

## Supporting information

### Green-emitting iridium complexes containing pyridine sulfonic acid as ligands for efficient OLEDs with extremely low efficiency roll-off

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#### S1 Instrument and details

<sup>1</sup>H NMR spectra were measured on Bruker AM 500 spectrometer. The high resolution electrospray ionization mass spectra (HR ESI-MS) were recorded on Bruker micrOTOF-Q III. UV-vis absorption and photoluminescence spectra were measured on Shimadzu UV-3100 and Hitachi F-4600 spectrophotometer at room temperature, respectively. The absolute photoluminescence quantum yields (PLQY) was measured with HORIBA FL-3 fluorescence spectrometer. Cyclic voltammetry measurements were carried out using chi600 electrochemical workstation with Fc<sup>+</sup>/Fc as the standard at the rate of 0.1 V s<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on Pyris 1 DSC under nitrogen at a heating rate 10 °C min<sup>-1</sup>. The decay lifetimes were measured with Edinburg FLS980 lifetime and steady state spectrometer.

X-ray crystallographic measurements of the single crystals were carried out on Bruker APEX-II CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT<sup>1</sup> program in order to reduce the highly redundant data sets. Data were collected using a narrow-frame method with scan width of 0.30° in  $\omega$  and an exposure time of 5 s per frame. Absorption corrections were applied using SADABS<sup>2</sup> supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the program SHELXS-2014<sup>3</sup>. The positions of metal atoms and their first coordination spheres were located from direct-Emaps, other non-hydrogen atoms were found in

alternating difference Fourier syntheses and least-squares refinement cycles and during the final cycles refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of  $U_{iso}$ .

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of  $15 \Omega \text{ sq}^{-1}$ . Before device fabrication, ITO glasses were cleaned by detergent and rinsed in deionized water for 20 min, and then let the surface dry thoroughly. The deposition rates for organic materials, LiF and Al are about 0.1, 0.01 and  $0.1 \text{ nm s}^{-1}$ , respectively. The emitters and host were co-evaporated from different sources under the vacuum level lower than  $6 \times 10^{-4}$  mbar. The effective area of the emitting diode is  $0.1 \text{ cm}^2$ . The characteristics of the devices were measured with a programmable KEITHLEY 2400 with a calibrated silicon diode in a dark container. The electroluminescence was measured by F-4600 spectrophotometer.

## S2 Experiment procedures

### 2.1 Synthesis of ancillary ligand

NaOH (0.29, 7.19 mmol) was added to a solution of pyridine-2-sulfonic acid (1.04 g, 6 mmol) in 20 ml  $\text{CH}_3\text{OH}$  and stirred for 0.5 h at room temperature. Then, the solution was evaporated under reduced pressure and the residue was washed with 10 ml diethyl ether twice to afford the product as white solid.

### 2.2 General synthesis of Ir(III) complexes

The mixture of Ir(III) chloro-bridged dimer (1.03 mmol) and ancillary ligand (0.51 mmol) in 15 ml 2-ethoxyethanol was refluxed for 8 h under nitrogen. After the reaction was completed, the solvent was evaporated and the product was isolated with column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to obtain yellow solid. The complexes were purified by vacuum sublimation.

Ir1 (yield 71%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.17 (dd,  $J = 5.8, 0.7 \text{ Hz}$ , 1H), 8.16 (d,  $J = 7.5 \text{ Hz}$ , 1H), 8.01 (ddd,  $J = 7.8, 4.6, 1.6 \text{ Hz}$ , 2H), 7.98 (d,  $J = 7.9 \text{ Hz}$ , 1H), 7.94 – 7.86 (m, 3H), 7.72 (dd,  $J = 13.0, 8.1 \text{ Hz}$ , 2H), 7.61 (ddd,  $J = 5.5, 1.4, 0.7 \text{ Hz}$ , 1H), 7.38 (dt,  $J = 3.1, 1.5 \text{ Hz}$ , 1H), 7.37 – 7.34 (m, 1H), 7.25 (dd,  $J = 8.1, 1.1 \text{ Hz}$ , 1H), 7.22 – 7.15 (m, 2H), 6.47 (s, 1H), 6.25 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.80, 164.05, 157.70, 148.99, 148.78, 147.28, 147.13, 146.61, 142.99, 139.34, 138.35, 137.70, 137.42, 127.42, 126.79, 124.39, 123.35, 123.08, 122.89, 122.51, 119.11, 118.90, 118.70, 118.20.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.81 (3 H), -62.93 (3 H). MS (HR ESI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{18}\text{N}_3\text{SIrO}_3$   $[\text{M} + \text{Na}]^+ = 818.06$ , found 818.05.

Ir2 (yield 63%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.25 (dd,  $J = 5.8, 1.1$  Hz, 1H), 8.42 (d,  $J = 8.5$  Hz, 1H), 8.36 (d,  $J = 8.5$  Hz, 1H), 8.15 (d,  $J = 7.6$  Hz, 1H), 8.01 (td,  $J = 7.8, 1.5$  Hz, 1H), 7.97 (dd,  $J = 5.8, 1.1$  Hz, 1H), 7.89 (ddd,  $J = 8.9, 7.5, 1.7$  Hz, 1H), 7.87 – 7.82 (m, 1H), 7.51 (d,  $J = 4.8$  Hz, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.34 (m, 3H), 7.15 (ddd,  $J = 7.2, 5.8, 1.2$  Hz, 1H), 6.85 (t,  $J = 7.8$  Hz, 1H), 6.82 (t,  $J = 7.9$  Hz, 1H), 6.44 (d,  $J = 7.6$  Hz, 1H), 6.14 (d,  $J = 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.35, 162.68, 157.73, 149.21, 148.84, 146.99, 146.62, 144.28, 138.42, 137.35, 137.08, 135.26, 127.87, 127.34, 126.72, 124.46, 122.83, 122.22, 121.13, 120.34.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.06 (3 H), -57.42 (3 H). MS (HR ESI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{18}\text{N}_3\text{SiIrO}_3$   $[\text{M} + \text{Na}]^+ = 818.06$ , found 818.06.

### 2.3 NMR spectra

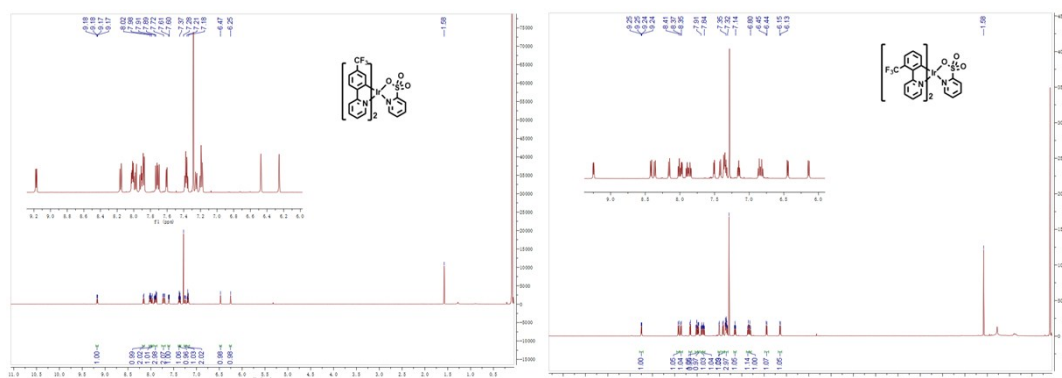


Fig. S1  $^1\text{H}$  NMR spectra of the complexes.

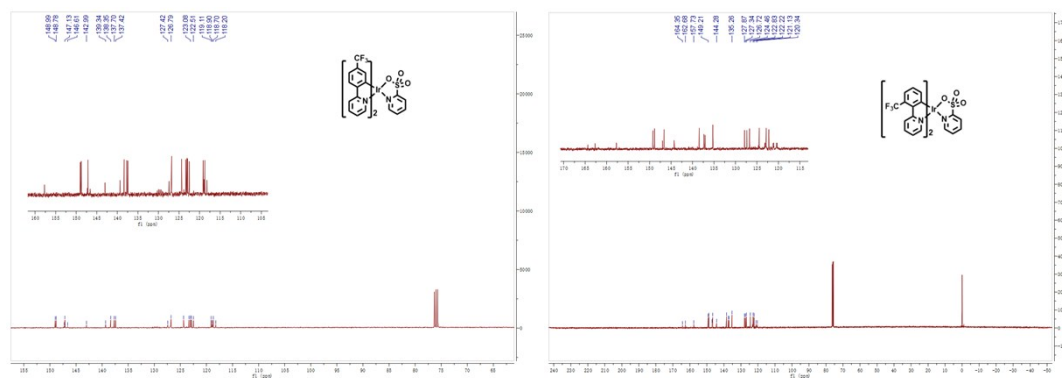


Fig.S2  $^{13}\text{C}$  NMR spectra of the complexes.

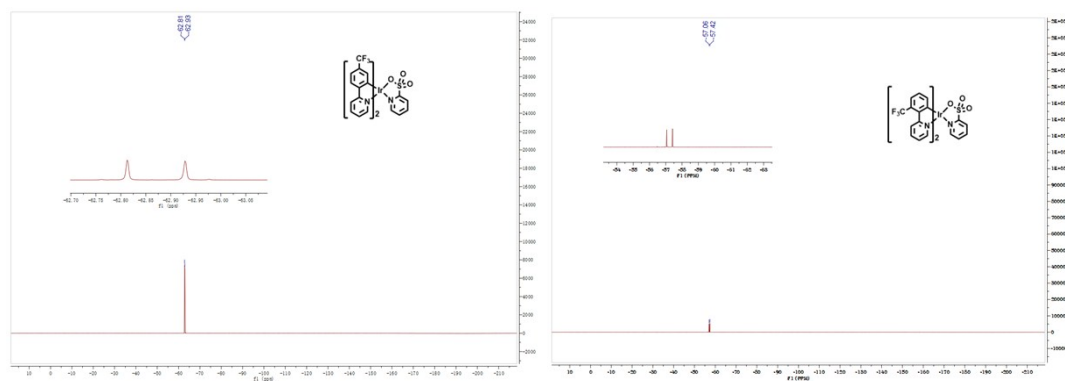


Fig.S3  $^{19}\text{F}$  NMR spectra of the complexes.

### S3 X-ray crystallographic data and theoretical calculation data

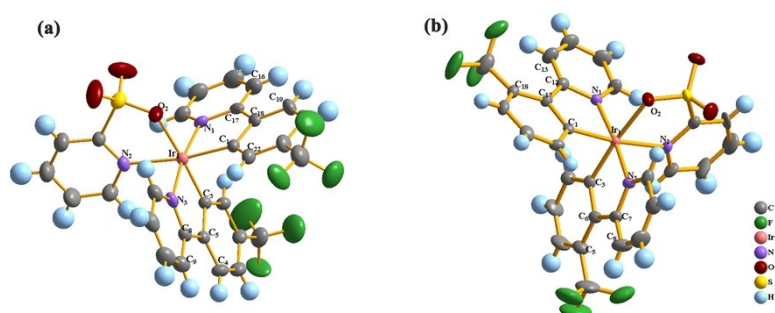


Fig. S4 Thermal ellipsoidal diagram of: (a) Ir1; (b) Ir2. Ellipsoids are drawn at 30% probability level.

Table S1 crystallographic data of Ir1 and Ir2

	Ir1	Ir2
formula	$\text{C}_{29}\text{H}_{18}\text{N}_3\text{O}_3\text{F}_6\text{SIr}$	$\text{C}_{29}\text{H}_{18}\text{N}_3\text{O}_3\text{F}_6\text{SIr}$
Formula weight	794.72	794.72
Temperature/K	296.15	296.15
Crystal system	triclinic	orthorhombic
Space group	$\text{P}\bar{1}$	$\text{P}_{bca}$
$a$ (Å)	13.4753(12)	9.0788(8)
$b$ (Å)	14.2487(13)	19.4903(17)
$c$ (Å)	16.5970(15)	31.615(3)
$\alpha$ °	106.9973(17)	90
$\beta$ °	94.9688(17)	90
$\gamma$ °	107.8771(15)	90
$V/\text{Å}^3$	2845.4(4)	5594.2(8)
$Z$	4	8
$\rho_{\text{calc}} \text{ g/cm}^3$	1.855	1.887
$\mu$ (Mo $\text{K}\alpha$ )/ $\text{mm}^{-1}$	4.842	4.925
$F(000)$	1536	3072
Reflns collected	15995	13367

Unique	9946	4851
Data/restraints/parameters	9946/486/847	4851/0/376
GOF on $F^2$	0.984	1.177
$R_I^a$ , $wR_2^b$ [ $I > 2\sigma(I)$ ]	0.0408, 0.0975	0.0558, 0.1084
$R_I^a$ , $wR_2^b$ (all data)	0.0626, 0.1090	0.0785, 0.1155

$$R_I^a = \frac{\sum ||F_o| - |F_c||}{\sum F_o}, \quad wR_2^b = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

**Table S2** selected bond lengths and angles of Ir1 and Ir2

Ir1		Ir2	
Selected bonds	Bond Lengths (Å)	Selected bonds	Bond Lengths (Å)
Ir <sub>1</sub> N <sub>1</sub>	2.041(6)	Ir <sub>1</sub> C <sub>3</sub>	1.981(11)
Ir <sub>1</sub> N <sub>3</sub>	2.039(6)	Ir <sub>1</sub> C <sub>1</sub>	2.007(10)
Ir <sub>1</sub> C <sub>3</sub>	1.987(8)	Ir <sub>1</sub> N <sub>2</sub>	2.166(5)
Ir <sub>1</sub> C <sub>1</sub>	2.011(7)	Ir <sub>1</sub> N <sub>1</sub>	2.037(8)
Ir <sub>1</sub> O <sub>2</sub>	2.201(6)	Ir <sub>1</sub> N <sub>3</sub>	2.026(8)
Ir <sub>1</sub> N <sub>2</sub>	2.173(6)	Ir <sub>1</sub> O <sub>2</sub>	2.196(8)
Selected Angles	(°)	Selected Angles	(°)
N <sub>1</sub> Ir <sub>1</sub> O <sub>2</sub>	94.4(2)	C <sub>3</sub> Ir <sub>1</sub> C <sub>1</sub>	89.4(4)
N <sub>1</sub> Ir <sub>1</sub> N <sub>2</sub>	99.0(2)	C <sub>3</sub> Ir <sub>1</sub> N <sub>2</sub>	95.8(4)
N <sub>3</sub> Ir <sub>1</sub> N <sub>1</sub>	170.7(2)	C <sub>3</sub> Ir <sub>1</sub> N <sub>1</sub>	97.4(4)
N <sub>3</sub> Ir <sub>1</sub> O <sub>2</sub>	93.1(3)	C <sub>3</sub> Ir <sub>1</sub> N <sub>3</sub>	80.2(4)
N <sub>3</sub> Ir <sub>1</sub> N <sub>2</sub>	87.7(2)	C <sub>3</sub> Ir <sub>1</sub> O <sub>2</sub>	174.3(4)
N <sub>2</sub> Ir <sub>1</sub> O <sub>2</sub>	79.4(2)	C <sub>1</sub> Ir <sub>1</sub> N <sub>2</sub>	172.9(3)
C <sub>3</sub> Ir <sub>1</sub> N <sub>1</sub>	92.1(3)	C <sub>1</sub> Ir <sub>1</sub> N <sub>1</sub>	79.6(4)
C <sub>3</sub> Ir <sub>1</sub> O <sub>2</sub>	173.5(2)	C <sub>1</sub> Ir <sub>1</sub> N <sub>3</sub>	95.2(4)
C <sub>3</sub> Ir <sub>1</sub> N <sub>3</sub>	80.3(3)	C <sub>1</sub> Ir <sub>1</sub> O <sub>2</sub>	94.6(4)
C <sub>3</sub> Ir <sub>1</sub> N <sub>2</sub>	100.1(3)	N <sub>2</sub> Ir <sub>1</sub> O <sub>2</sub>	80.5(3)
C <sub>3</sub> Ir <sub>1</sub> C <sub>1</sub>	90.0(3)	N <sub>1</sub> Ir <sub>1</sub> N <sub>2</sub>	95.0(3)
C <sub>1</sub> Ir <sub>1</sub> N <sub>1</sub>	80.7(3)	N <sub>1</sub> Ir <sub>1</sub> O <sub>2</sub>	87.2(3)
C <sub>1</sub> Ir <sub>1</sub> O <sub>2</sub>	90.5(3)	N <sub>3</sub> Ir <sub>1</sub> N <sub>2</sub>	90.4(3)
C <sub>1</sub> Ir <sub>1</sub> N <sub>3</sub>	93.8(3)	N <sub>3</sub> Ir <sub>1</sub> N <sub>1</sub>	174.3(4)
C <sub>1</sub> Ir <sub>1</sub> N <sub>2</sub>	169.9(3)	N <sub>3</sub> Ir <sub>1</sub> O <sub>2</sub>	95.5(3)
C <sub>16</sub> -C <sub>17</sub> -C <sub>18</sub> -C <sub>19</sub>	7.0(14)	C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	-9.3(21)
C <sub>9</sub> -C <sub>8</sub> -C <sub>5</sub> -C <sub>4</sub>	0.5(13)	C <sub>13</sub> -C <sub>12</sub> -C <sub>17</sub> -C <sub>18</sub>	1.5(20)

## S4 Properties characterization

**Table S4** Absolute photoluminescence quantum yield of the complexes

Complex	Absolute photoluminescence quantum yield		
	In solution	Doped in 2,6-DczPPy (8%)	Doped in TCTA(8%)
Ir1	3.50%	41.84%	49.46%
Ir2	5.87%	69.64%	40.34%

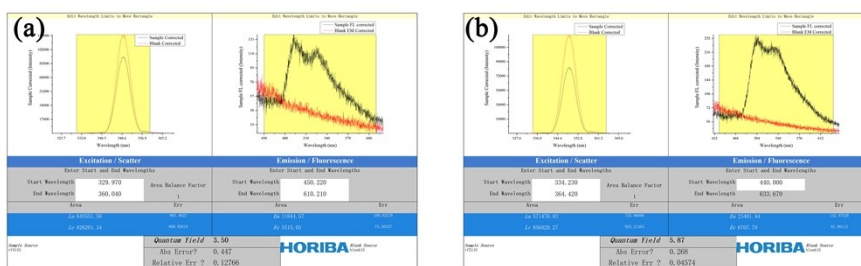


Fig. S5 Absolute photoluminescence quantum yield of (a) Ir1, (b) Ir2 in CH<sub>2</sub>Cl<sub>2</sub> solution.

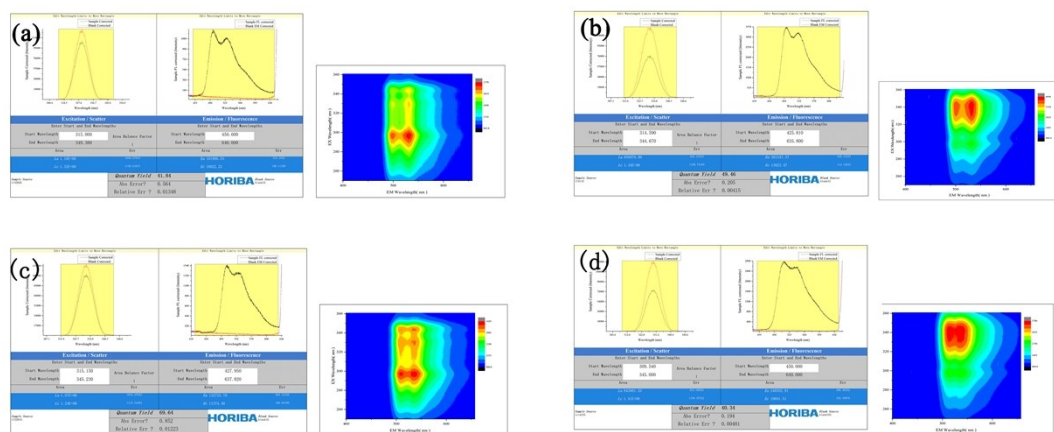


Fig. S6 Absolute photoluminescence quantum yield of (a) Ir1 doped in 2,6-DczPPy; (b) Ir1 doped in TCTA; (c) Ir2 doped in 2,6-DczPPy; (d) Ir2 doped in TCTA and correlative 3D excitation-emission spectra.

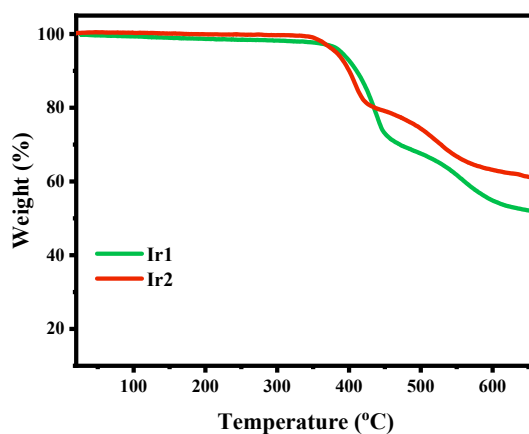


Fig.S7 TGA curves of the complexes at a heating rate of 10 °C min<sup>-1</sup>.

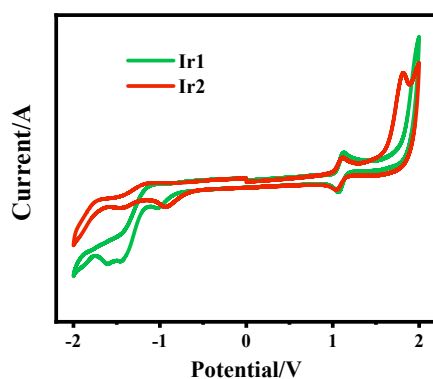


Fig. S8 The cyclic voltammogram curves of Ir1 and Ir2 in degassed CH<sub>3</sub>CN at room temperature.

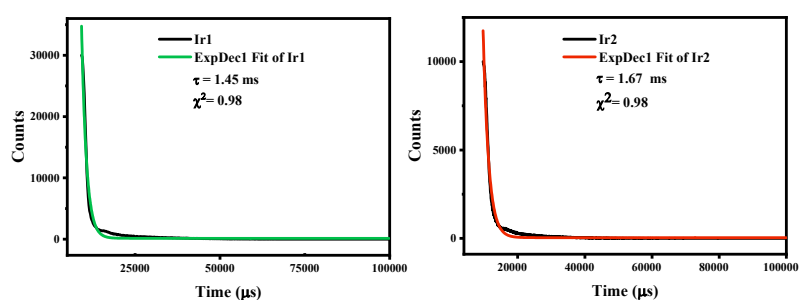


Fig. S9 Phosphorescence lifetime curves of the complexes in CH<sub>2</sub>Cl<sub>2</sub> solution.

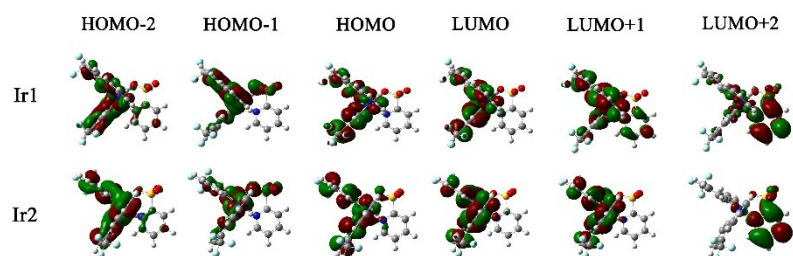


Fig. S10 The optimized structures and electron cloud distributions of several molecular orbitals (MOs).

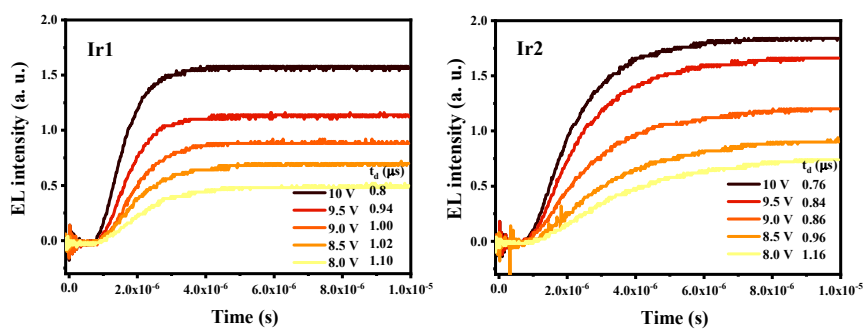


Fig. S11 The transient EL signals of Ir1 and Ir2.

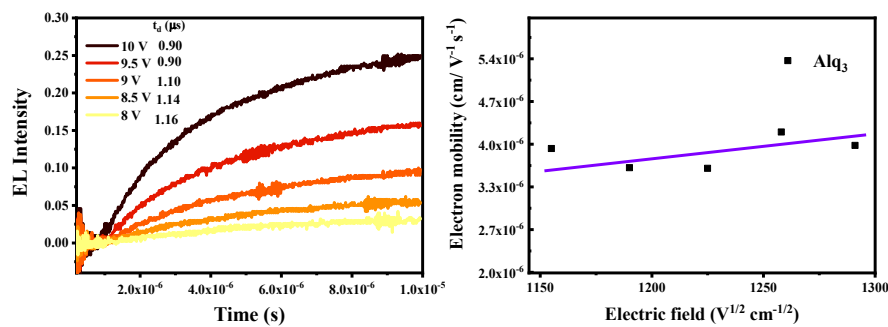


Fig. S12 the transient EL signals and electron mobility of Alq<sub>3</sub> as a function of the square of the electric field

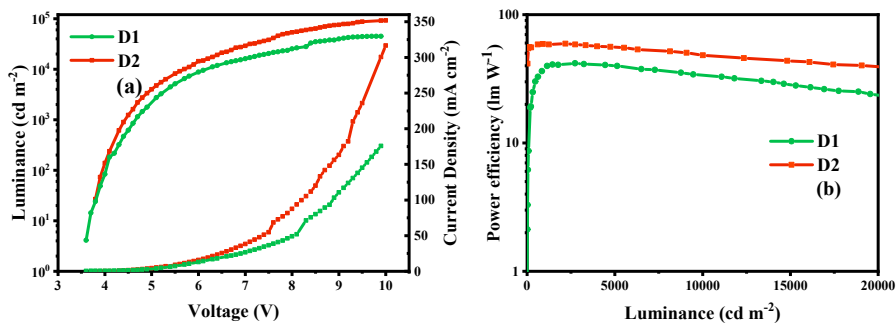


Fig. S13 characteristics of devices D1 and D2: (a) luminance-voltage-current density ( $L$ - $V$ - $J$ ) curves; (b) power efficiency-luminance ( $\eta_p$ - $L$ ) curves.

## S5 References

1. *SAINT-Plus, version 6.02*, Bruker Analytical X-ray System, Madison, WI, 1999.
2. G. M. Sheldrick, *SADABS, An empirical absorption correction program, Bruker Analytical X-ray Systems, Madison, WI, 1996.*
3. G. M. Sheldrick, *SHELXTL-2014*, Universität of Göttingen, Göttingen, Germany, 2014.