

Electronic Supplementary Information

Figure S1. The synthetic routes of complexes **1-4**.

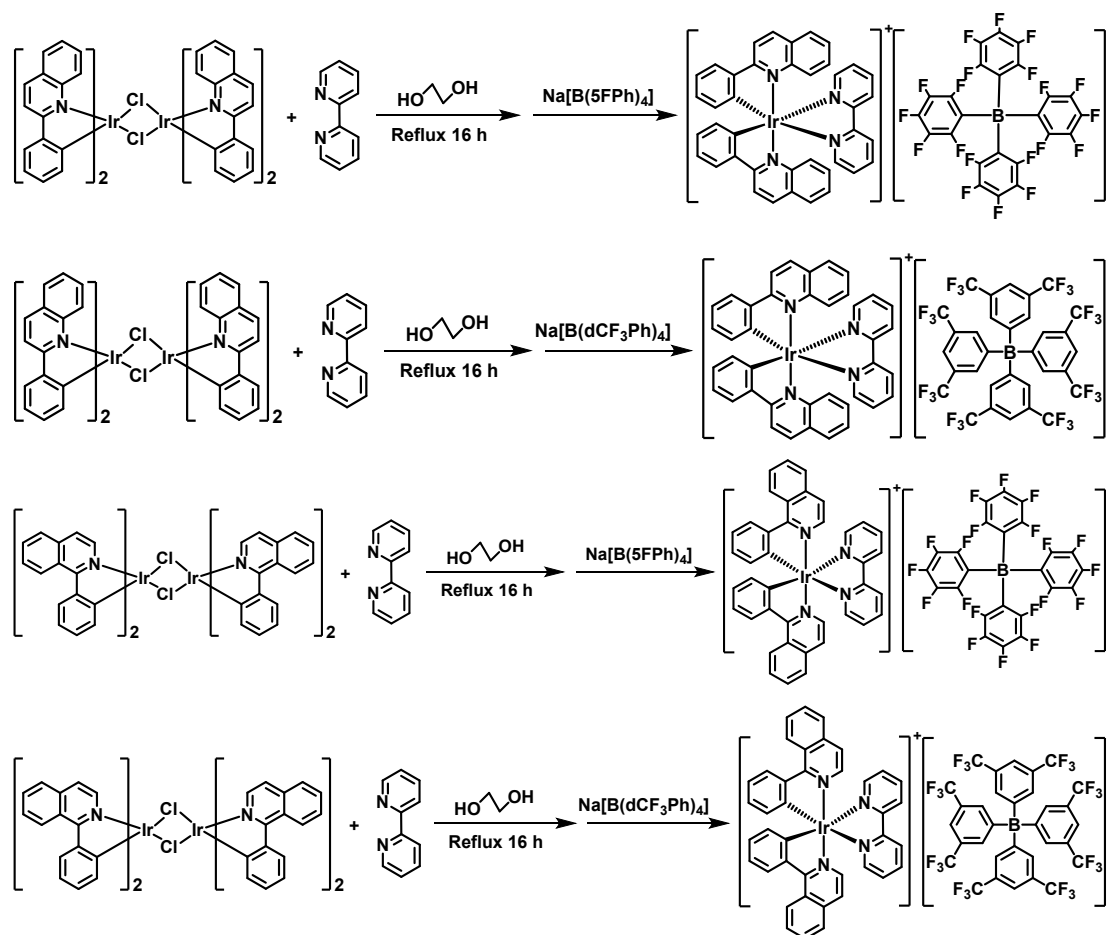


Figure S2. Schematic of the material design strategy.

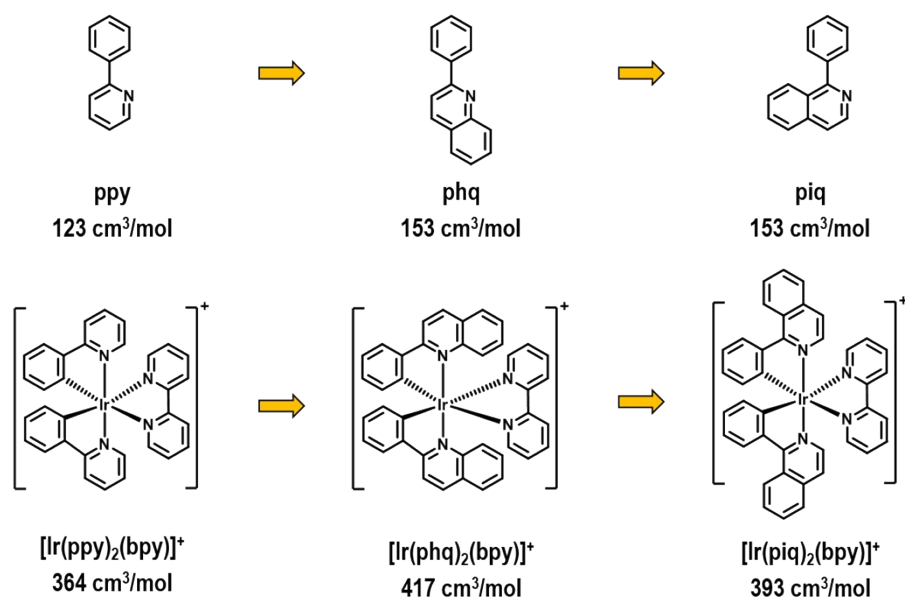


Figure S3. The excited state lifetimes of complexes **1-4** in neat films at room temperature.

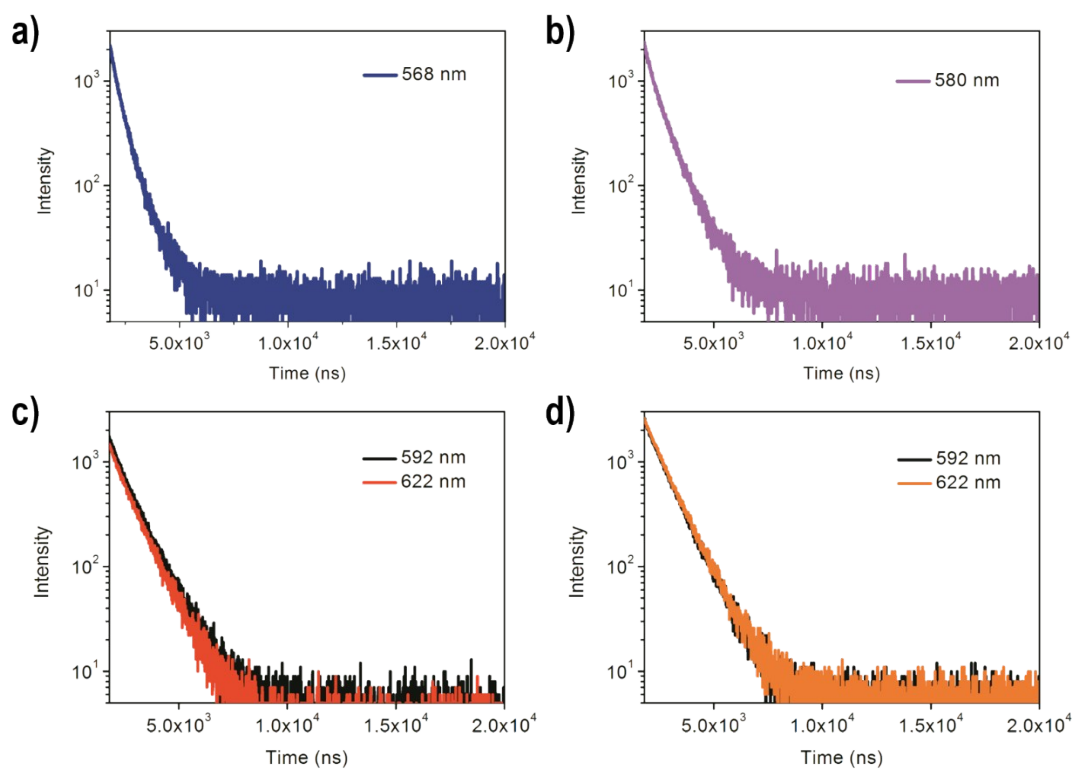


Figure S4. The excited state lifetimes of complexes **1-4** in acetonitrile glass at 77 K.

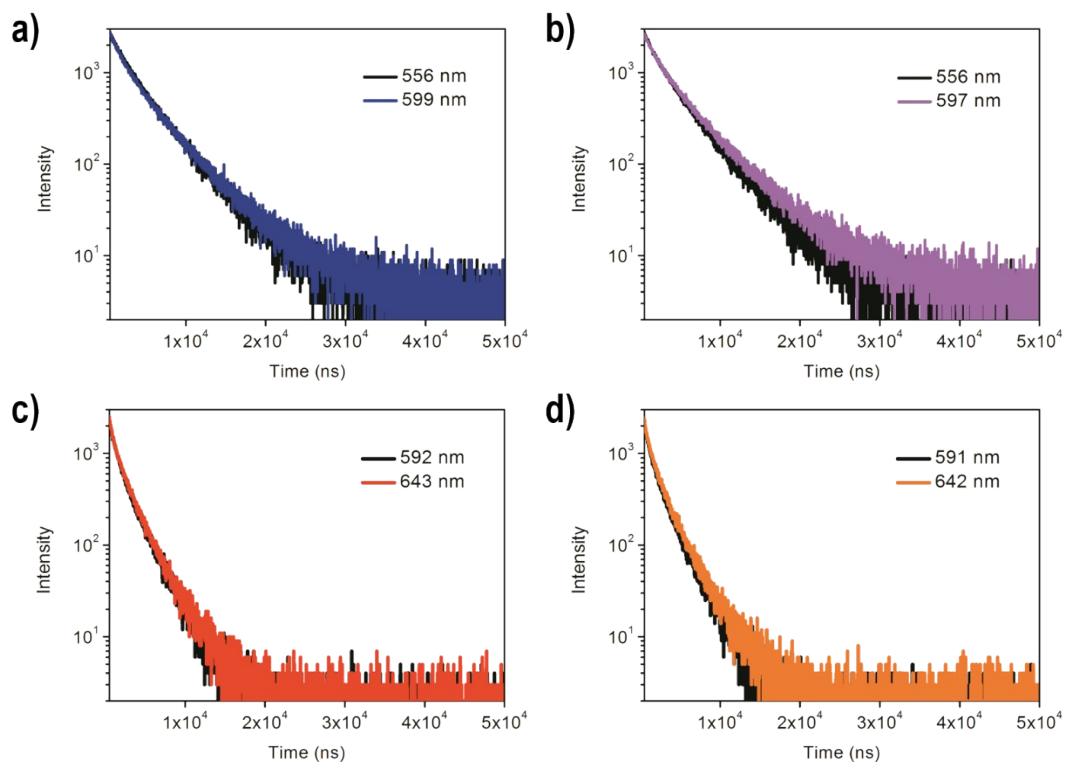


Figure S5. OLED characteristics. (a) J - V , (b) L - V and (c) CE - L characteristics, (d) EL spectra of ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/DIC-TRZ: x % Complex **1** (12 nm)/BPBiPA (50 nm)/LiF (1 nm)/Al (150 nm) with varying dopant concentrations.

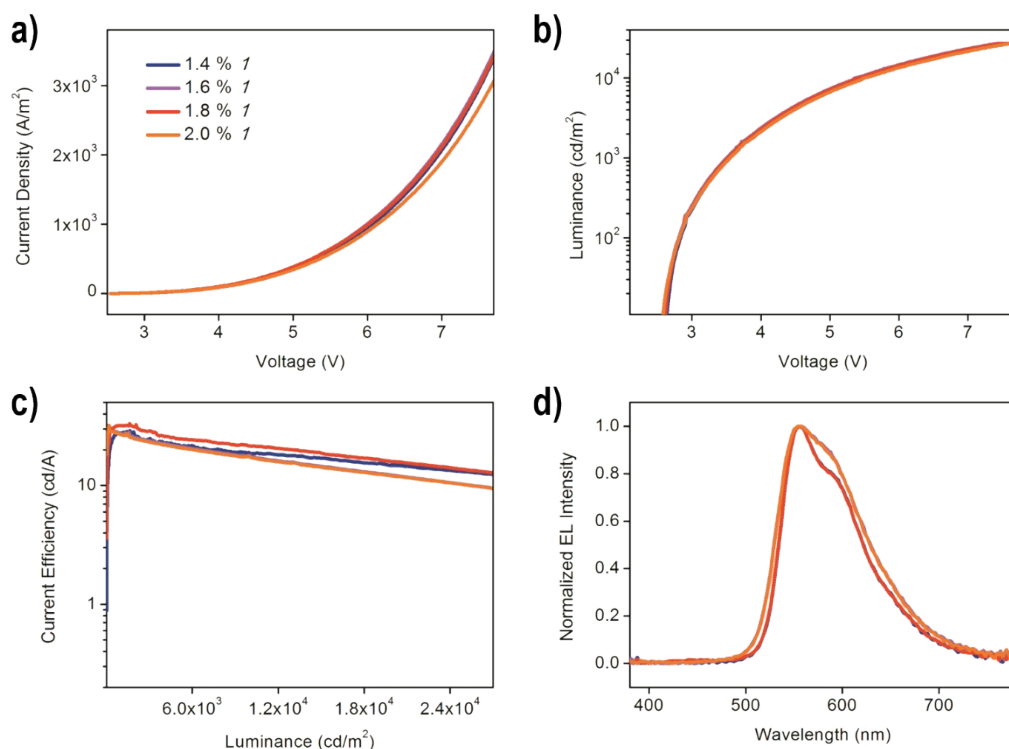


Figure S6. OLED characteristics. (a) *J*-*V*, (b) *L*-*V* and (c) CE-*L* characteristics, (d) EL spectra of ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/DIC-TRZ: *x* % Complex **2** (12 nm)/BPBiPA (50 nm)/LiF (1 nm)/Al (150 nm) with varying dopant concentrations.

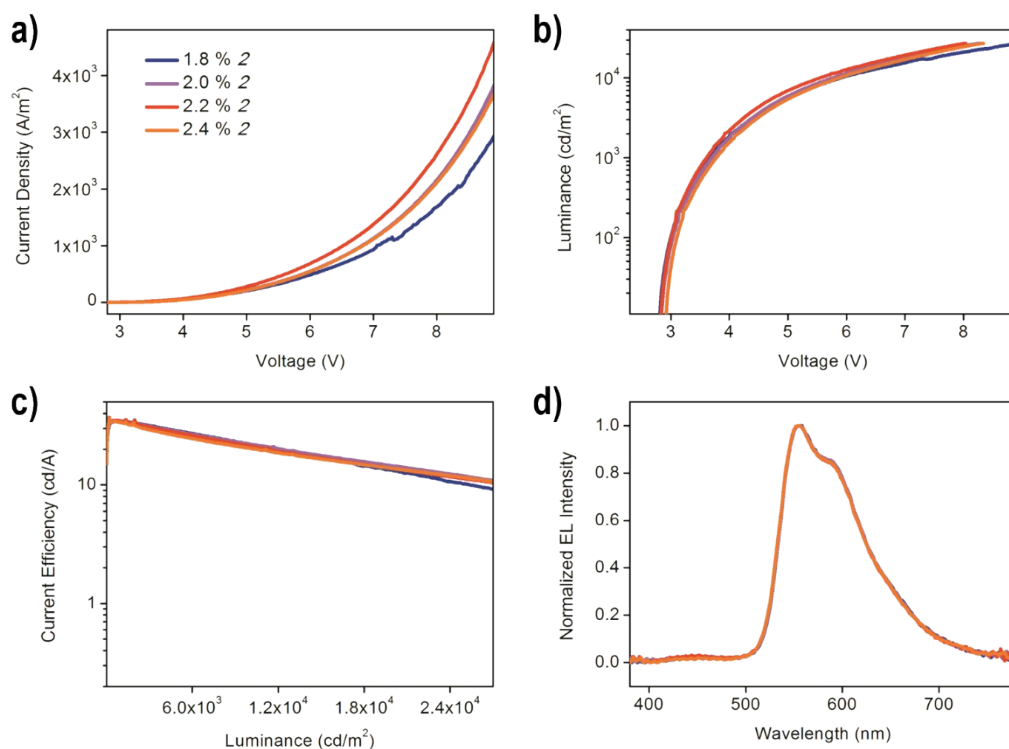


Figure S7. OLED characteristics. (a) *J*-*V*, (b) *L*-*V* and (c) CE-*L* characteristics, (d) EL spectra of ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/DIC-TRZ: *x* % Complex **3** (12 nm)/BPBiPA (50 nm)/LiF (1 nm)/Al (150 nm) with varying dopant concentrations.

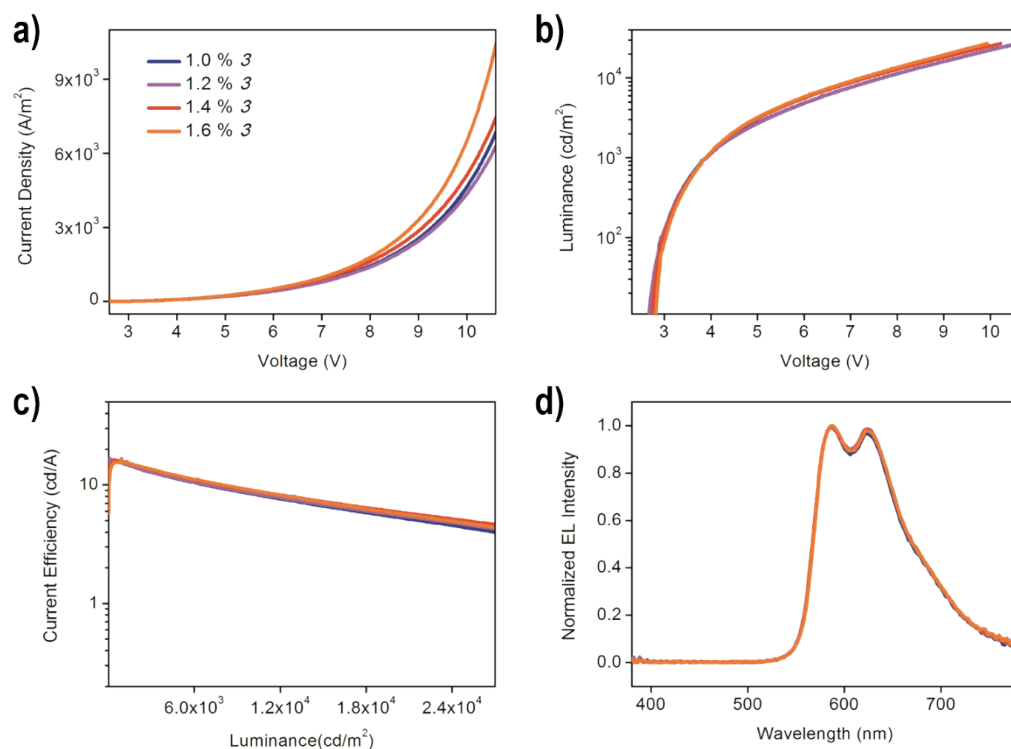


Figure S8. OLED characteristics. (a) *J*-*V*, (b) *L*-*V* and (c) CE-*L* characteristics, (d) EL spectra of ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/DIC-TRZ: *x* % Complex **4** (12 nm)/BPBiPA (50 nm)/LiF (1 nm)/Al (150 nm) with varying dopant concentrations.

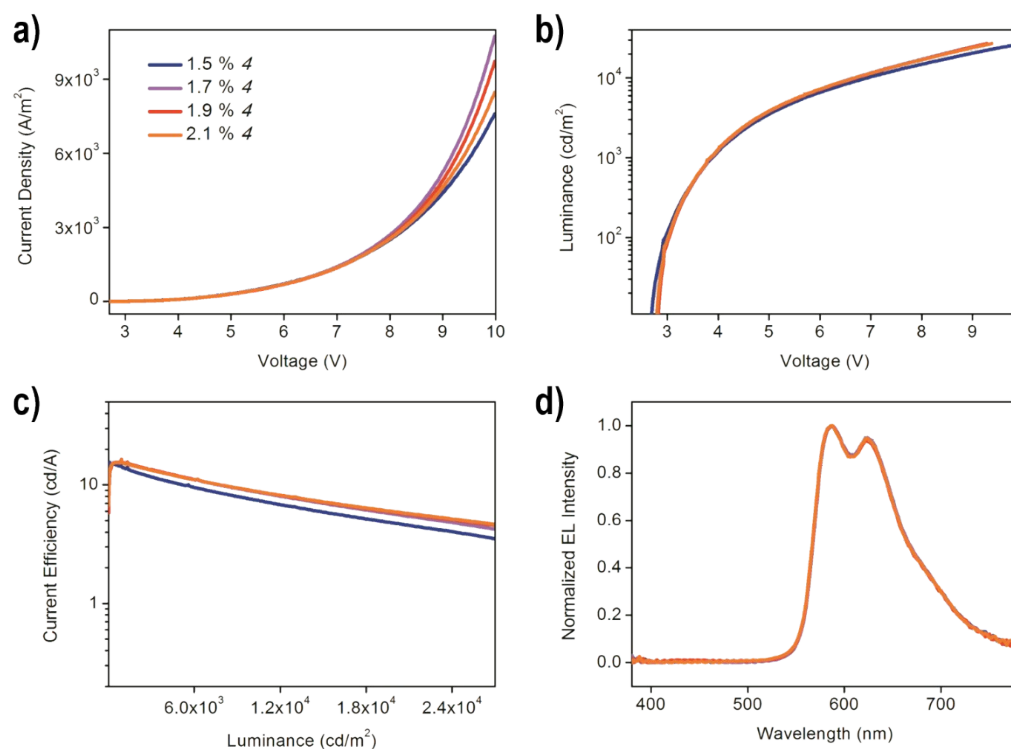


Table S1. Summary of the reported device performance of selected OLEDs based on cationic iridium(III) complexes.

Polychromatic Dopant	V_{on}^a [V]	Max CE ^b [cd/A]	Max EQE ^c [%]	Max PE ^d [lm/W]	Max L ^e [cd/m ²]	λ_{EL}^f [nm]	CIE ^g (x, y)	Reference
[Ir(dFppy) ₂ (pzpy)][PF ₆]	4.1	2.5	/	/	2.0×10 ³	458	(0.16, 0.27)	6
[Ir(dFppy) ₂ (dppmmi)][PF ₆]	7.2	3.4	/	/	7.3×10 ²	478	(0.20, 0.38)	10
[Ir(ppy) ₂ (Phpyim)][PF ₆]	4.4	25.3	8.1	/	38.5×10 ³	526	(0.34, 0.56)	7
[Ir(ppy) ₂ (EHCAF)][PF ₆]	8.4	23.7	6.8	5.3	11.9×10 ³	540	(0.37, 0.58)	14
[Ir(ppy) ₂ (bpy)][B(5FPh) ₄]	4.4	24.3	8.1	12.9	>27.1×10 ³	550	(0.42, 0.54)	15
[Ir(L) ₂ (N [^] N)][PF ₆]	5.0	19.7	6.5	18.4	15.6×10 ³	565	(0.44, 0.47)	13
[Ir(phq) ₂ (bpy)][B(5FPh) ₄]	2.2	33.1	11.1	32.2	>27.3×10 ³	556, 591 (<i>sh</i>)	(0.47, 0.51)	This work
[Ir(phq) ₂ (bpy)][B(dCF ₃ Ph) ₄]	2.5	37.0	13.7	37.5	>27.3×10 ³	560, 589 (<i>sh</i>)	(0.48, 0.51)	This work
[Ir(piq) ₂ (bpy)][B(5FPh) ₄]	2.2	16.8	10.3	18.1	>27.3×10 ³	588, 624 (<i>sh</i>)	(0.59, 0.40)	This work
[Ir(piq) ₂ (bpy)][B(dCF ₃ Ph) ₄]	2.4	16.4	9.9	14.2	>27.3×10 ³	588, 624 (<i>sh</i>)	(0.59, 0.40)	This work
[Ir(npy) ₂ (c-phen)][PF ₆]	6.8	10.0	7.1	/	3.2×10 ³	618	(0.57, 0.40)	9
[Ir(npy) ₂ (o-phen)][PF ₆]	8.6	9.1	6.5	/	2.3×10 ³	620	(0.57, 0.40)	9

^a V_{on} , turn-on voltage (at the luminance of 1 cd/m²). ^b CE, current efficiency. ^c EQE, external quantum efficiency. ^d PE, power efficiency. ^e L, luminance. ^f λ_{EL} , EL wavelength, *sh* denotes the shoulder wavelength. ^g CIE, Commission Internationale de l'Elairage.