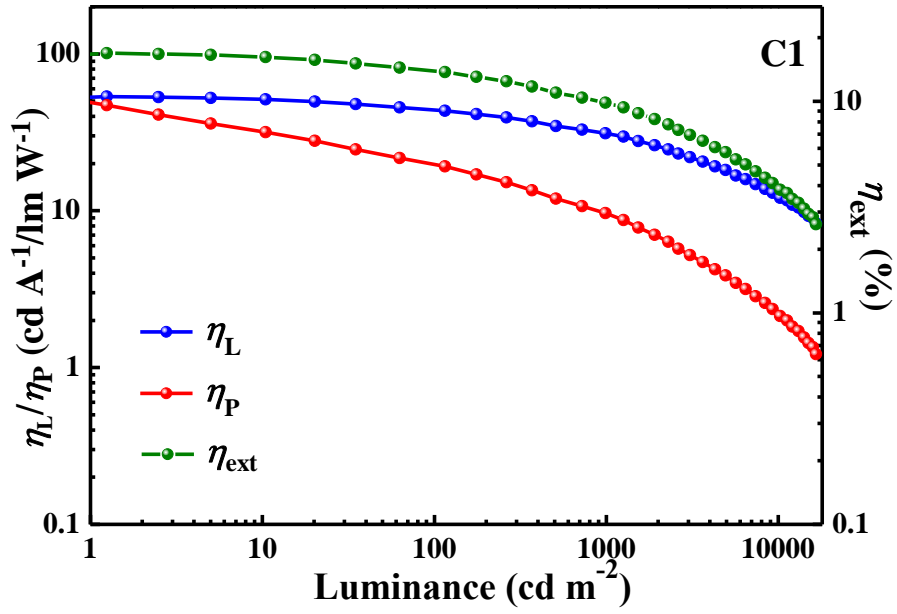


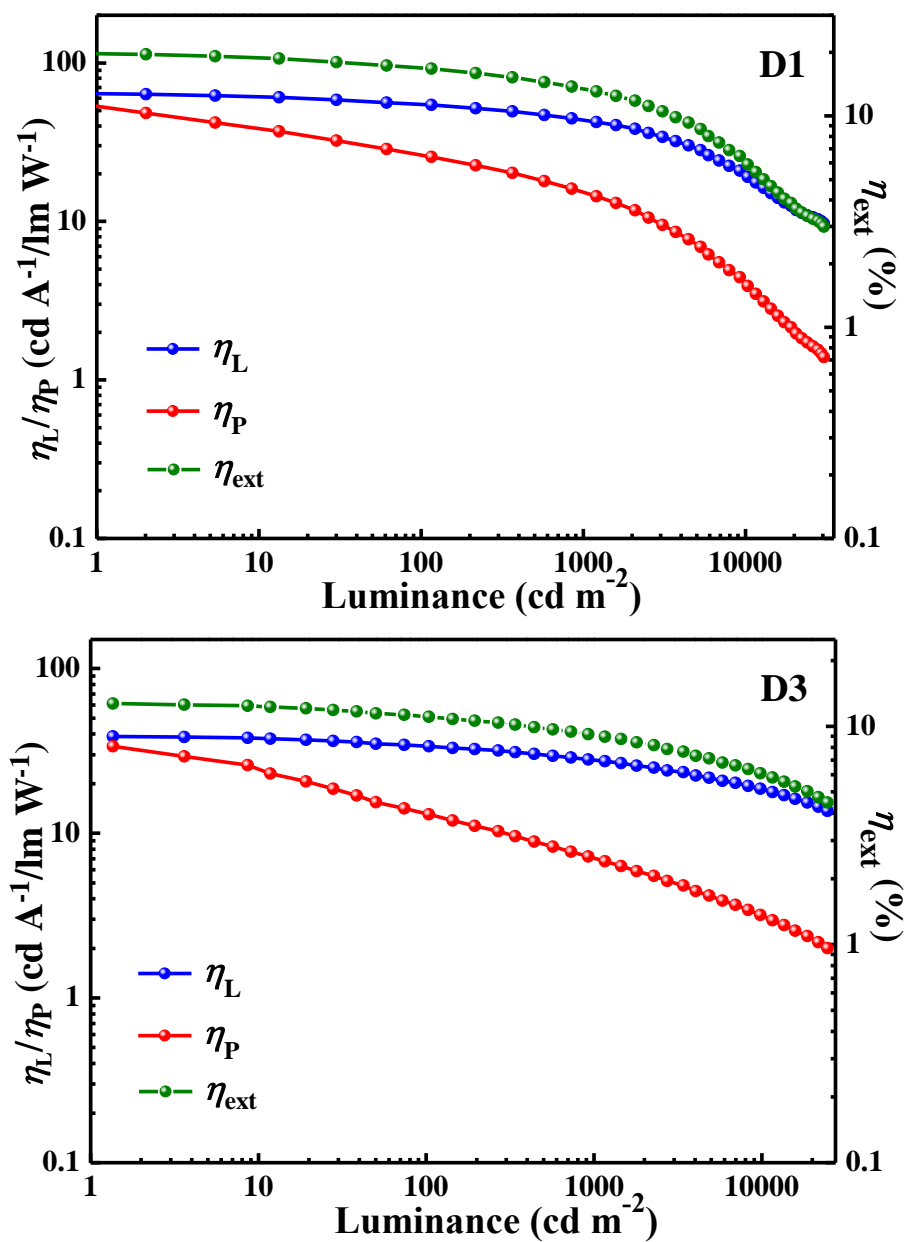
**Fig. S6** The Current density-Voltage-Luminance ( $J-V-L$ ) curves for the devices except the optimized ones.











**Fig. S7** Relationship between the electroluminescence efficiency and luminance for the devices except the optimized ones.

**Table 1** The coordinate covalent bonds length based on the TD-DFT calculations

complexes	coordinate covalent bonds	bond length(Å)
Ir3-1	Ir-C (ppy)	2.02865
	Ir-N (ppy)	2.18316
Ir3-2	Ir-C (ppy)	2.02817
	Ir-N (ppy)	2.18394
Ir2-1	Ir-O1 (acac)	2.19689
	Ir-O2 (acac)	2.20403
Ir2-2	Ir-O1 (acac)	2.19751
	Ir-O2 (acac)	2.20506