

Electronic Supplementary Information (ESI)

Rational design of orange-red iridium(III) complexes by isomer engineering strategy for improved performance of white organic light-emitting diodes

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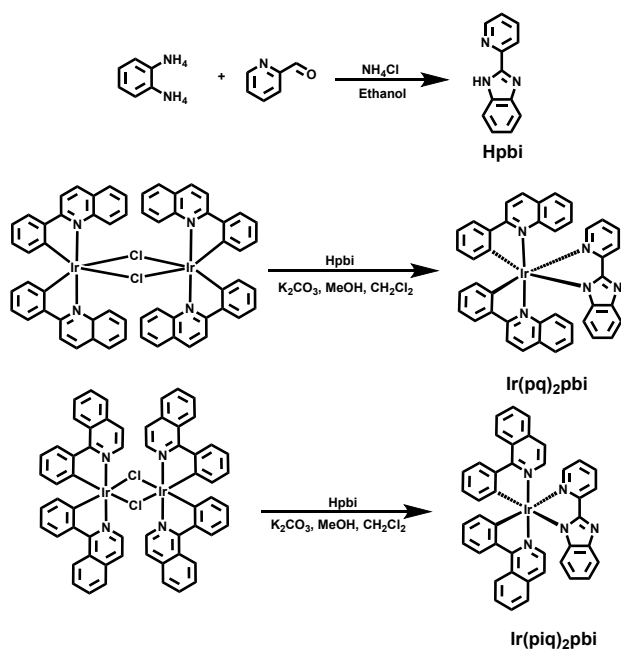


Fig. S1 The synthesized process of ancillary ligand and designed iridium(III) complexes.

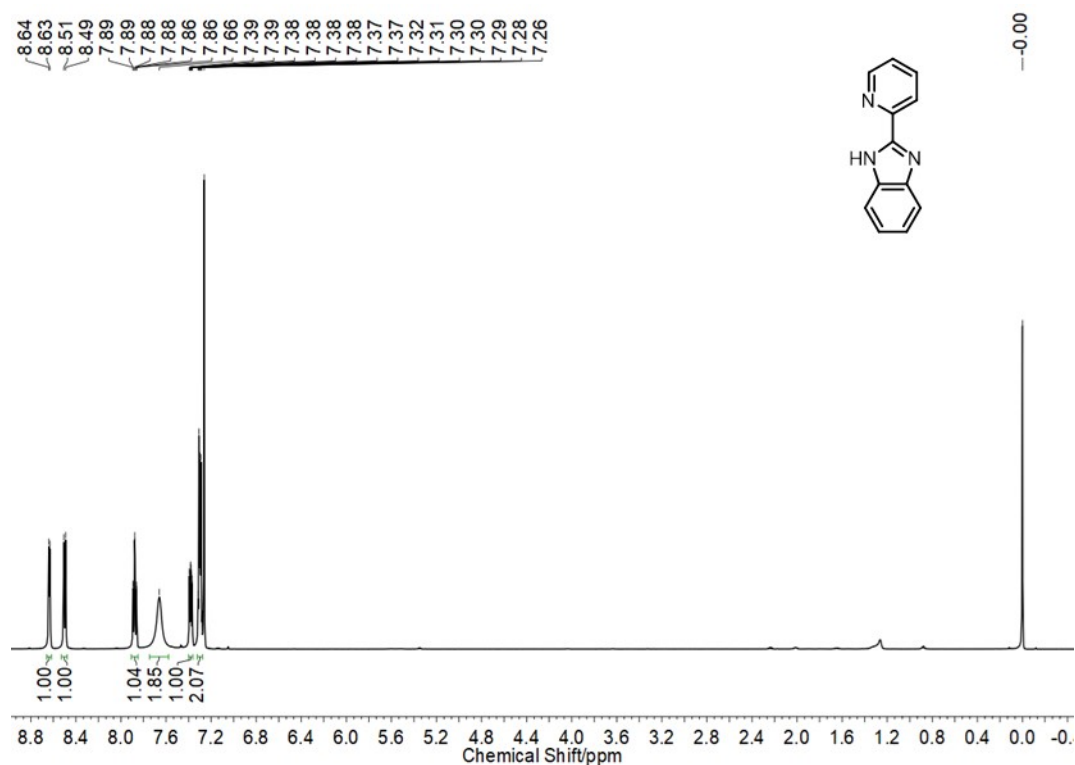


Fig. S2 ¹H NMR spectrum of auxiliary ligand Hpbi.

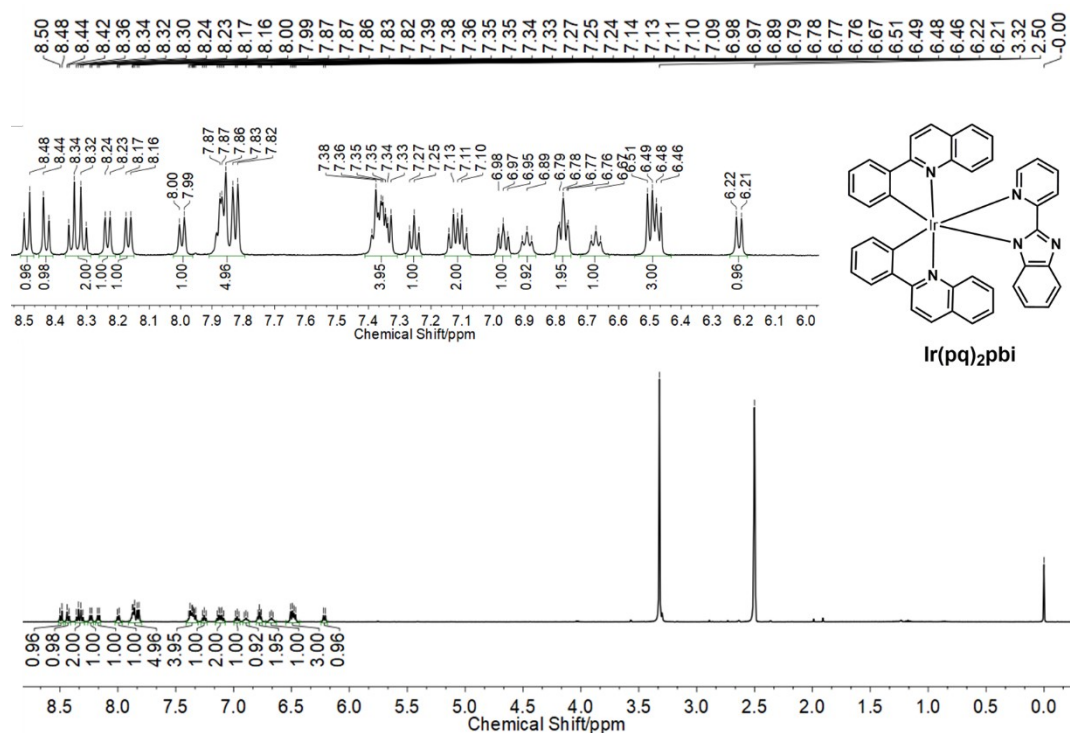


Fig. S3 ¹H NMR spectrum of complex **Ir(pq)₂bpi**.

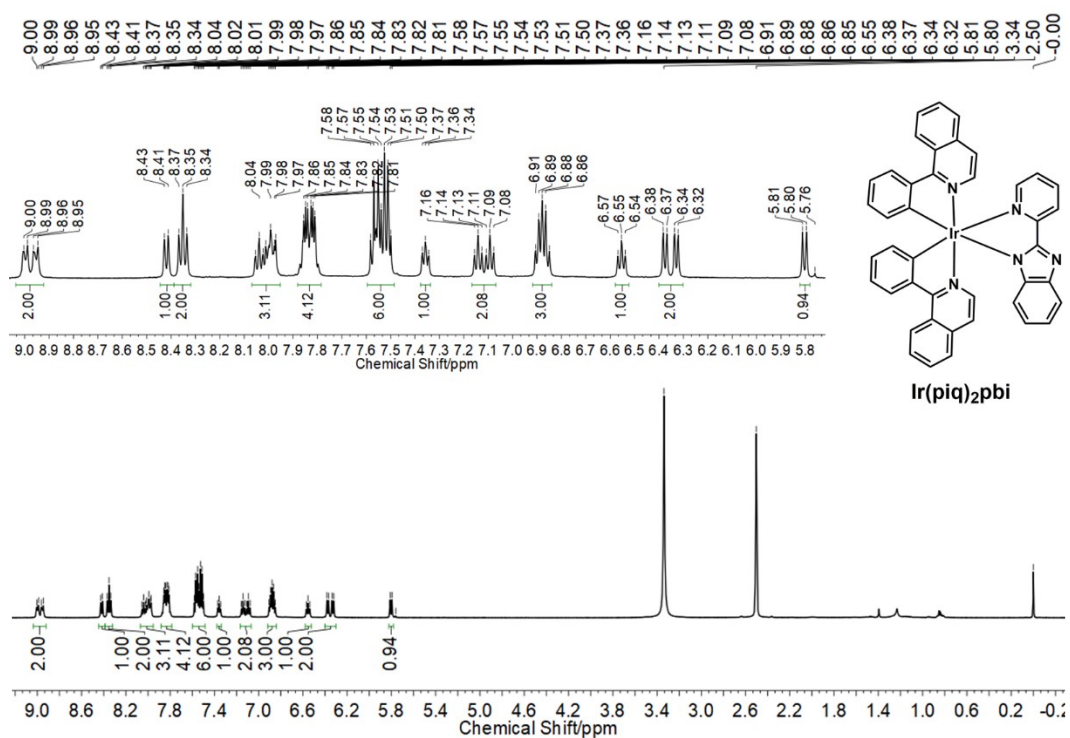


Fig. S4 ¹H NMR spectrum of complex **Ir(piq)₂bpi**.

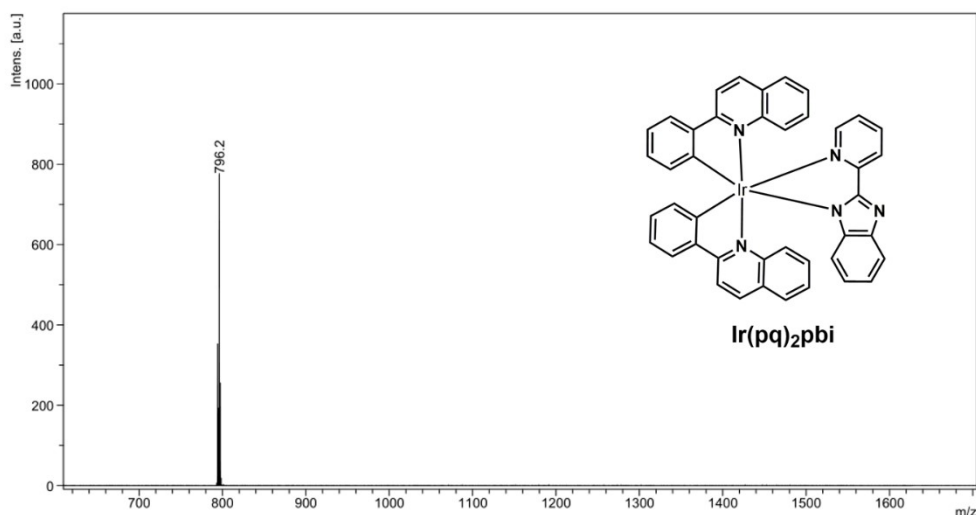


Fig. S5 Mass spectrum of complex **Ir(pq)₂pbi**.

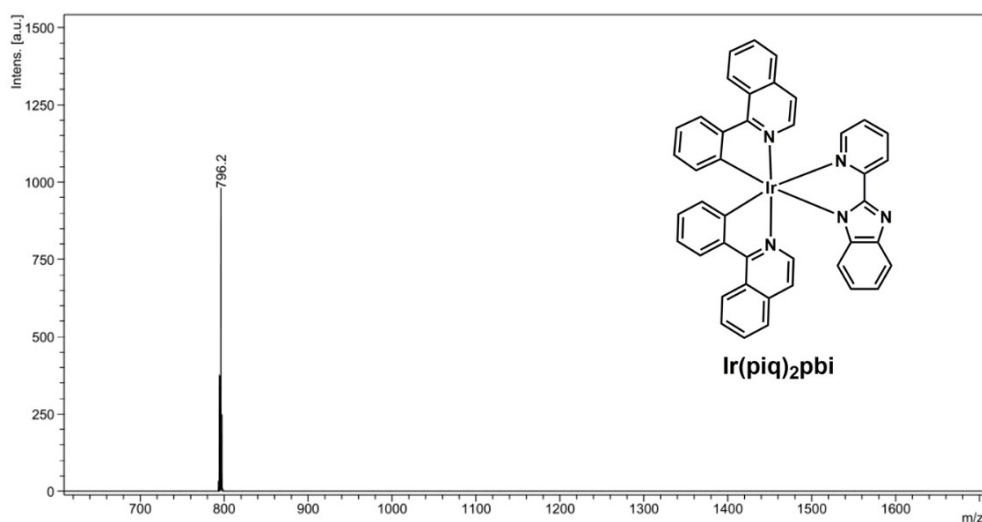


Fig. S6 Mass spectrum of complex **Ir(piq)₂pbi**.

Table S1 Crystallographic summary of single crystals for **Ir(pq)₂pbi** and **Ir(piq)₂pbi**.

	Ir(piq)₂pbi	Ir(pq)₂pbi
Empirical formula	C ₄₂ H ₂₈ IrN ₅	C ₄₂ H ₂₈ IrN ₅
Formula weight	795.90	794.89
Temperature/K	173.0	173.0
Crystal system	monoclinic	triclinic
Space group	<i>C2/c</i>	<i>P-1</i>
<i>a</i> /Å	38.4774(17)	15.8437(7)
<i>b</i> /Å	10.4809(5)	17.0679(7)
<i>c</i> /Å	19.2732(8)	17.3454(8)

$\alpha/^\circ$	90	75.672(2)
$\beta/^\circ$	116.6730(10)	70.044(2)
$\gamma/^\circ$	90	64.469(2)
Volume/ \AA^3	6945.3(5)	3950.4(3)
Z	8	4
ρ_{cal} (g/cm ³)	1.522	1.337
μ (Cu K α)/mm ⁻¹	7.724	6.790
$F(000)$	3144.0	1568.0
Reflections collected	29612	68833
Independent reflections	5722 [R _{int} = 0.0432, R _{sigma} = 0.0335]	13021 [R _{int} = 0.0853, R _{sigma} = 0.0565]
Goodness-of-fit on F ²	1.080	1.066
Final R indexes [I >= 2 σ (I)]	R _I = 0.0269, wR ₂ = 0.0725	R _I = 0.0558, wR ₂ = 0.1424
Final R indexes [all data]	R _I = 0.0277, wR ₂ = 0.0731	R _I = 0.0712, wR ₂ = 0.1528

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad {}^b wR_2 = \frac{|\sum w(|F_o|^2 - |F_c|^2)|}{\sum w(F_o^2)^{1/2}}$$

Table S2 Selected bonds lengths and angles for **Ir(pq)₂pbi** and **Ir(piq)₂pbi**.

	Ir(pq)₂pbi	Ir(pq)₂pbi
Selected bonds	Bond length (\AA)	Bond length (\AA)
Ir-C(1)	1.989(8)	1.997(3)
Ir-C(16)	1.959(9)	1.999(3)
Ir-N(1)	2.094(7)	2.039(3)
Ir-N(2)	2.079(7)	2.034(3)
Ir-N(3)	2.170(7)	2.122(3)
Ir-N(5)	2.194(6)	2.174(3)
Selected angles	($^\circ$)	($^\circ$)
C(1)-Ir-N(1)	79.8(3)	79.3(12)
C(16)-Ir-N(2)	79.8(3)	79.7(12)
N(3)-Ir-N(5)	74.8(2)	75.9(10)
N(1)-Ir-N(2)	171.0(3)	172.8(10)
C(1)-Ir-N(3)	169.7(3)	173.9(12)
C(16)-Ir-N(5)	172.8(3)	171.6(12)

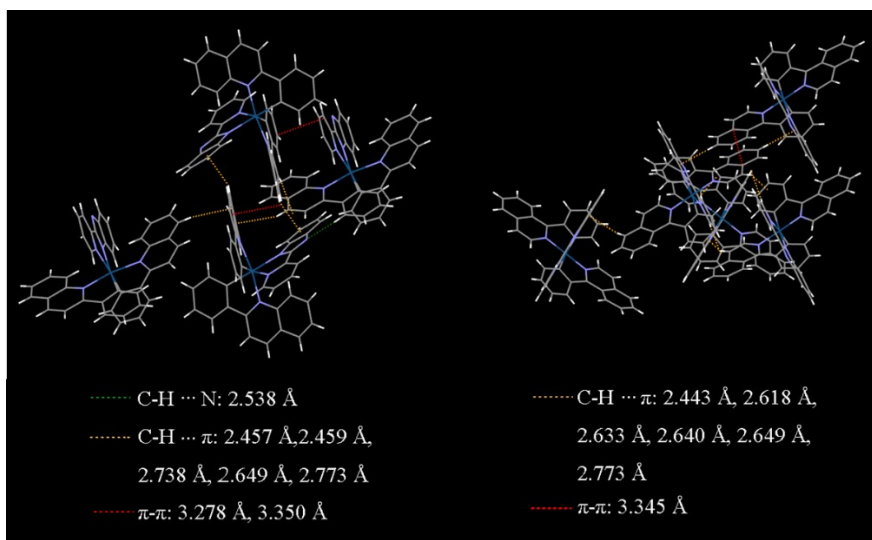


Fig. S7 The packing diagrams of complexes $\text{Ir}(\text{pq})_2\text{pbi}$ (left) and $\text{Ir}(\text{piq})_2\text{pbi}$ (right).

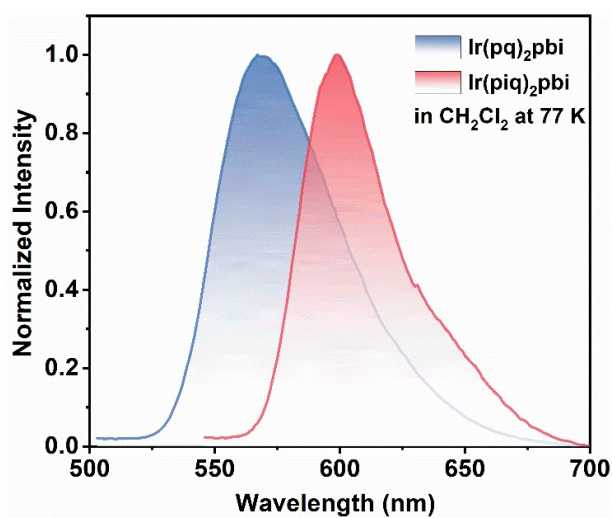


Fig. S8 Normalized PL spectra of $\text{Ir}(\text{pq})_2\text{pbi}$ and $\text{Ir}(\text{piq})_2\text{pbi}$ in CH_2Cl_2 at 77 K.

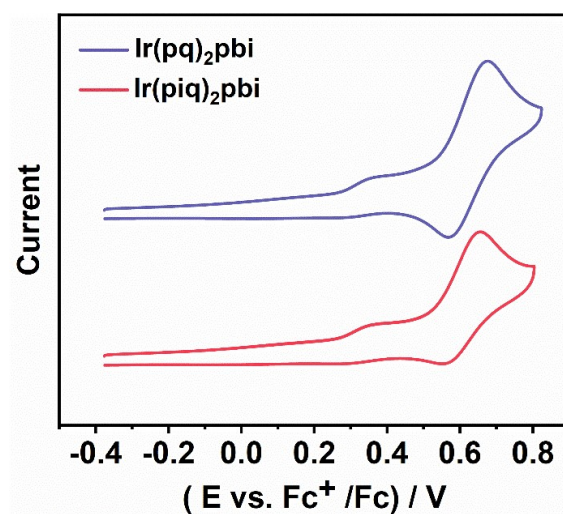
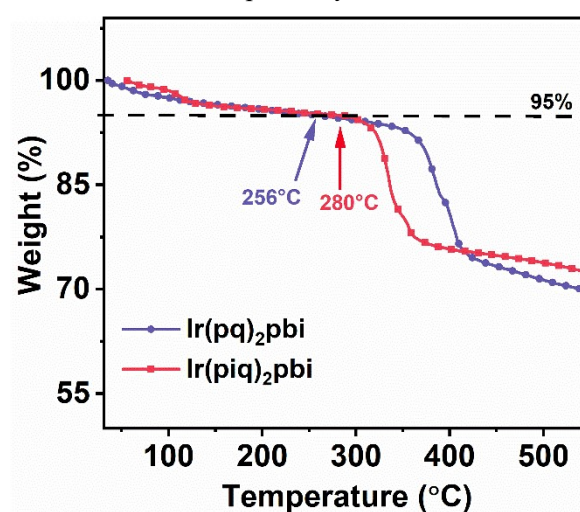
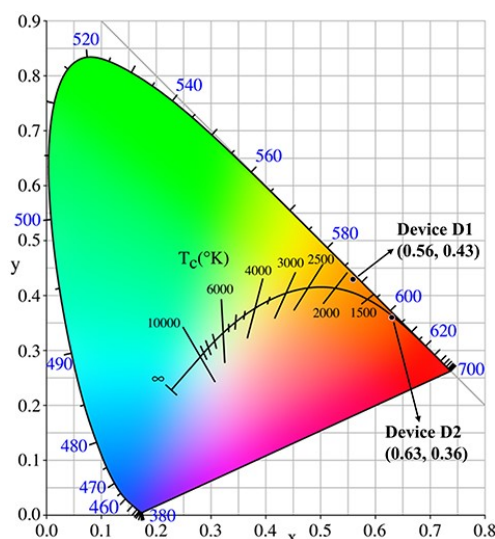


Fig. S9 CV curves of complexes $\text{Ir}(\text{pq})_2\text{pbi}$ and $\text{Ir}(\text{piq})_2\text{pbi}$ in CH_2Cl_2 .

Table S3 Excitation energy and major electronic configuration for complexes**Ir(pq)₂pbi** and **Ir(piq)₂pbi**.

Complex	λ_{cal} (nm)	λ_{Expt} (nm)	E (eV)	Configuration	Assignments	³ MLCT(%)
Ir(pq)₂pbi	545	565	2.28	H→L (45%)	³ MLCT/ ³ LLCT	18.61
				H-3→L (38%)	³ MLCT/ ³ LC/ ³ LLCT	
Ir(piq)₂pbi	651	594, 636	1.90	H→L (64%)	³ MLCT/ ³ LLCT	17.35
		H-3→L (19%)		³ MLCT/ ³ LC/ ³ LLCT		

“H” and “L” denote HOMO and LUMO, respectively.

**Fig. S10** TGA curves of complexes **Ir(pq)₂pbi** and **Ir(piq)₂pbi**.**Fig. S11** CIE coordinates of devices **D1** and **D2** based on complexes **Ir(pq)₂pbi** and

Ir(piq)₂pbi at 6 V.

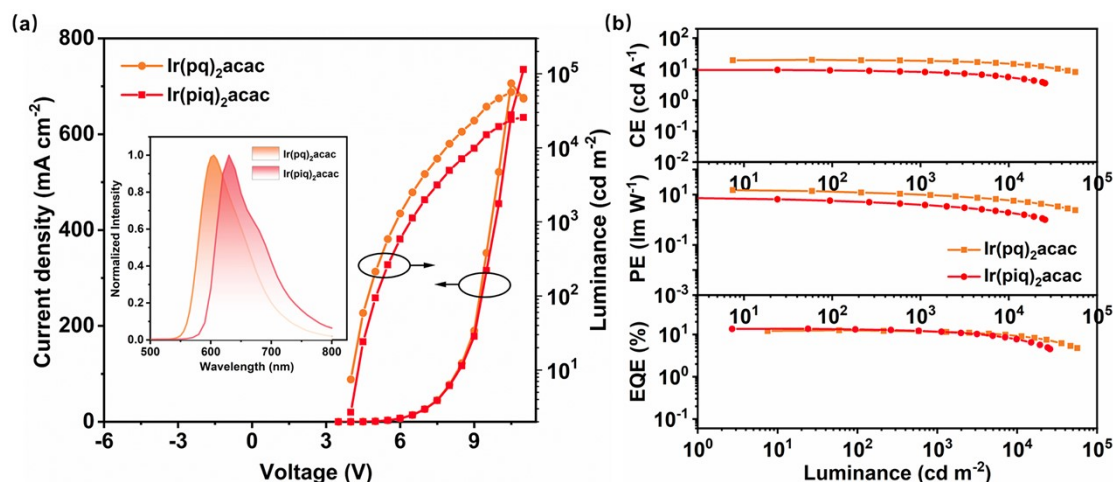


Fig. S12 (a) J-V-L curves, inset: EL spectra; (b) η_c -L, η_p -L and η_{ext} -L curves for devices based iridium(III) complexes **Ir(pq)₂acac** and **Ir(piq)₂acac** [The device structure is ITO/MoO₃ (3 nm)/TAPC (35 nm)/TCTA (5 nm)/26DCzPPy: **Ir(pq)₂acac** or **Ir(piq)₂acac** (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al].

Table S4 Summary of device performances of **Ir(pq)₂acac** and **Ir(piq)₂acac**.

Device	$V_{turn-on}^a$ (V)	L_{max} (cd m ⁻²)	η_c^b (cd A ⁻¹)	η_p^b (lm W ⁻¹)	η_{ext}^b (%)	CIE ^c (x, y)
Ir(pq)₂acac	3.6	56591	19.8/18.5	15.0/9.9	12.5/11.6	(0.62, 0.37)
Ir(piq)₂acac	3.5	25729	9.3/8.0	7.2/3.9	13.6/11.6	(0.68, 0.31)

^a Turn on the voltage at 1 cd m⁻²; ^b measured efficiency values in the order: maximum, then at 1000 cd m⁻²; ^c Measured at 6 V.

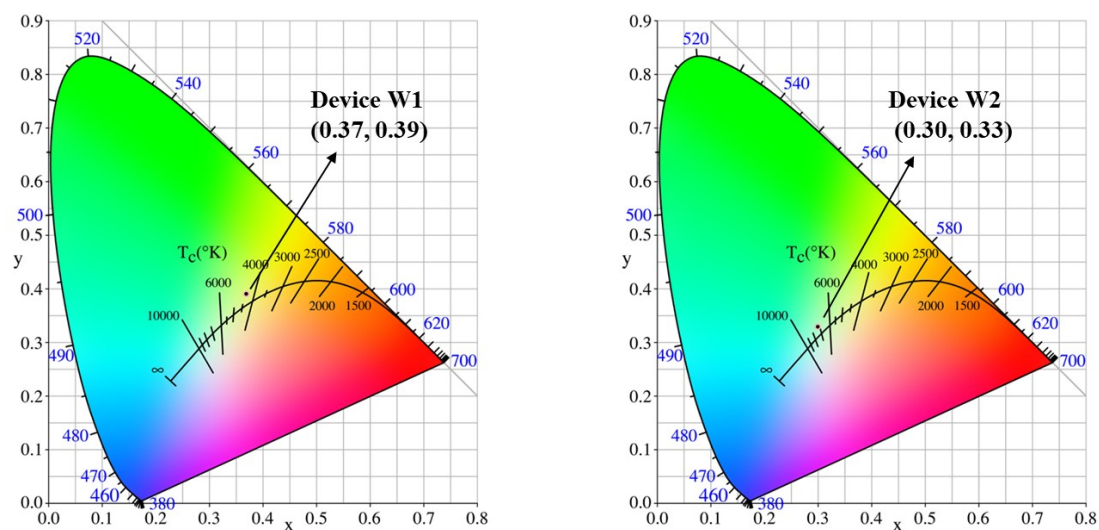


Fig. S13 CIE coordinates of devices **W1** and **W2** at 6 V.

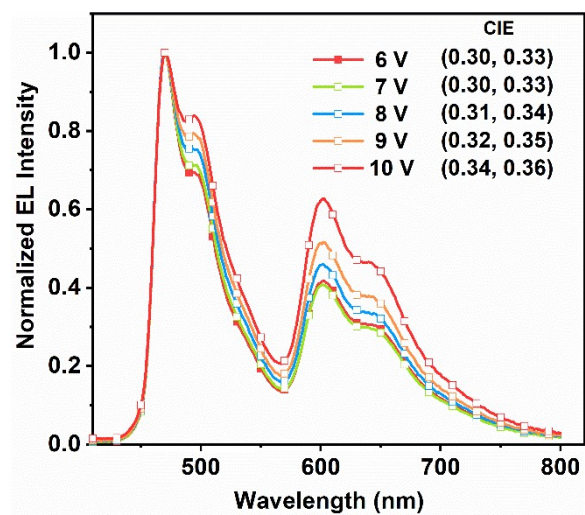


Fig. S14 EL spectra for W2.