Supporting Information (SI)

Iridium(III) complexes incorporating thieno[2,3-*d*]pyrimidine units for efficient orange-to-yellow electroluminescence with low efficiency roll-off

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Contents

S1. General information

NMR measurements were conducted on a Bruker AM 400 spectrometer. High resolution electrospray mass spectra (HR-MS) were measured on G6500 from Agilent. Absorption photoluminescence spectra were measured on a UV-3100 and a Hitachi F-4600 photoluminescence spectrophotometer. Cyclic voltammetry measurements were conducted on an MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-$AgNO_3$ (0.1 M) in CH_3CN as the reference electrode, tetra-*n*-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^+/Fc as the external standard, the scan rate was 0.1 V/s. The absolute photoluminescence quantum yields and the decay lifetimes of the compounds were measured with HORIBA FL-3 fluorescence spectrometer. Thermogravimetric analysis was performed on a Pyris 1 DSC under nitrogen at a heating rate of 10 °C min^{-1}. The single crystal of the complex was carried out on a Bruker SMART CCD diffractometer using monochromated Mo Ka radiation (λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections.

S2. OLEDs fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω sq^{-1}. The deposition rate for organic compounds is 1-2 Å s^{-1}. The phosphor and the host (2,6DCzPPy) were co-evaporated to form emitting layer from two separate sources. The cathode consisting of LiF/Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å s^{-1} and then by evaporation of Al metal with a rate of 3 Å s^{-1}.

The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in the air without device encapsulation. On the basis of the uncorrected photoluminescence (PL) and electroluminescence (EL) spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer. The external quantum efficiencies (EQE) of EL devices were calculated based on the photo energy measured by the photodiode.

S3. NMR spectra

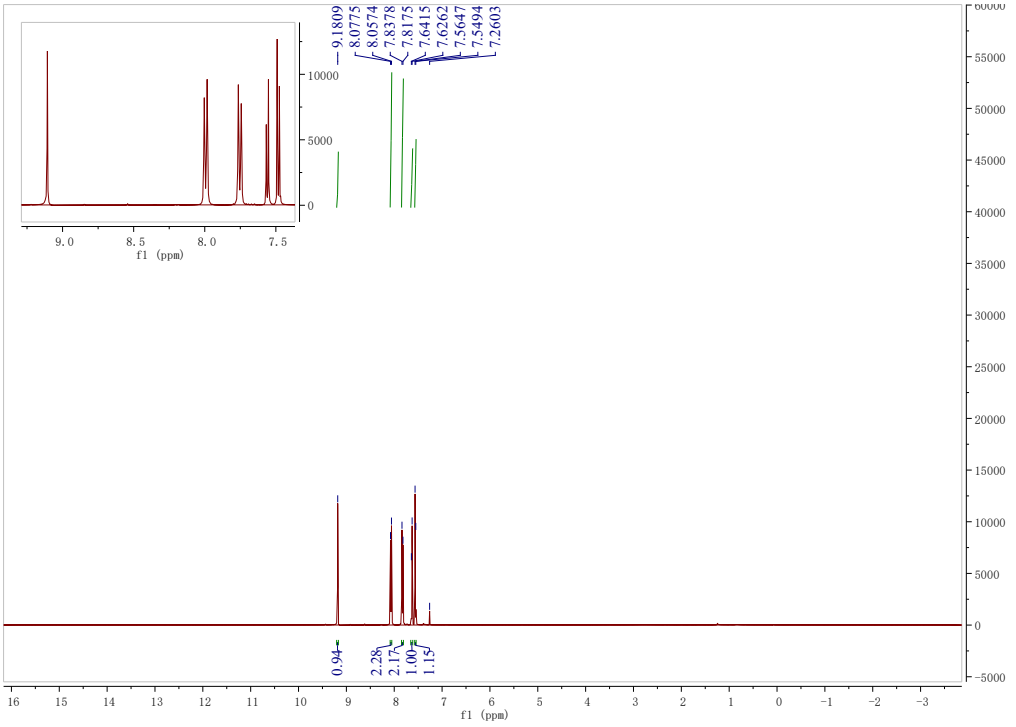

Fig. S1 The ^{1}H NMR spectrum of 4tfptp in $CDCl_3$.

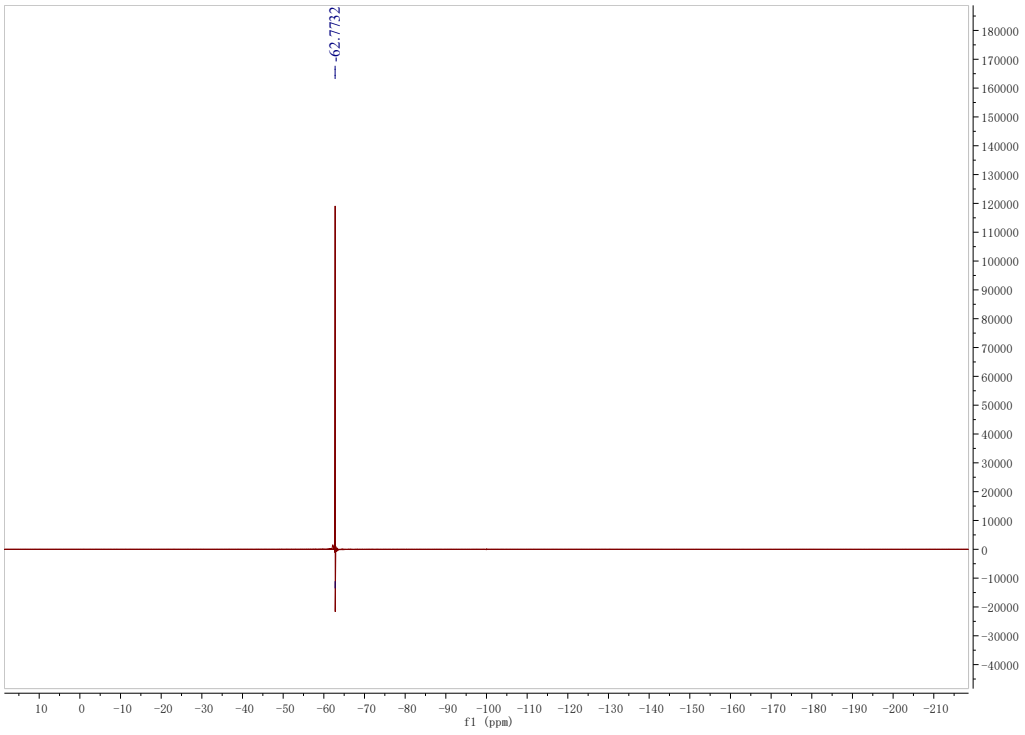

Fig. S2 The ^{19}F NMR spectrum of 4tfptp in $CDCl_3$.

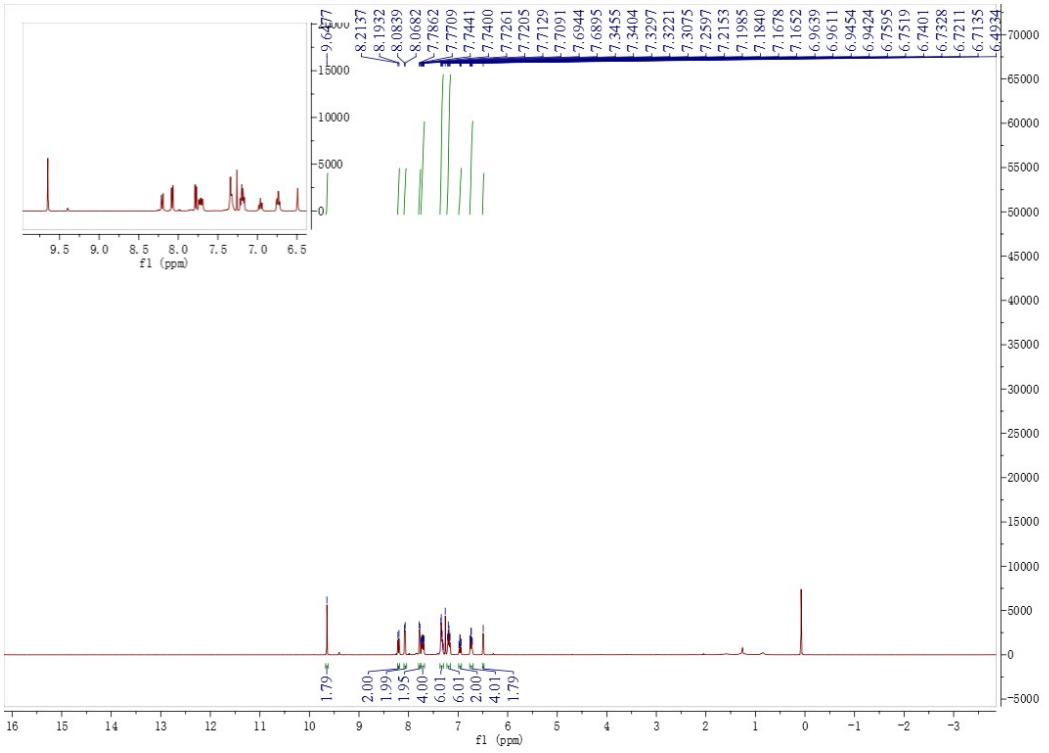

Fig. S3 The ^{1}H NMR spectrum of $(4tfptp)_2Ir(tpip)$ in $CDCl_3$.

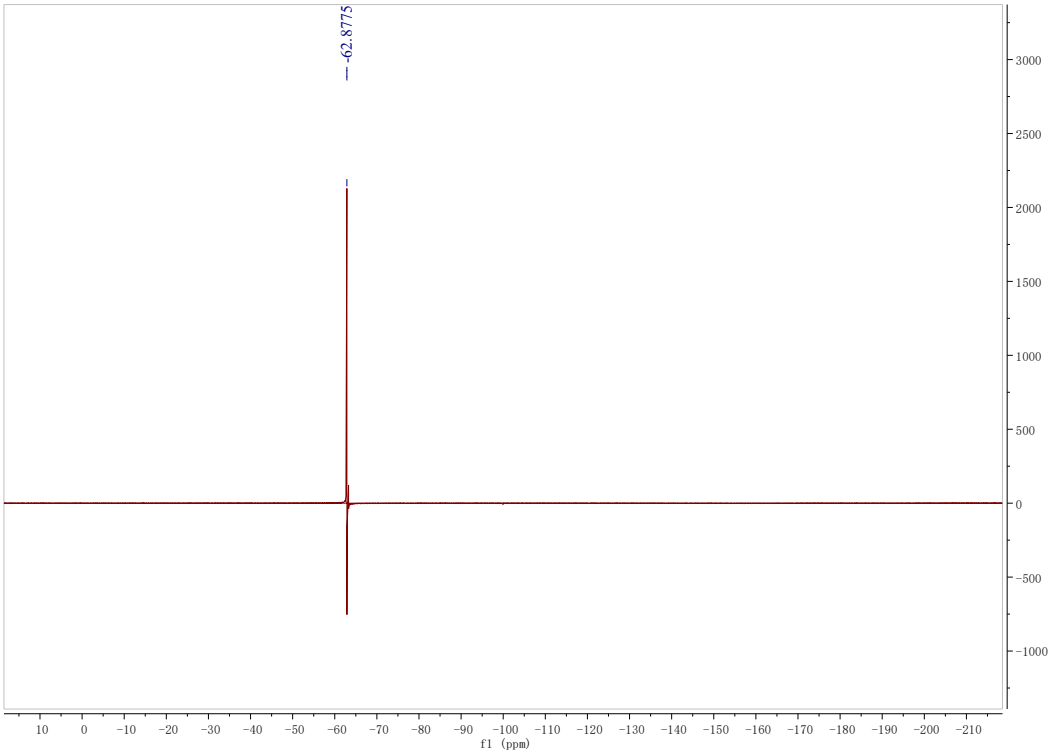

Fig. S4 The ^{19}F NMR spectrum of $(4tfptp)_2Ir(tpip)$ in $CDCl_3$.

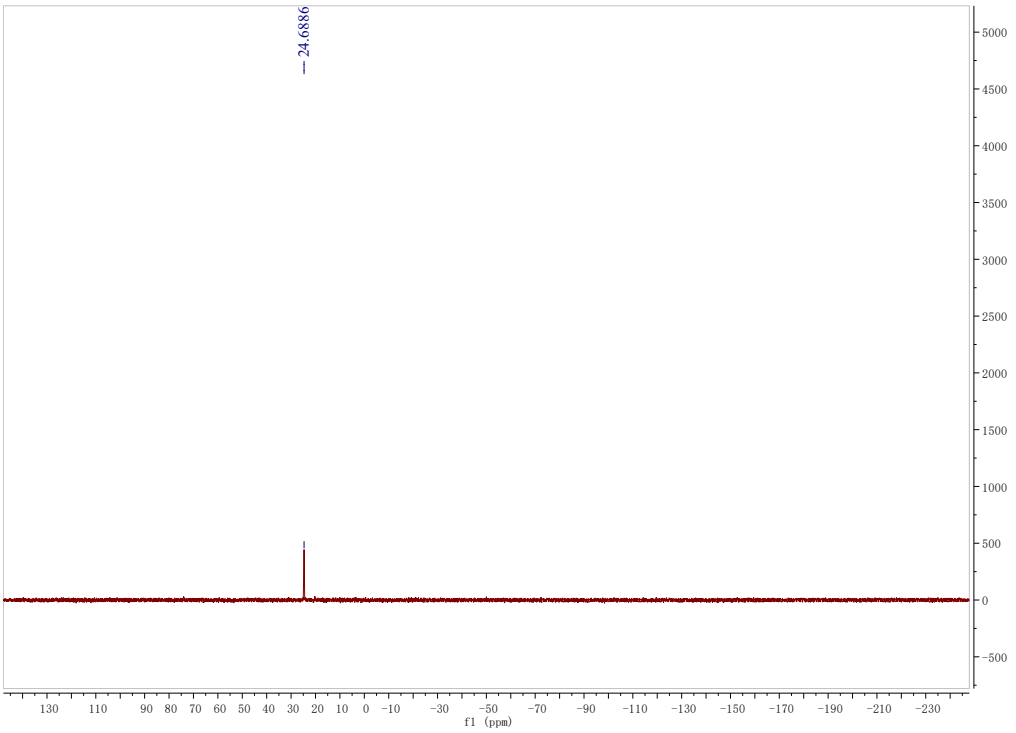

Fig. S5 The ^{31}P NMR spectrum of $(4tfptp)_2Ir(tpip)$ in $CDCl_3$.

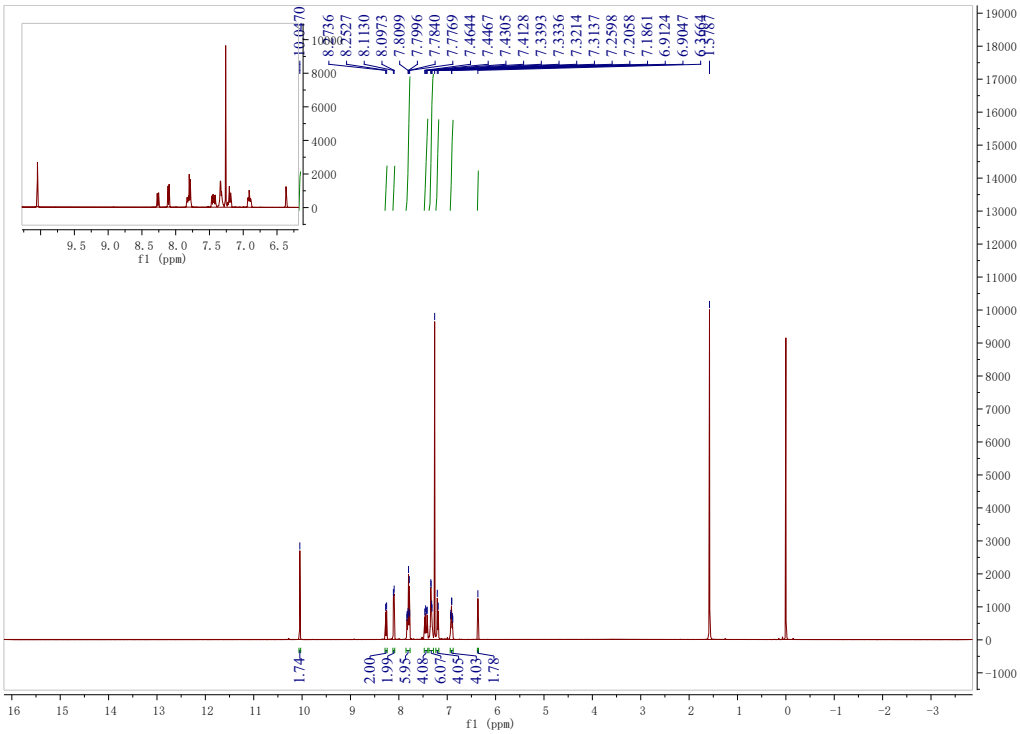

Fig. S6 The ^{1}H NMR spectrum of $(4tfptp)_2Ir(Stpip)$ in $CDCl_3$.

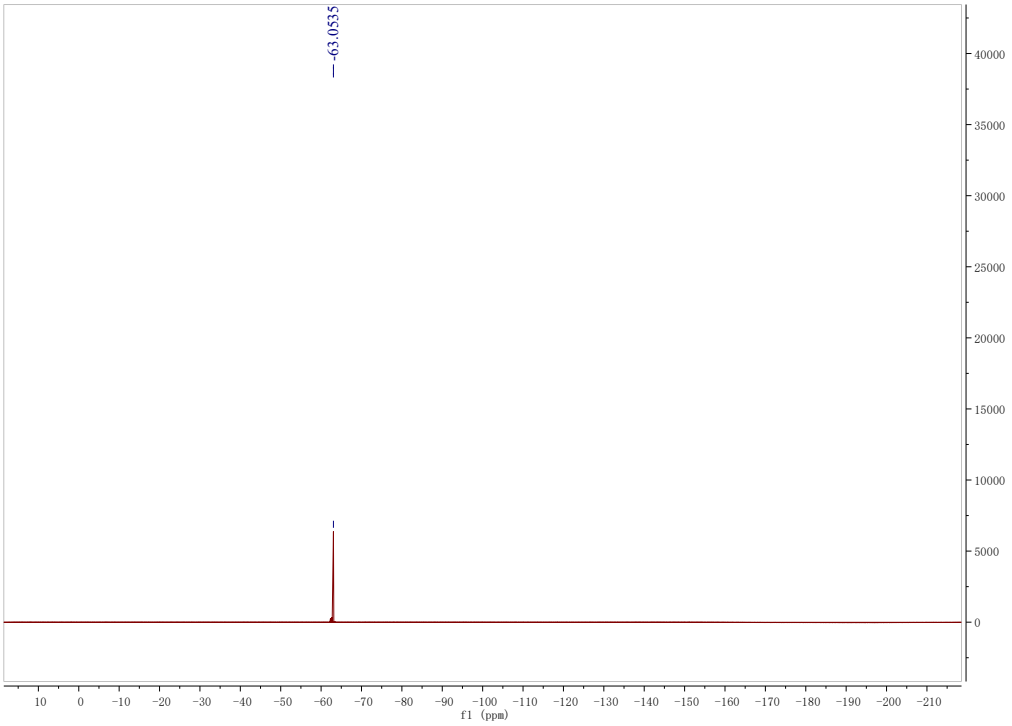

Fig. S7 The ^{19}F NMR spectrum of $(4tfptp)_2Ir(Stpip)$ in $CDCl_3$.

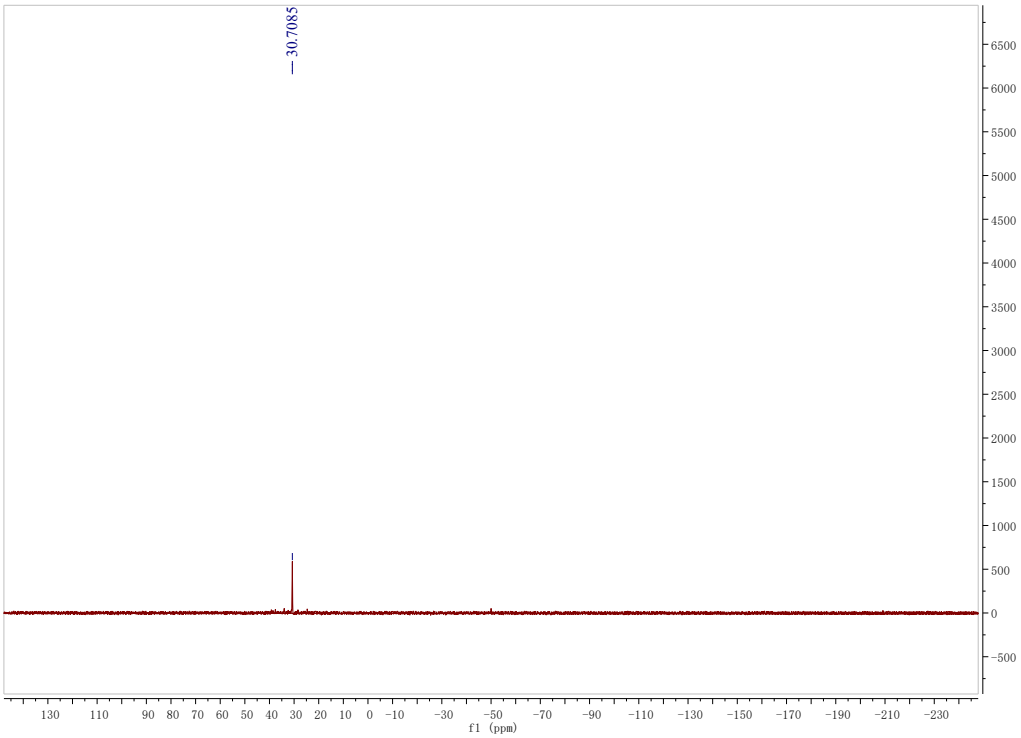

Fig. S8 The ^{31}P NMR spectrum of $(4tfptp)_2Ir(Stpip)$ in $CDCl_3$.

S4. X-ray crystallographic data

Table S1. The crystallographic data of $(4tfptp)_2Ir(Stpip)$.

	$(4tfptp)_2Ir(Stpip)$
Formula	$C_{50}H_{33}F_6IrN_5P_2S_4$
Formula weight	1200.19
T (K)	193.0
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.5647(12)
b (Å)	26.471(3)
c (Å)	15.2254(14)
α (deg)	90
β (deg)	92.320(4)
γ (deg)	90
V (Å3)	4657.0(8)
Z	4
$\rho_{calculated}$ (g/cm^3)	1.712
μ (Mo Kα) (mm^{-1})	5.745
F (000)	2372.0
Range of transm factors (deg)	5.83 to 107.826
Reflns collected	24070
Unique(R_{int})	10387(0.0676)
$R_1{}^a$, $wR_2{}^b$ [I > 2s(I)]	0.0342, 0.0897
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0393, 0.0932
GOF on F^2	1.052
CCDC No.	2158550

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$

Table S2. Selected bond lengths and angles of $(4tfptp)_2Ir(Stpip)$.

Selected Bonds	Bond length (Å)
Ir1-C1	2.006(4)
Ir1-C2	2.009(3)
Ir1-N1	2.049(3)
Ir1-N2	2.060(3)
Ir1-S1	2.4944(9)
Ir1-S2	2.4753(10)
Selected angles	(°)
C1-Ir1-N1	79.59(13)
C2-Ir1-N2	79.51(13)
S1-Ir1-S2	90.94(3)

S5. Thermal stability

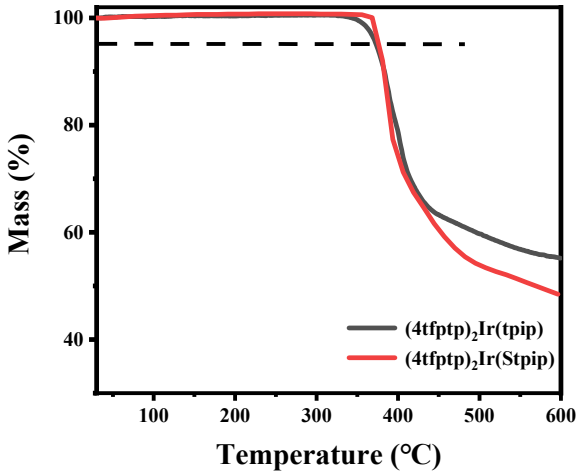

Fig. S9 TGA curves of Ir(III) complexes.

S6. Photophysical measurement

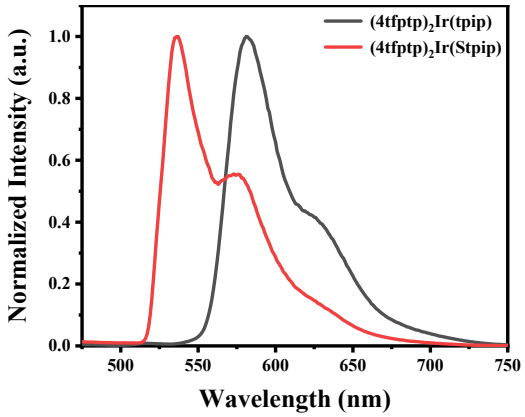

Fig. S10 Normalized PL spectra of Ir(III) complexes in DCM at 77 K.

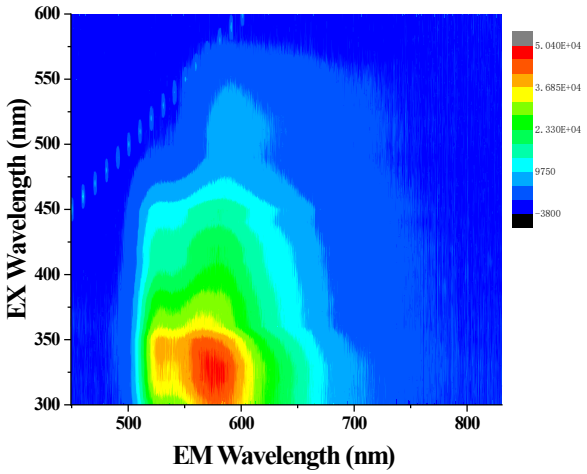

Fig. S11 3D excitation-emission correlation map of $(4tfptp)_2Ir(tpip)$ in DCM solutions (10^{-5} M).

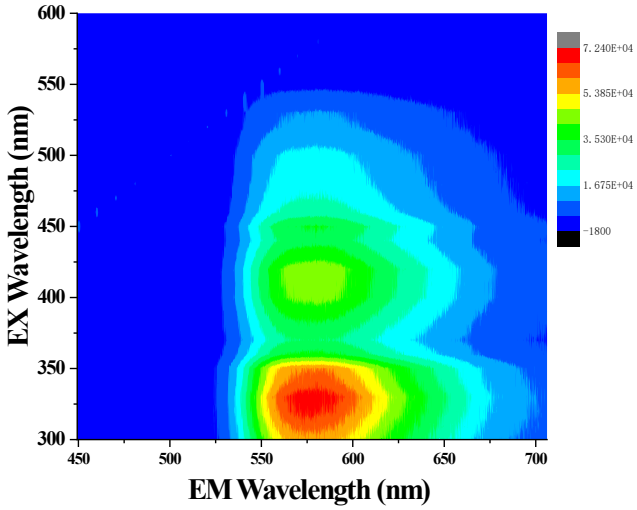

Fig. S12 3D excitation-emission correlation map of $(4tfptp)_2Ir(Stpip)$ in DCM solutions (10^{-5} M).

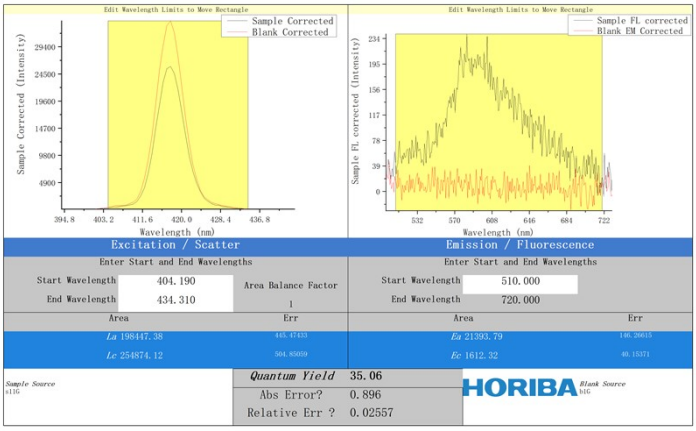

Fig. S13 The photoluminescence quantum yield of $(4tfptp)_2Ir(tpip)$ in degassed DCM solution (10^{-5} M).

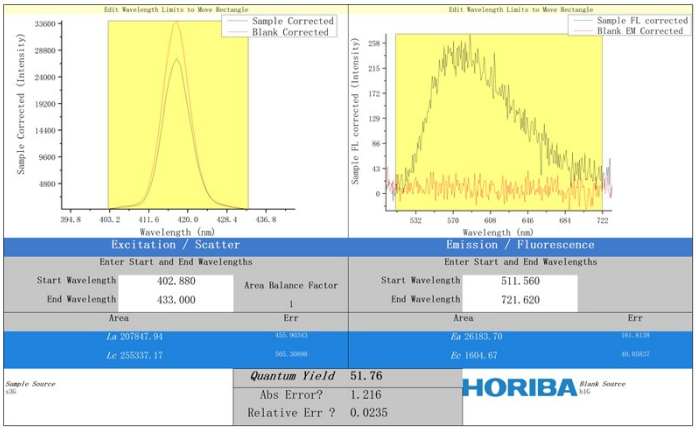

Fig. S14 The photoluminescence quantum yield of $(4tfptp)_2Ir(Stpip)$ in degassed DCM solution (10^{-5} M).

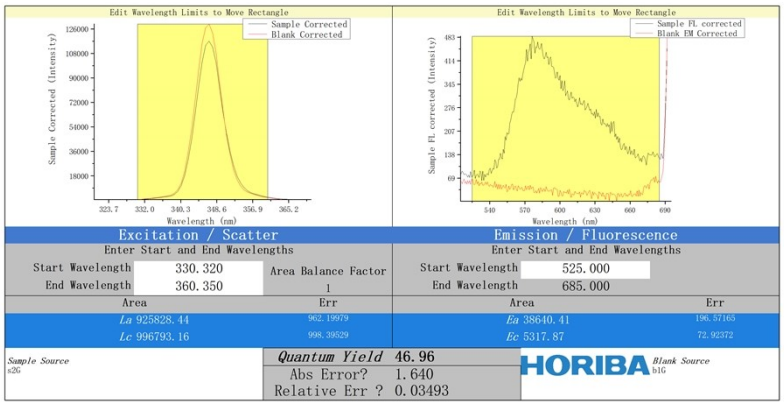

Fig. S15 The photoluminescence quantum yield of $(4tfptp)_2Ir(tpip)$ in co-doped film (5 wt% in 2,6DCzPPy).

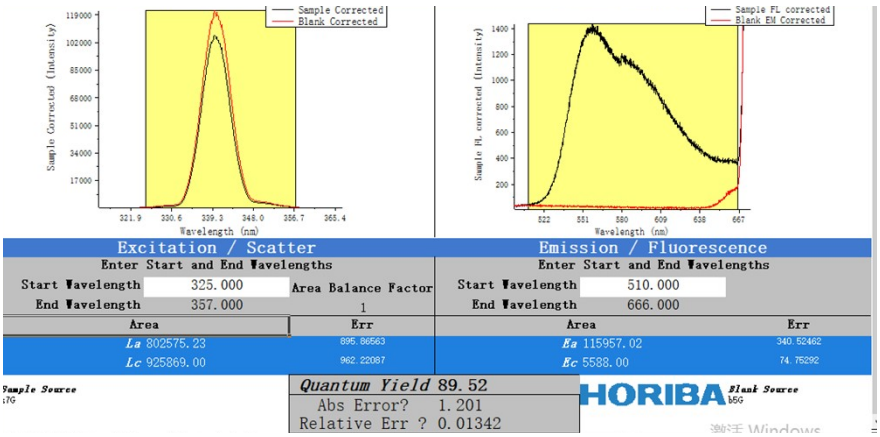

Fig. S16 The photoluminescence quantum yield of $(4tfptp)_2Ir(Stpip)$ in co-doped film (5 wt% in 2,6DCzPPy).

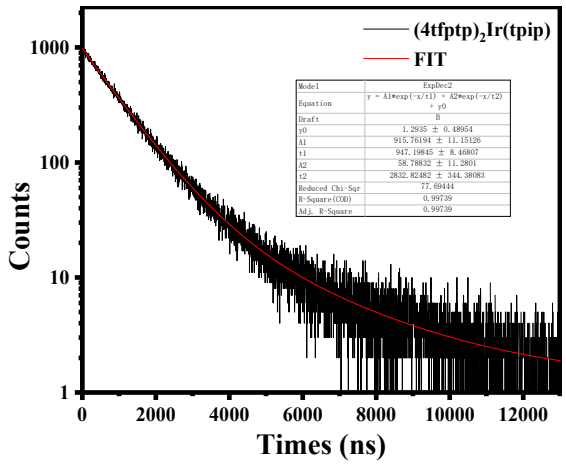

Fig. S17 The phosphorescence lifetime and fitted curves of $(4tfptp)_2Ir(tpip)$ in degassed DCM solution (10^{-5} M).

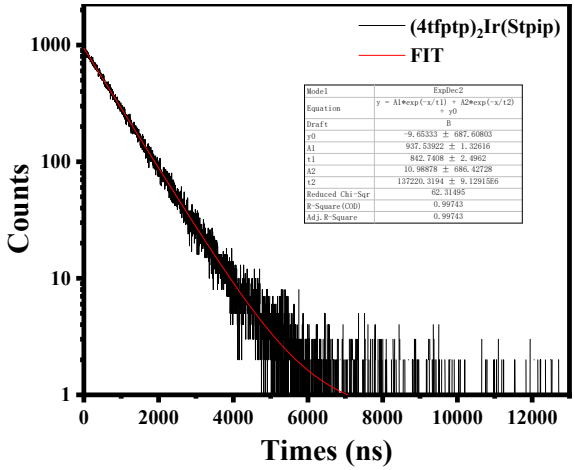

Fig. S18 The phosphorescence lifetime and fitted curves of $(4tfptp)_2Ir(Stpip)$ in degassed DCM solution (10^{-5} M).

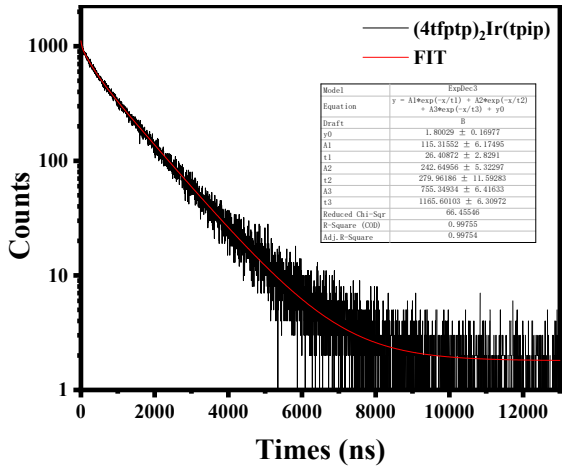

Fig. S19 The phosphorescence lifetime and fitted curves of $(4tfptp)_2Ir(tpip)$ in co-doped film (5 wt% in 2,6DCzPPy).

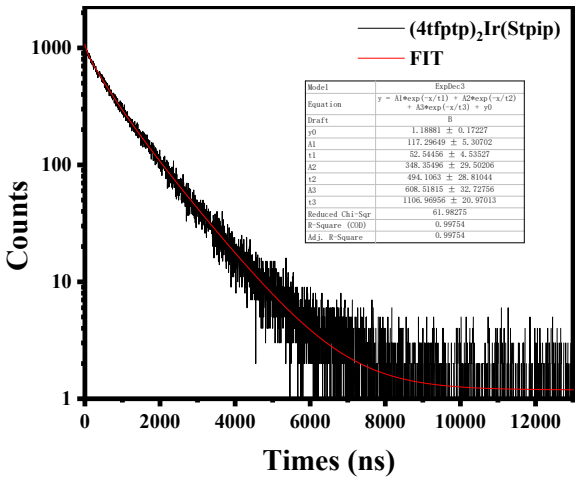

Fig. S20 The phosphorescence lifetime and fitted curves of $(4tfptp)_2Ir(Stpip)$ in co-doped film (5 wt% in 2,6DCzPPy).

S7. Electrochemical measurement

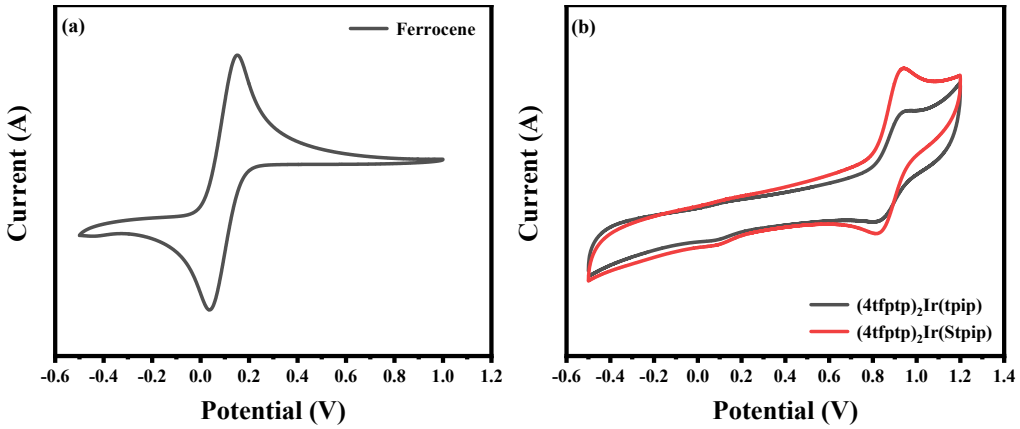

Fig. S21 CV curves: (a) Fc and (b) two Ir(III) complexes in deaerated CH_3CN solutions (10^{-5} M).

S8. Device electroluminescence spectra

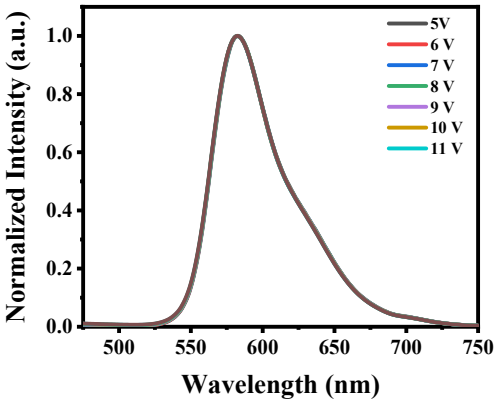

Fig. S22 EL spectra of D1 taken at various voltages from 5 to 11 V.

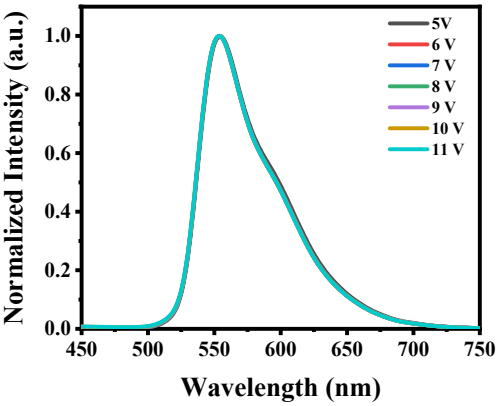

Fig. S23 EL spectra of D2 taken at various voltages from 5 to 11 V.

S9. IR spectra

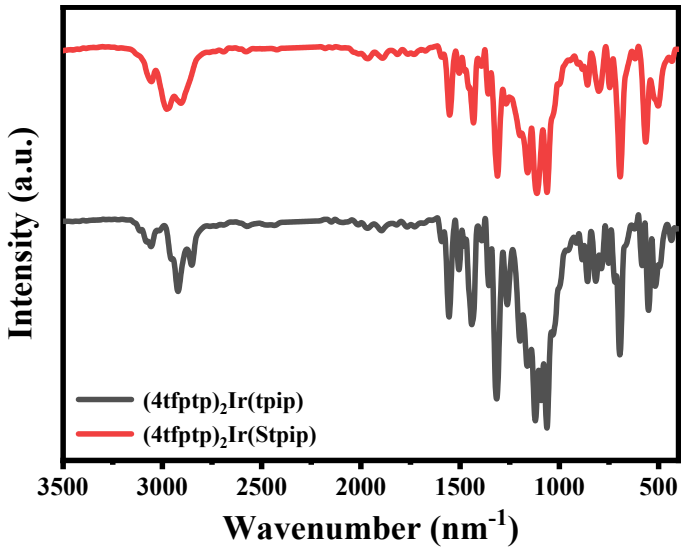

Fig. S24 IR spectra of $(4tfptp)_2Ir(tpip)$ and $(4tfptp)_2Ir(Stpip)$.