

Supporting Information

Rational Design and Characterization of Heteroleptic Phosphorescent Iridium(III) Complexes for Highly Efficient Deep-Blue OLEDs

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Synthesis and Characterization Details:

Dfpypy and Medfpypy were synthesized by Suzuki coupling following the method reported by Lee et al.^{S1} The iridium dimer complexes [(dfpypy)₂Ir(μ-Cl)]₂ and [(Medfpypy)₂Ir(μ-Cl)]₂ were synthesized using IrCl₃·3H₂O according to the standard literature method.^{S2}

Synthesis of Fptz : Picolinonitrile (2.08 g, 20 mmol) and sodium methoxide (120 mg, 2 mmol) in ethanol (40 ml) were stirred at room temperature for 12 h, then NH₄Cl (1.28 g) was added and the solution was refluxed with stirring for 5 h then cooled to room temperature. The precipitate was filtered and the filtrate was evaporated under reduced pressure and the residue dried in vacuum to give picolinimidamide hydrochloride (3.1 g). Ethyl trifluoroacetate (2.84 g, 20.0 mmol) and hydrazine hydrate (1.5 g, 80%, 24.0 mmol) in THF (12.0 mL) were refluxed for 1.5 h. After the solution had cooled to room temperature, picolinimidamide hydrochloride (3.1 g) and NaOH (0.8 g) were added, and the mixture was refluxed for 5 h. The mixture was cooled to room temperature, the precipitate was filtered and the filtrate was evaporated under reduced pressure to give a crude residue which was purified by column chromatography on silica gel (eluent EtOAc-hexane, 1:5 v/v) to obtain **Fptz** as a canary yellow solid (3.59 g, yield 84%). Characterization data were in agreement with those in the literature.^{S3}

Synthesis of Ir(dfpypy)₂(Fptz) (Ir1): Fptz (0.86 g, 4.0 mmol) and tetrabutylammonium hydroxide (TBAOH: 1.6 g, 50%, 3.0 mmol) were dissolved in dichloromethane (60 mL). The

mixture was refluxed for 30 min and the solution was cooled to room temperature, then $[(dfppy)_2Ir(\mu-Cl)]_2$ ^{S3,S4} (1.25 g, 1.0 mmol) was added. The solution was stirred for 8 h at 30 °C and then cooled to room temperature. The mixture was quenched with water, and the organic phase was extracted with dichloromethane. After drying over Na₂SO₄, the dichloromethane solution was concentrated and the residue was purified by column chromatography on Al₂O₃ gel (eluent tetrahydrofuran-chloroform = 5:1 v/v) to give **Ir1** as a yellow powder, (1.18 g, 75%). ¹H NMR (500 MHz, CDCl₃) δ 8.63 (d, J = 7.6 Hz, 1H), 8.35 (dd, J = 17.3, 8.3 Hz, 2H), 8.06 (t, J = 7.8 Hz, 1H), 7.92 (dd, J = 13.8, 7.2 Hz, 2H), 7.81 (d, J = 5.2 Hz, 1H), 7.76 (d, J = 6.0 Hz, 1H), 7.48 (d, J = 5.4 Hz, 1H), 7.42–7.36 (m, 1H), 7.20 (t, J = 6.6 Hz, 1H), 7.09 (dd, J = 12.5, 6.2 Hz, 1H), 5.80 (s, 1H), 5.67 (s, 1H). Elemental analysis: found C, 42.93%; H, 1.80%; N, 14.23%; calc. for C₂₈H₁₄F₇IrN₈: C, 42.70%; H, 1.79%; N, 14.23%. MS m/z: 787.8 [M⁺] (calcd: 788.1).

Synthesis of Ir(Medfppy)₂(Fptz) (Ir2): The complex was prepared by the same method as described for **Ir1**, using $[(Medfppy)_2Ir(\mu-Cl)]_2$ ^{S3} (1.28 g, 2.0 mmol), Fptz (0.86 g, 4.0 mmol) and TBAOH (1.6 g, 50%, 3 mmol), and isolated as a yellow powder (1.15 g, 71%). ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 18.7 Hz, 2H), 7.98 (td, J = 7.9, 1.2 Hz, 1H), 7.75 (d, J = 5.2 Hz, 1H), 7.54 (d, J = 6.0 Hz, 1H), 7.32–7.27 (m, 2H), 6.95 (d, J = 5.4 Hz, 1H), 6.86 (d, J = 5.5 Hz, 1H), 5.80 (s, 1H), 5.67 (s, 1H), 2.56 (s, 6H). Elemental analysis: found C, 44.36%; H, 2.20%; N, 13.70%; calc. for C₃₀H₁₈F₇IrN₈: C, 44.17%; H, 2.22%; N, 13.74%. MS m/z: 815.6 [M⁺] (calcd: 815.7).

Theoretical Calculations:

The ground state geometries were fully optimized by the density functional theory (DFT)^{S5} method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional^{S6} (B3LYP) and 6-31G** basis set using the Gaussian 03 software package.^{S7}

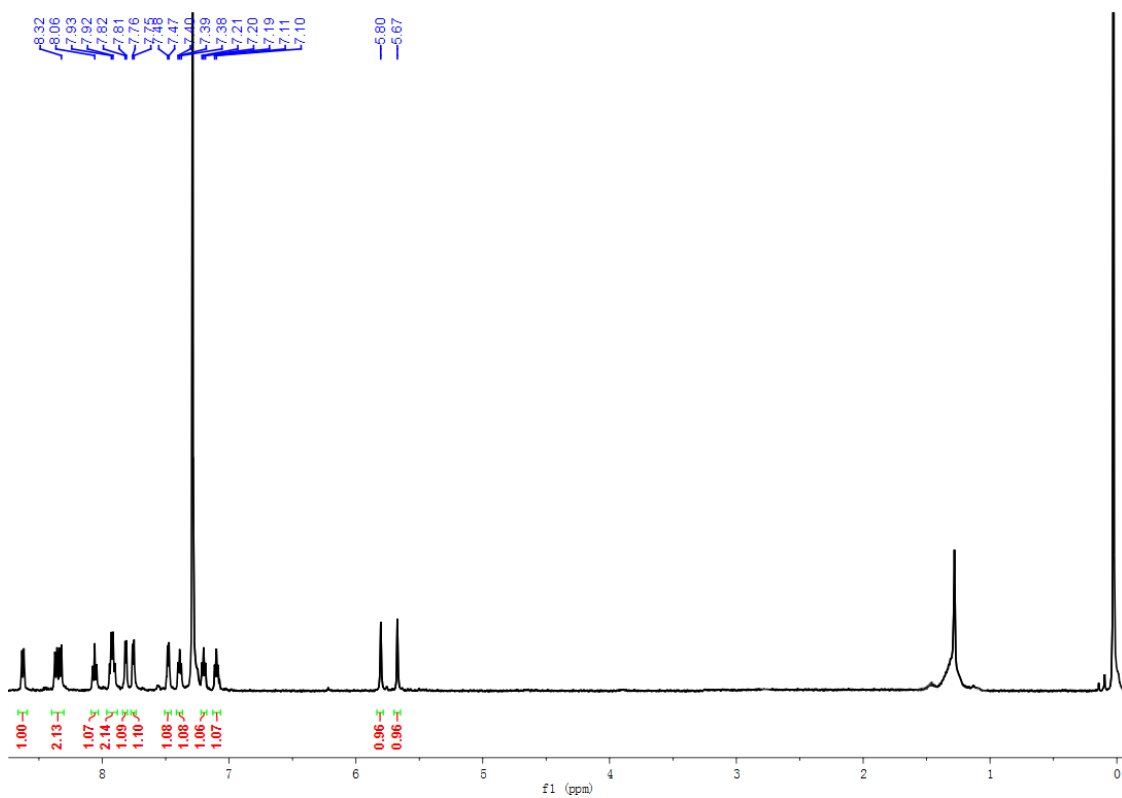


Figure S1. ^1H NMR spectrum of **Ir1** in CDCl_3 .

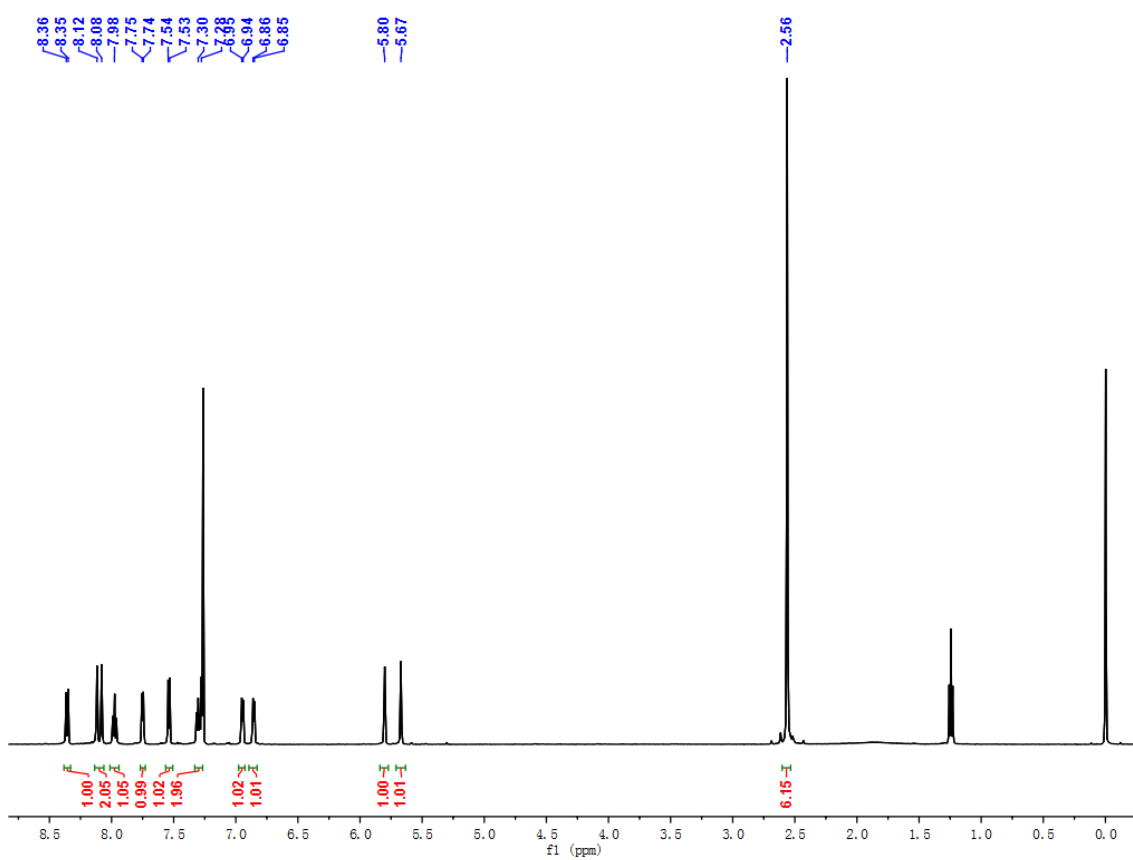


Figure S2. ^1H NMR spectrum of **Ir2** in CDCl_3 .

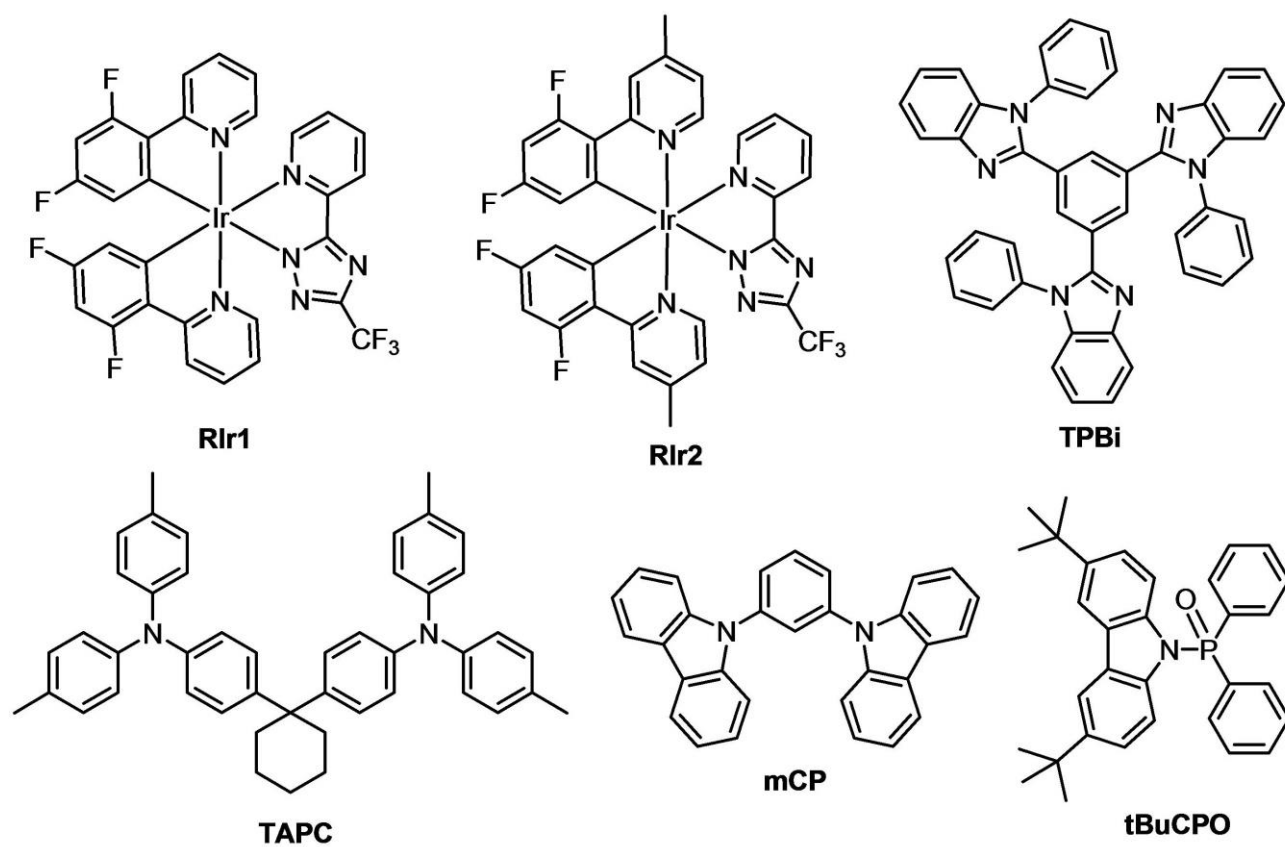


Figure S3. Chemical formulae of the reference complexes (RIr1 and RIr2) studied for comparison with Ir1 and Ir2, and the materials used in device preparation.

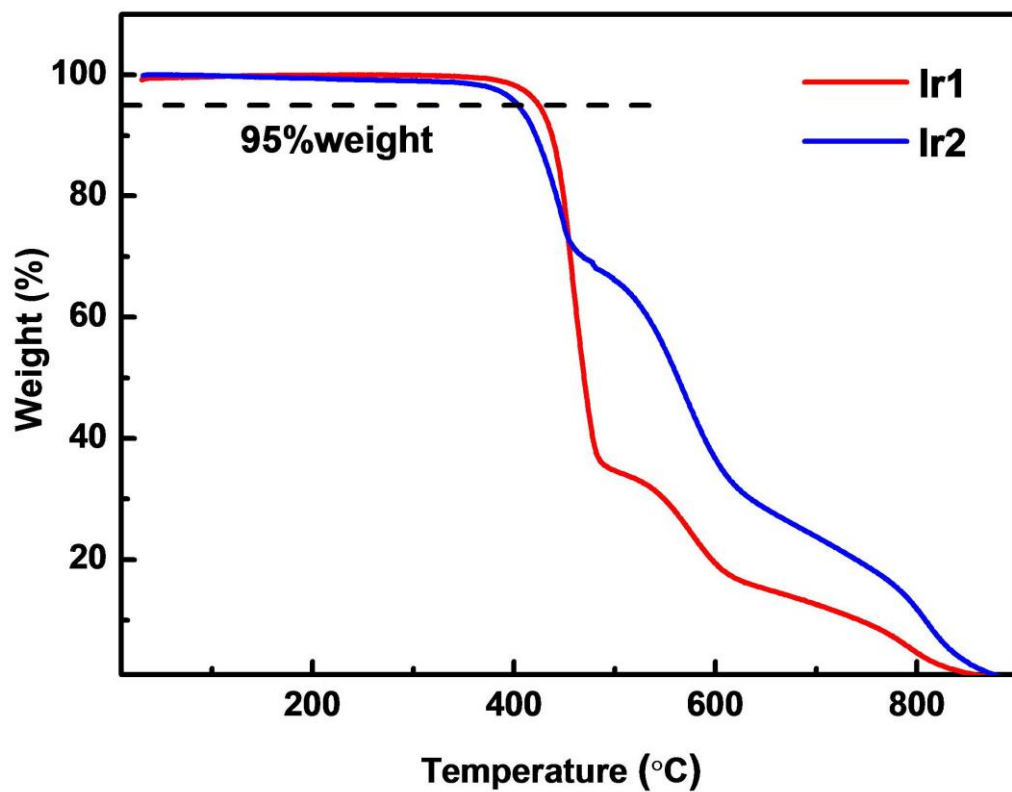


Figure S4. TGA graphs of Ir1 and Ir2.

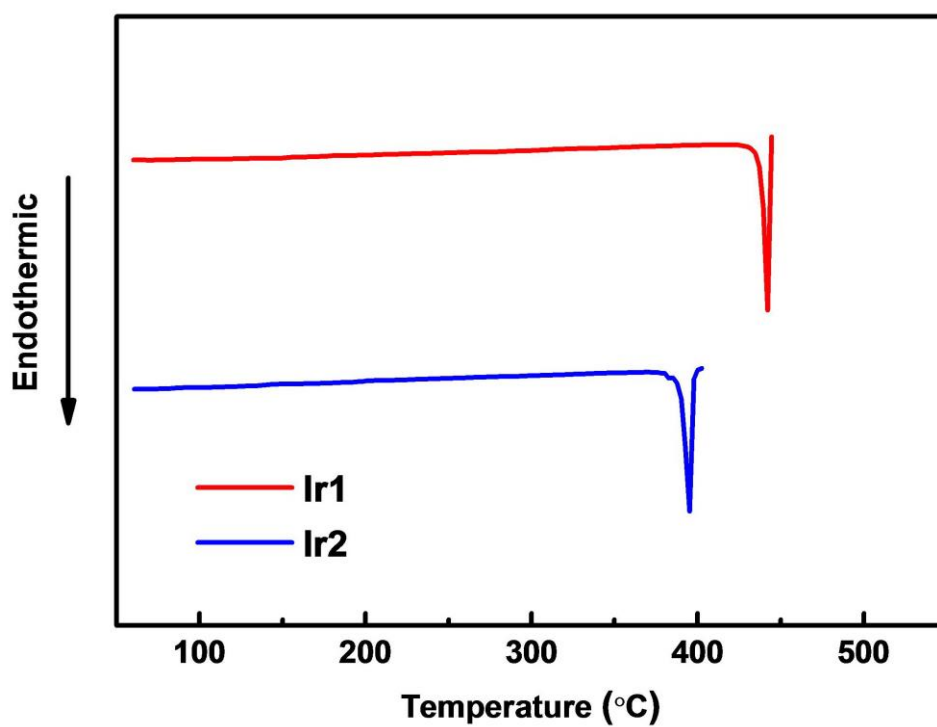


Figure S5. DSC graphs of Ir1 and Ir2.

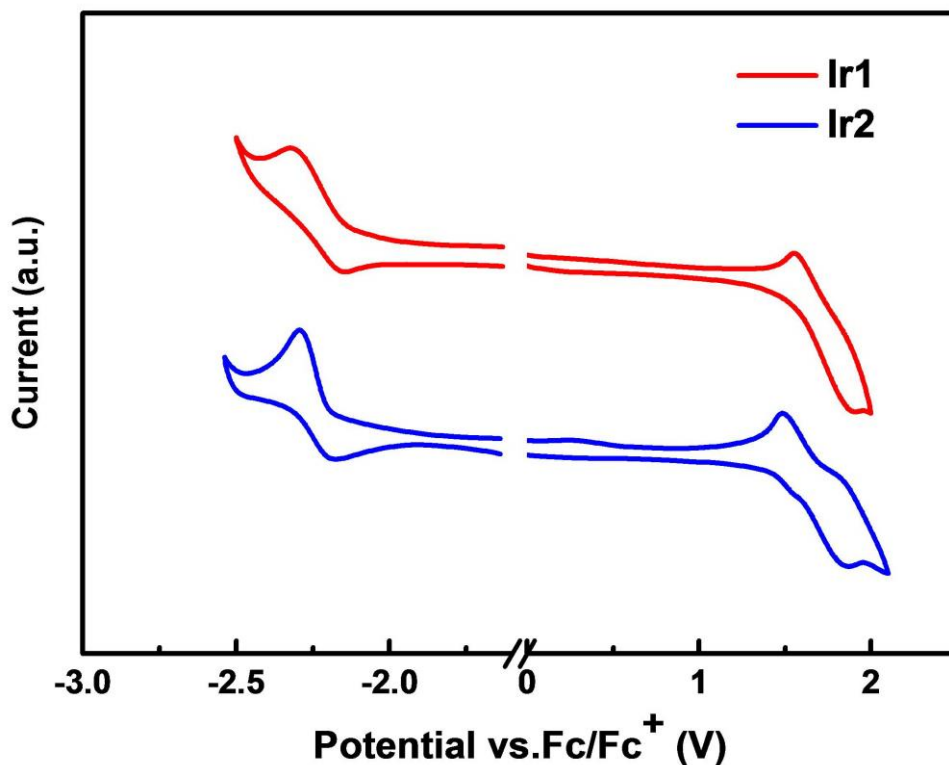


Figure S6. Cyclic voltammograms of complexes **Ir1** and **Ir2** recorded in dichloromethane for oxidation and in acetonitrile for reduction.

Single Crystal X-ray Structures:

Single crystals suitable for X-ray structural analysis were obtained by vacuum sublimation. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo K α radiation. The structures were solved by direct methods using the SHELXTL programs and refined with full-matrix least-squares on F^2 .^{S8} Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The corresponding CCDC reference numbers are 1052634 for **Ir1** and 1052689 for **Ir2**: the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement parameters for complexes **Ir1** and **Ir2**.

Complexes	Ir1	Ir2
Formula	C ₂₈ H ₁₄ F ₇ IrN ₈	C ₃₀ H ₁₈ F ₇ IrN ₈
molecular weight	788.1	815.72

crystal system	Monoclinic	Monoclinic
space group	C 2/c	P 2 ₁ /n
crystal size [mm ³]	0.38×0.34×0.31	0.21×0.20×0.18
a [Å]	32.451(7)	10.423(2)
b [Å]	10.272(2)	16.123(3)
c [Å]	15.874(3)	17.439(4)
α[o]	90.00	90.00
β[o]	92.58(3)	96.28(3)
γ[o]	90.00	90.00
V [Å ³]	5286.0(19)	2913.1(10)
Z	8	4
ρ _{calc} [g/cm ³]	1.980	1.860
temp (K)	293(2)	293(2)
μ [mm ⁻¹]	5.138	4.665
reflections collected	24901	26687
independent reflections	6023	6602
RF, R _w (F ²) (all data)	0.0381, 0.0689	0.0560, 0.0719
RF, R _w (F ²) [I > 2σ(I)]	0.0256, 0.0566	0.0361, 0.0665
GOF	1.068	1.072
CCDC	1052634	1052689

$$R_F = \Sigma ||F_o - F_c| / \Sigma |F_o|. R_w(F^2) = [\Sigma w|F_o^2 - F_c^2|^2 / \Sigma w(F_o^4)]^{1/2}$$

Table S2. Selected bond lengths (Å) and angles (deg) of **Ir1** and **Ir2**.

Ir1		Ir2	
bond lengths (Å)		bond lengths (Å)	
Ir(1)-C(10)	2.009(4)	Ir(1)-C(10)	2.005(4)
Ir(1)-C(20)	2.008(4)	Ir(1)-C(21)	1.981(4)Å
Ir(1)-N(1)	2.051(3)	Ir(1)-N(1)	2.040(4)

Ir(1)-N(3)	2.055(3)	Ir(1)-N(3)	2.055(4)
Ir(1)-N(5)	2.170(3)	Ir(1)-N(5)	2.169(4)
Ir(1)-N(6)	2.119(3)	Ir(1)-N(6)	2.101(3)
angles (deg)		angles (deg)	
C(10)-Ir(1)-N(1)	80.27(14)	C(10)-Ir(1)-N(1)	80.23(18)
C(20)-Ir(1)-N(3)	80.08(14)	C(21)-Ir(1)-N(3)	80.00(17)
N(6)-Ir(1)-N(5)	76.36(12)	N(6)-Ir(1)-N(5)	75.99(14)
C(10)-Ir(1)-N(6)	170.57(13)	C(10)-Ir(1)-N(6)	171.28(17)
C(20)-Ir(1)-N(5)	176.60(13)	C(21)-Ir(1)-N(5)	176.10(15)
N(3)-Ir(1)-N(5)	96.95(12)	N(3)-Ir(1)-N(5)	97.27(16)

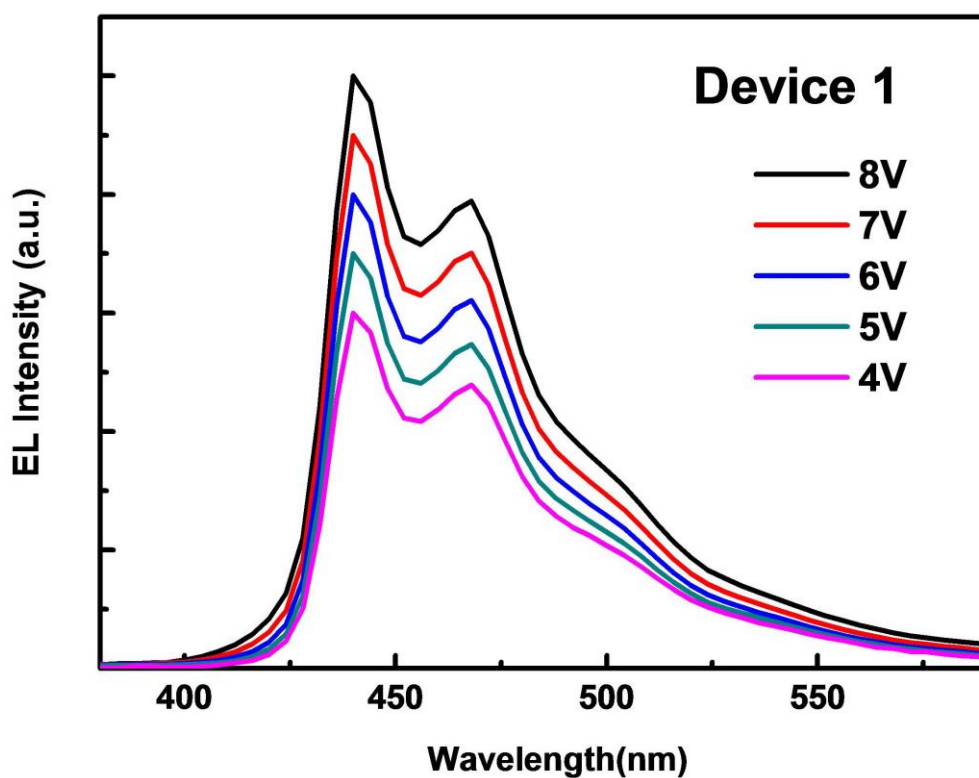


Figure S7. EL spectra of Device 1 based on Ir1 at different driving voltages.

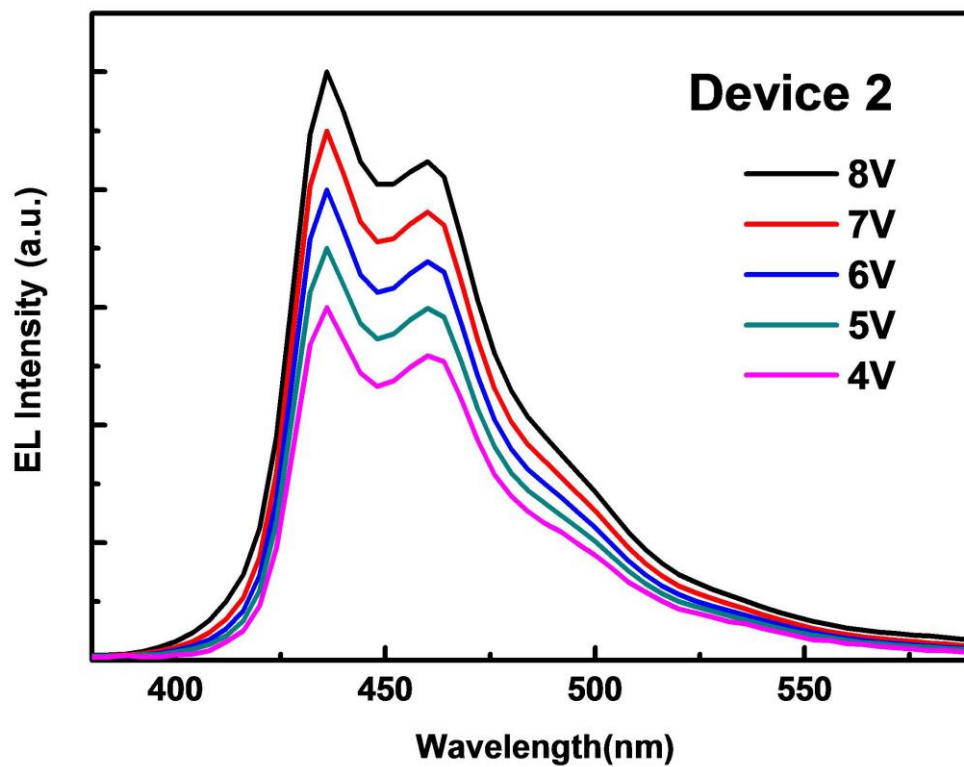


Figure S8. EL spectra of Device 2 based on Ir2 at different driving voltages.

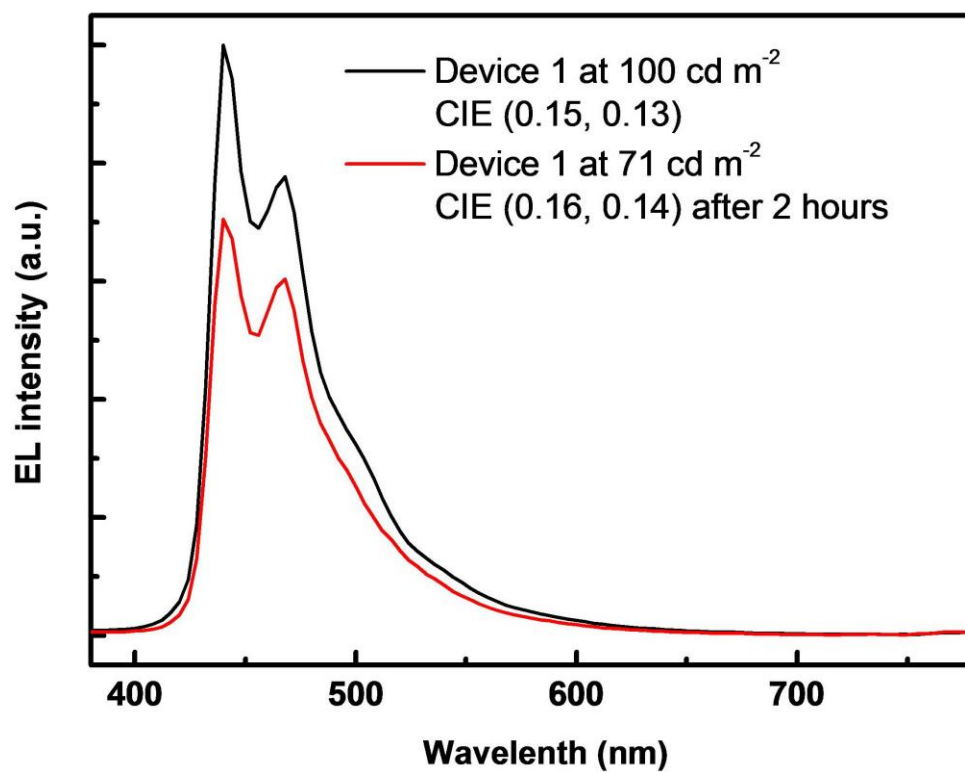


Figure S9. EL spectra of Device 1 based on Ir1 at 100 cd m^{-2} before and after continuous operation for 2 hours.

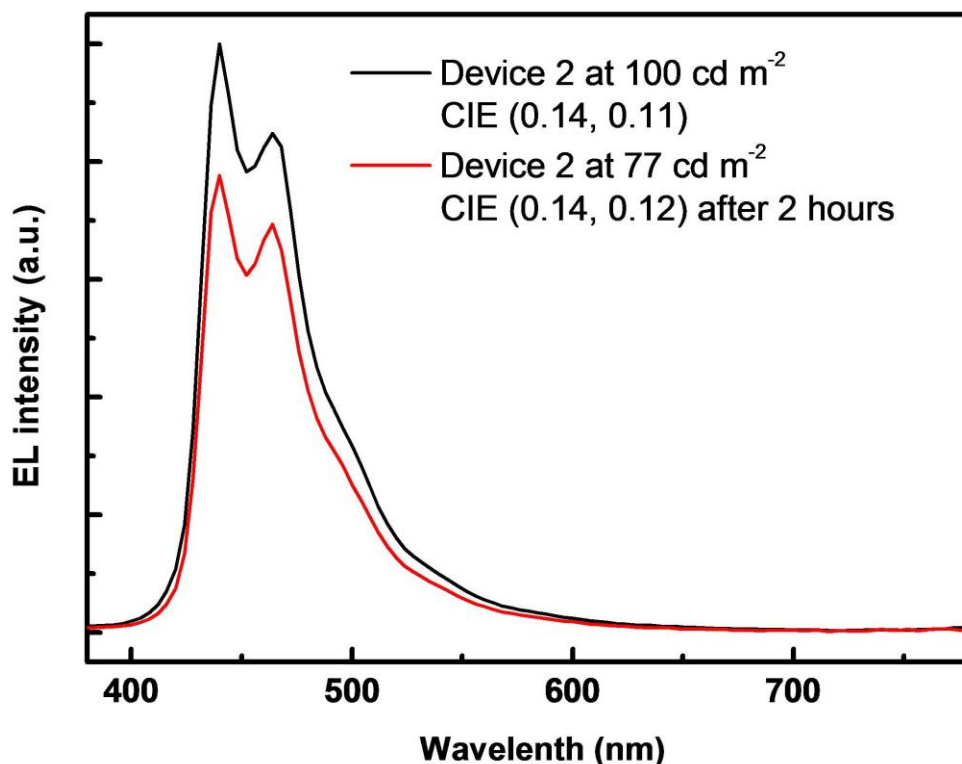


Figure S10. EL spectra of Device 2 based on Ir2 at 100 cd m^{-2} before and after continuous operation for 2 hours.

References for the Supporting Information :

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S8 (a) SHELXTL, Version 5.1; Siemens Industrial Automation, Inc., 1997. (b) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, 1997.