Supporting Information

Syntheses of compounds

*Preparation of Ligand **L1***: A solution of 2-aminothiophenol (275 mg, 2.20 mmol), **L1a** (500 mg, 1.84 mmol) and *p*-toluenesulfonic acid monohydrate (PTSA) (50 mg, 0.18 mmol) in ethanol (8 mL) were reflux under nitrogen for six hours. After cooling, the solvent was removed under vacuum. The residue was poured into water and extracted with dichloromethane. The product was purified by column chromatograph over silica using petroleum ether and dichloromethane (3:1) as eluent to yield the pure product as pale yellow solid (150 mg, 21.6 %). APCI-MS (*m*/*z*): 377.0 $[M+H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 8.28-8.26 (d, *J* =8.0 Hz, 1H), 8.16-8.14 (d, *J* =8.0 Hz, 1H), 8.13-8.11 (d, *J* =8.0 Hz, 1H), 7.92 (d, *J* =8.0 Hz, 1H), 7.69-7.59 (m, 4H), 7.55-7.34 (m, 7H).

*Preparation of Ligand **L2***: A mixture of **L2a** (575 mg, 1.11 mmol), 2-bromobenzothiazole (243 mg, 1.14 mmol) and $Pd(PPh_3)_4$ (66 mg, 0.055 mmol) in toluene (15 mL), ethanol (5 mL) and 2 M aqueous Na_2CO_3 solution (2.8 mL, 5.5 mmol) was degassed by pump. The solution was heated at 80 °C for 18 h under argon. After cooling, dichloromethane and water were added. The organic layer was separated and washed with diluted HCl and brine, then dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether and dichloromethane (4:1) as eluent to yield the pure product as white solid (380 mg, 64 %). TOF-MS-EI (*m*/*z*):

523.8 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.78 (d, *J* =8.0 Hz, 1H), 7.60 (s, 1H), 7.24-7.22 (d, *J* =8.0 Hz, 1H), 7.17-7.14 (m, 1H), 7.12-7.10 (d, *J* =8.0 Hz, 2H), 7.03-6.97 (m, 3H), 6.91-6.87 (m, 1H), 6.71-6.69 (d, *J* =8.0 Hz, 1H), 2.05-2.00 (m, 2H), 1.89-1.85 (m, 2H), 1.26-0.97 (m, 20H), 0.82-0.78 (m, 6H), 0.72-0.64 (m, 4H).

*Preparation of Ligand **L3***: A mixture of **L3a** (237 mg, 0.82 mmol), 2-bromobenzothiazole (160 mg, 0.75 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in toluene (5 mL), ethanol (1 mL) and 2 M aqueous K_2CO_3 solution (1.8 mL, 3.75 mmol) was degassed by pump. The solution was heated at 80 °C for 12 h under argon. After cooling, dichloromethane and water were added. The organic layer was separated and washed with diluted HCl and brine, then dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether and dichloromethane (4:1) as eluent to yield the pure product as white solid (192 mg, 68 %). MALDI-TOF-MS (*m*/*z*): 376 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24-8.22 (d, *J* =8.0 Hz, 1H), 8.19-8.17 (m, 2H), 8.07-8.05 (d, *J* =8.0 Hz, 1H), 8.00-7.98 (d, *J* =8.0 Hz, 1H), 7.90-7.88 (d, *J* =8.0 Hz, 1H), 7.68-7.61 (m, 4H), 7.55-7.31 (m, 6H).

*General Procedure for Synthesis of the Iridium Complexes **1** and **3***: $IrCl_3 \cdot 3H_2O$ (1 mmol) and the ligand (**L1** or **L2**) (2.3 mmol) were added in a 16 mL of mixture of 2-ethoxyethanol and water (v/v=3:1). The mixture was refluxed under nitrogen for 24 h and cooled to room temperature. The orange precipitate was collected by filtration and washed with water, ethanol and hexane. The solid was completely dried under reduced pressure to give the corresponding crude chloro-bridged dimer complex.

Without further purification, the dimer was added in a mixture of the corresponding ligand (**L1** or **L2**) (1 mmol), silver trifluoromethane sulfonate (1 mmol), and diglyme (10 ml) and the mixture was stirred under a nitrogen atmosphere at 160 °C for 20 h. The mixture was allowed to cool to room temperature, and then isolated by column chromatography over silica gel with petroleum ether/dichloromethane as mobile phase to produce pure iridium complex.

1: Yield 37 %. MALDI-TOF-MS (*m*/*z*): 1318.2 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 3H), 8.02-8.00 (d, *J* =8.0 Hz, 3H), 7.78-7.76 (d, *J* =8.0 Hz, 3H), 7.33-7.29 (m, 6H), 7.24-7.22 (d, *J* =8.0 Hz, 3H), 7.17-7.13 (m, 3H), 6.92-6.90 (d, *J* =8.0 Hz, 12H), 6.66-6.62 (m, 6H), 6.31-6.27 (m, 3H), 6.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.9, 157.1, 152.7, 143.8, 140.4, 136.8, 133.9, 132.3, 128.7, 126.8, 126.1, 125.8, 124.7, 124.1, 122.2, 120.0, 119.6, 119.3, 118.0, 115.5, 109.6. Calcd for $C_{75}H_{45}IrN_6S_3$: C, 68.31; H, 3.44; N, 6.37. Found: C, 68.27; H, 3.62; N, 6.41.

3: Yield 22 %. MALDI-TOF-MS (*m*/*z*): 1760.0 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 3H), 8.12-8.10 (d, *J* =8.0 Hz, 3H), 8.05-8.03 (d, *J* =8.0 Hz, 3H), 7.92-7.90 (d, *J* =8.0 Hz, 3H), 7.80-7.78 (d, *J* =8.0 Hz, 3H), 7.77-7.74 (m, 3H), 7.52-7.48 (m, 3H), 7.41-7.35 (m, 9H), 2.09-2.01 (m, 12H), 1.20-1.23 (m, 60H), 0.80-0.76 (m, 18H), 0.68-0.60 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.4, 157.0, 152.7, 151.8, 144.1, 143.4, 141.0, 139.9, 132.5, 127.4, 126.9, 126.6, 126.3, 124.0, 122.4, 122.1, 120.6, 120.2, 119.5, 54.0, 40.5, 31.8, 30.0, 29.5, 29.1, 23.8, 22.6, 14.1. Calcd for $C_{108}H_{132}IrN_3S_3$: C, 73.68; H, 7.56; N, 2.39. Found: C, 73.74; H, 7.71; N, 2.26.

*General Procedure for Synthesis of Iridium Complexes **2**, **4**, and **5***: A mixture of the chloro-bridged dimer complex (0.5 mmol), Na_2CO_3 (5 mmol), acetyl acetone (1.5 mmol), and 2-ethoxyethano (10 mL) was stirred under a nitrogen atmosphere at 130 °C for 24 h. After the solution was cooled to room temperature, the orange precipitate was filtered off and washed with water, ethanol and hexane. The crude product was purified by chromatography on silica gel using petroleum ether/dichloromethane as mobile phase.

2: Yield 41 %. MALDI-TOF-MS (*m*/*z*): 1042.8 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 2H), 8.17-8.15 (m, 2H), 7.98-7.96 (d, *J* =8.0 Hz, 2H), 7.90-7.88 (m, 2H), 7.47-7.44 (m, 4H), 7.22-7.20 (d, *J* =8.0 Hz, 4H), 7.17-7.02 (m, 12H), 6.35(s, 2H), 5.14(s, 1H), 1.79(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.6, 180.2, 151.1, 146.1, 140.1, 137.0, 134.6, 130.9, 128.9, 127.0, 126.1, 124.8, 122.0, 120.2, 119.2, 118.2, 114.6, 109.7, 101.6, 65.6, 28.4. Calcd for $C_{55}H_{37}IrN_4O_2S_2$: C, 63.38; H, 3.58; N, 5.38. Found: C, 63.17; H, 3.55; N, 5.47.

4: Yield 32 %. MALDI-TOF-MS (*m*/*z*): 1336.4 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14-8.12 (d, *J* =8.0 Hz, 2H), 7.96-7.94 (d, *J* =8.0 Hz, 2H), 7.56 (s, 2H), 7.47-7.44 (m, 4H), 7.21-7.19 (d, *J* =8.0 Hz, 2H), 7.15-7.06 (m, 6H), 6.74 (s, 2H), 5.19 (s, 1H), 1.85-1.80 (m, 8H), 1.78 (s, 6H), 1.25-0.90 (m, 40H), 0.84-0.72 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.6, 180.5, 152.2, 151.2, 144.1, 142.8, 140.5, 140.3, 131.2, 127.3, 127.1, 126.5, 125.7, 124.7, 122.8, 122.1, 120.3, 120.2, 120.0, 101.6, 54.0, 40.2, 31.8, 30.2, 29.3, 28.9, 28.4, 24.1, 23.7, 22.6, 14.0. Calcd for $C_{77}H_{95}IrN_2O_2S_2$: C, 69.17; H, 7.16; N, 2.10. Found: C, 69.31; H, 7.25; N, 2.03.

5: Yield 33 %. MALDI-TOF-MS (*m*/z): 1042.2 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.19 (d, *J* =8.0 Hz, 2H), 7.96-7.94 (d, *J* =8.0 Hz, 2H), 7.76 (s, 2H), 7.61-7.57 (m, 4H), 7.52-7.50 (d, *J* =8.0 Hz, 6H), 7.46-7.42 (m, 6H), 7.20-7.16 (m, 4H), 7.07 (s, 2H), 6.98-6.94 (m, 2H), 5.17 (s, 1H), 1.77(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.6, 180.6, 151.6, 141.9, 139.4, 137.6, 135.4, 131.4, 129.9, 127.4, 127.0, 126.3, 125.0, 122.2, 120.9, 120.4, 119.1, 109.1, 107.7, 101.7, 65.8, 28.5. Calcd for $C_{55}H_{37}IrN_4O_2S_2$: C, 63.38; H, 3.58; N, 5.38. Found: C, 63.19; H, 3.54; N, 5.47.

Supplementary figures

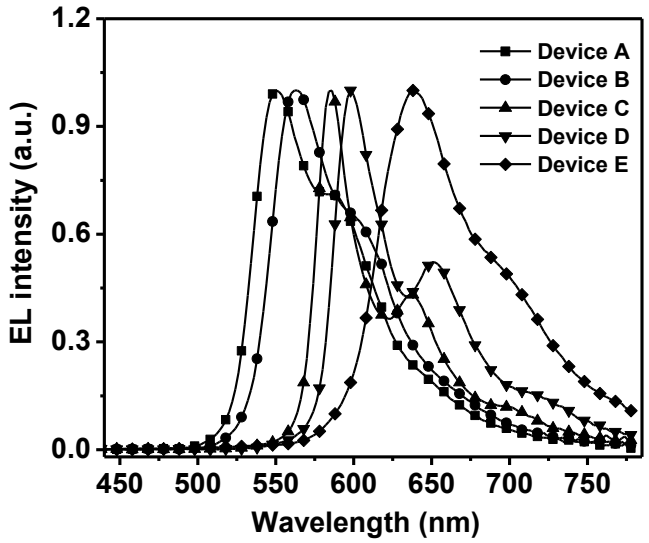

Figure S1. EL spectra of the devices A-E at 8 V.

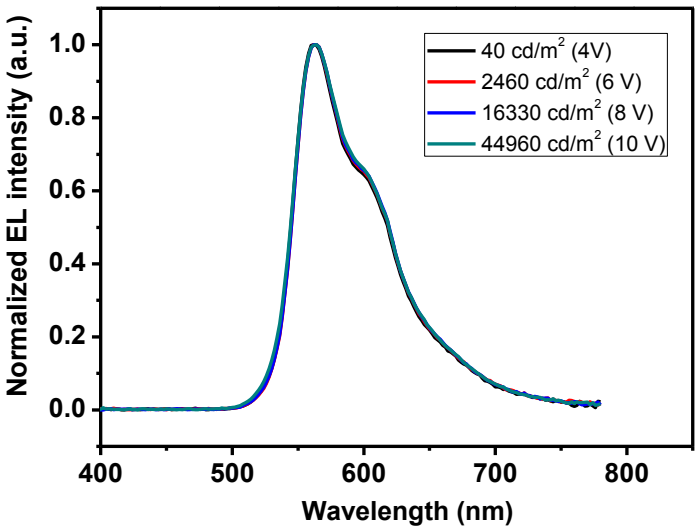

Figure S2. EL spectra for complex **2** based device B under different luminance.

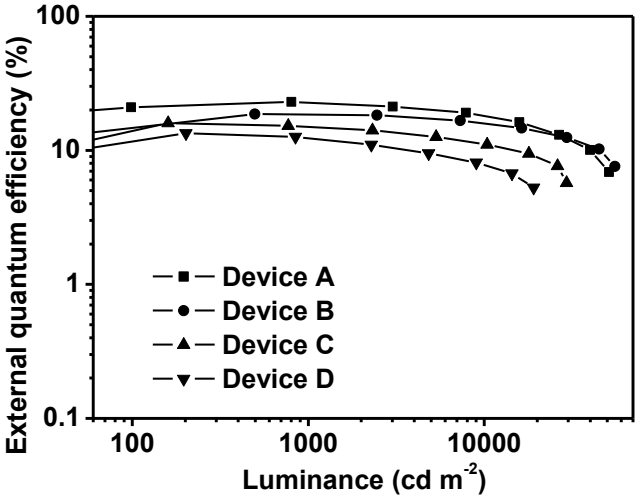

Figure S3. The plots of external quantum efficiency versus luminance for Device A-D.

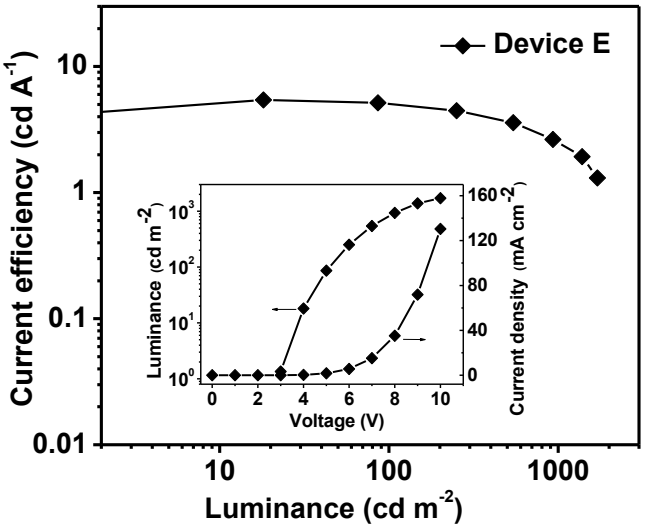

Figure S4. The plot of luminance efficiency versus luminance for device E. Insert: The luminance-voltage-current density (*L*-*V*-*J*) characteristics of device E.

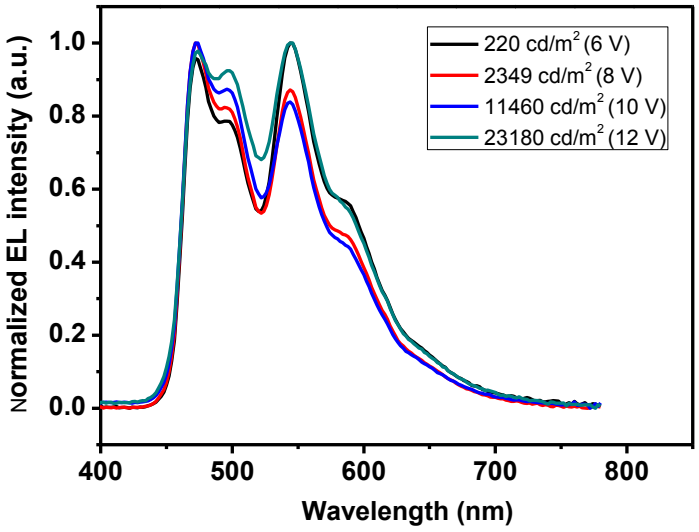

Figure S5. The EL spectra of the WOLED under different driving voltages and different luminance.