

Supporting Information

**Efficient 1-(thiophen-2-yl)isoquinoline-based ionic
iridophosphors with bulky counterion for solution-processed
deep-red electroluminescence**

Peng Tao,^{*a,b} Xiao-Kang Zheng,^a He Jiang,^a Xinghao Sheng,^a Yongjing
Deng,^c Yuk Yin Ian Chan,^a Qiang Zhao,^{*c} and Wai-Yeung Wong^{*a,b}

^a Department of Applied Biology and Chemical Technology and Research
Institute for Smart Energy, The Hong Kong Polytechnic University, Hung Hom,
Hong Kong, China.

^b The Hong Kong Polytechnic University Shenzhen Research Institute,
Shenzhen 518057, China.

^c State Key Laboratory of Organic Electronics and Information Displays,
Institute of Advanced Materials (IAM) & Institute of Flexible Electronics
(Future Technology), Nanjing University of Posts and Telecommunications,
Nanjing 210023, China.

Corresponding E-mails: pengtao@polyu.edu.hk (P. Tao);

iamqzhao@njupt.edu.cn (Q. Zhao); wai-yeung.wong@polyu.edu.hk (W.-Y.
Wong)

1. General Experimental Information

All operations were performed under an inert nitrogen atmosphere using standard Schlenk unless otherwise stated. All solvents were used after distillation and stored over activated molecular sieves (5 Å). All reagents and chemicals were purchased from commercial sources and used without further purification. The NMR spectra were recorded with a Bruker spectrometer at ambient temperature. Mass spectra were obtained on SHIMADZU matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MASS). The UV-vis absorption spectrum was recorded on an Agilent Cary UV-4000 spectrometer. Steady-state emission experiments at room temperature or 77 K were measured on an Edinburgh LFS-920 spectrometer. Excited-state lifetime studies were performed with an Edinburgh LFS-920 spectrometer with a hydrogen-filled excitation source. The data were analyzed by a software package provided by Edinburgh Instruments. The absolute quantum yields of the complex were determined through an absolute method by employing an integrating sphere. The solution was degassed by three freeze-pump-thaw cycles. Cyclic voltammetry measurements were carried out in CH₃CN (5×10⁻⁴ M) under Ar with a three-electrode cell configuration consisting of platinum working and counter electrodes and a Ag/AgCl (0.01 M in CH₃CN) reference electrode at room temperature. Tetra-*n*-butylammonium hexafluorophosphate (0.1 M in CH₃CN) was used as the supporting electrolyte. The redox potentials were recorded at a scan rate of 100 mV/s and are reported with reference to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

2. X-ray structure determination

The single crystals of **Irb** were obtained from the mixture of dichloromethane and methanol. The X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω - 2θ scan mode. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2000. All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Mercury. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference number for **Irb** is 2203809. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +441223336033; E-mail: deposit@ccdc.cam.ac.uk, or www: <http://www.ccdc.cam.ac.uk>).

3. EL Device Fabrication and Testing

The hole injection layer and light-emitting layer were prepared by the spin-coating method with the solution concentration at 10 mg mL⁻¹ and the rotation speed at 1000 rpm. Deep-red organic light-emitting diodes were fabricated with a configuration of ITO/*m*-PEDOT:PSS (70 nm)/ Bepp₂: **Ira** or **Irb** (6 wt% 40 nm)/TPBi (50 nm)/LiF (1 nm)/Al (100 nm). The ITO substrates were degassed in acetone, ethanol, and deionized water consecutively in an ultrasonic bath before UV-ozone treatment for 10 min. A layer of 70 nm thick *m*-PEDOT:PSS was spin-coated onto the ITO substrate and then baked at 120 °C for 10 min. Another baking at 120 °C for 10 min was conducted before spin-coating the emitting layer. Next, a 50 nm thick TPBi, acting as the electron transport layer, was deposited on the EML. After the evaporation of the composite LiF/Al cathode, all the devices were encapsulated with UV-curable resin. The current-voltage-luminance characteristics and the EL spectra were measured simultaneously by a customized software controlling a PR655 spectrascan spectrometer and a Keithley 2400 source measurement unit.

Table S1. Photophysical properties for **Ira** and **Irb** in CH₂Cl₂.

Complex	Absorption ^{a)}	Emission ^{b)}
	λ_{abs} [nm]	λ_{em} [nm]
Ira	225, 306, 347, 390, 480	630, 688 (sh)
Irb	225, 306, 347, 390, 480	630, 688 (sh)

^{a)}At 1.0×10^{-5} mol/L in CH₂Cl₂ at 298 K; ^{b)} At a concentration of 1.0×10^{-5} mol/L in CH₂Cl₂ at 77 K, sh refers to the shoulder emission, $\lambda_{\text{ex}} = 400$ nm.

Table S2. Photophysical properties for **Ira** and **Irb** in neat film.

Complex	λ_{em}^a [nm]	FWHM [nm]	τ^b [μs]	PLQY
Ira	641, 697 (sh)	119	$\tau_1 = 0.12$ (6%), $\tau_2 = 0.56$ (94%)	0.27
Irb	631, 685 (sh)	101	$\tau_1 = 0.31$ (19%), $\tau_2 = 0.85$ (81%)	0.34

^{a)} $\lambda_{ex} = 365$ nm, sh refers to the shoulder emission; ^{b)} $\lambda_{ex} = 375$ nm

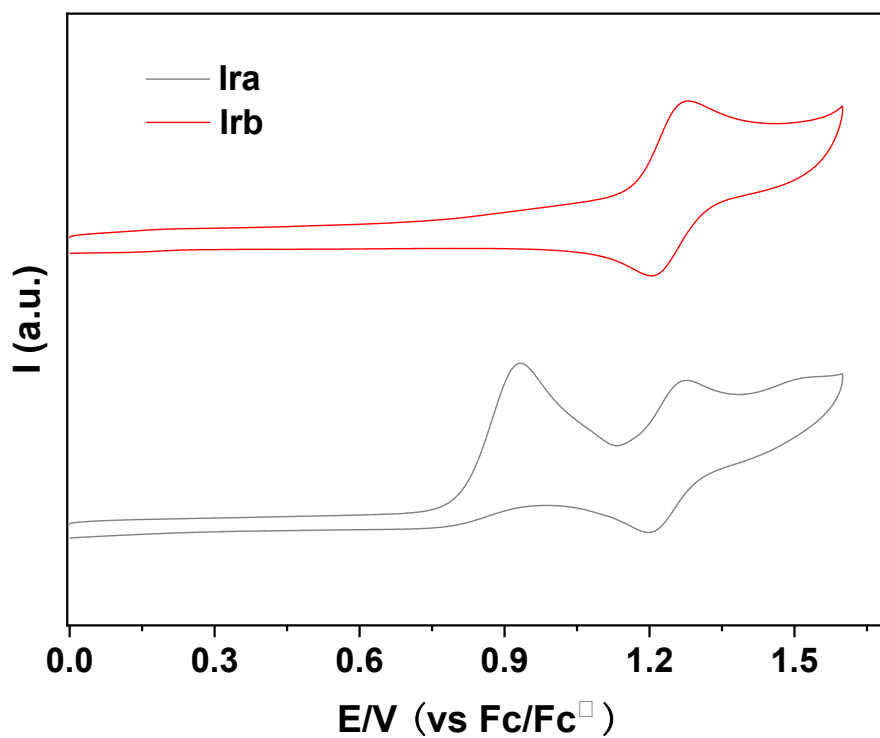


Figure S1. Cyclic voltammograms of **Ira** and **Irb** under a scan rate of 100 mV/s in CH_3CN under Ar.

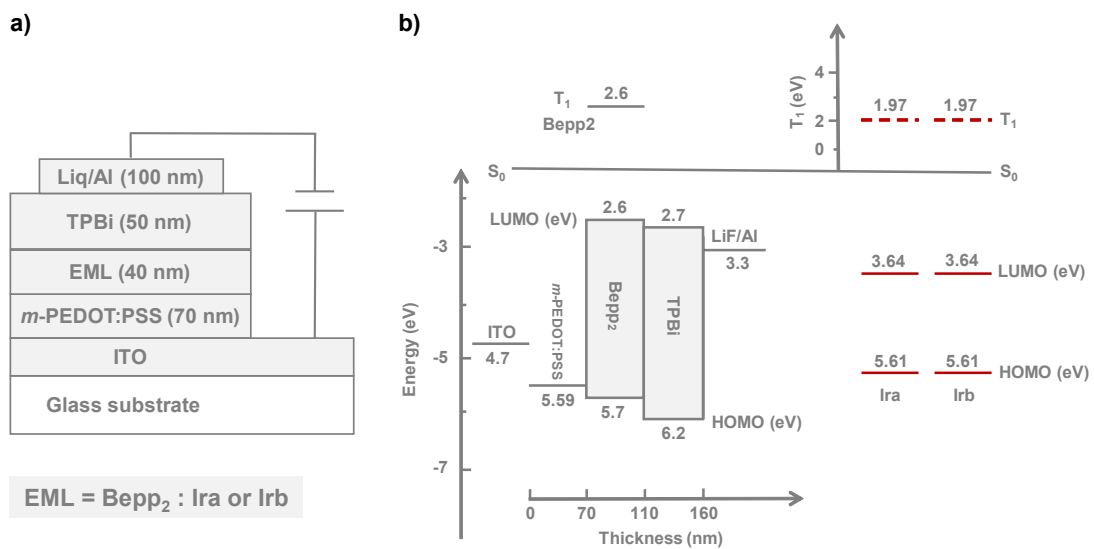


Figure S2. a) Device structures and b) schematic diagram of the energy levels of the deep-red devices.

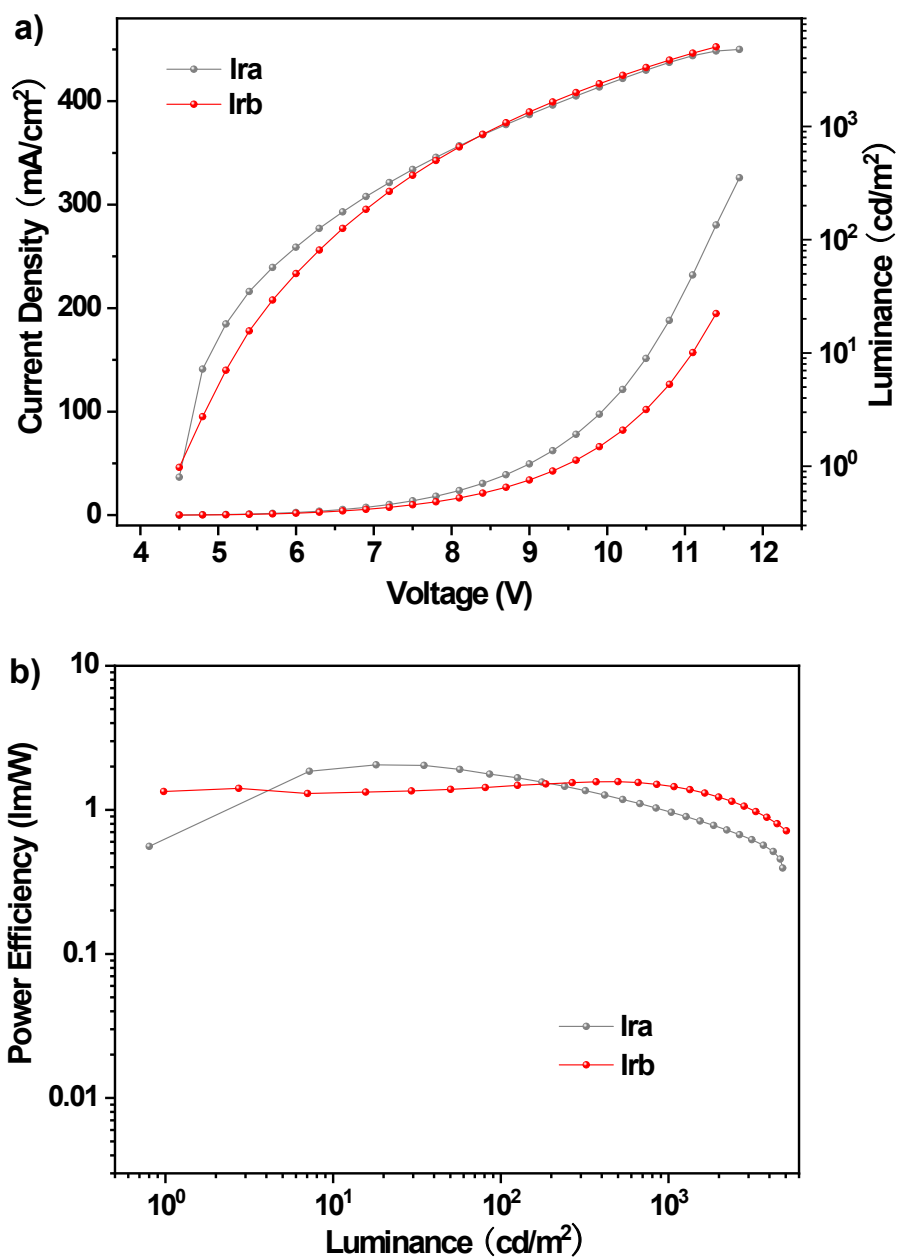


Figure S3. a) J-V-L curves and b) PE-L-EQE curves of the devices based on Ira and Irb.

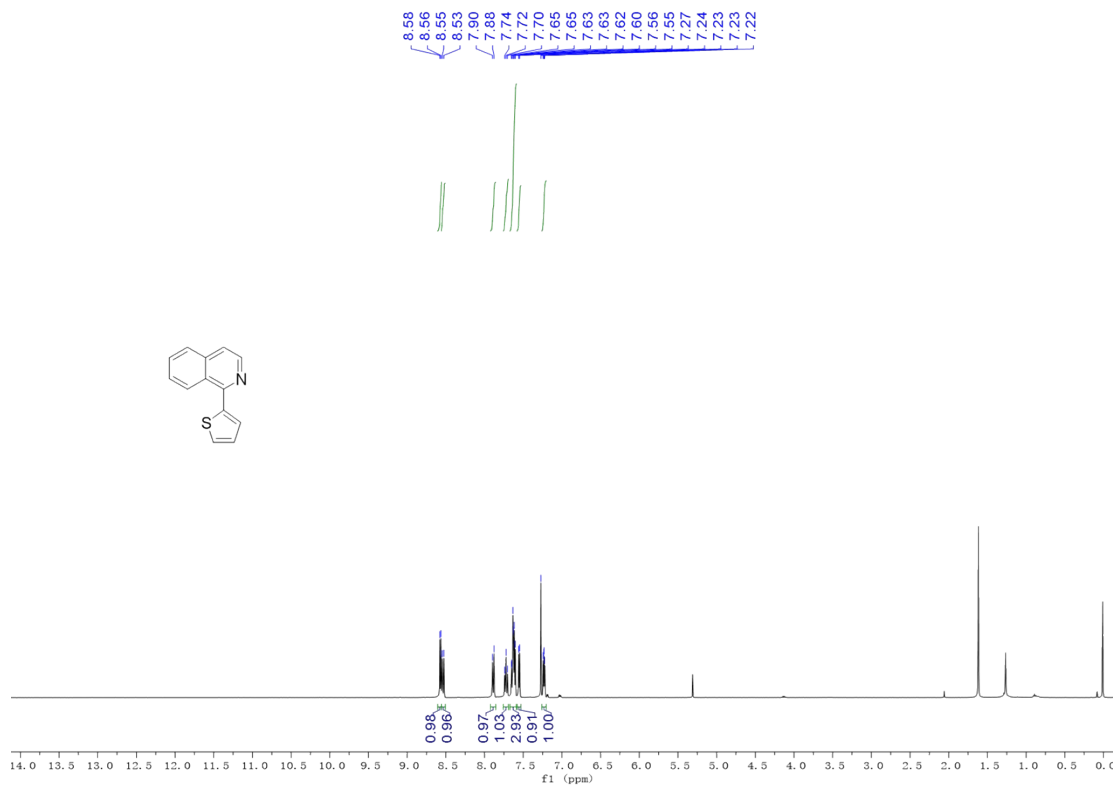


Figure S1. The ¹H NMR spectrum of 1-(thiophen-2-yl)isoquinoline.

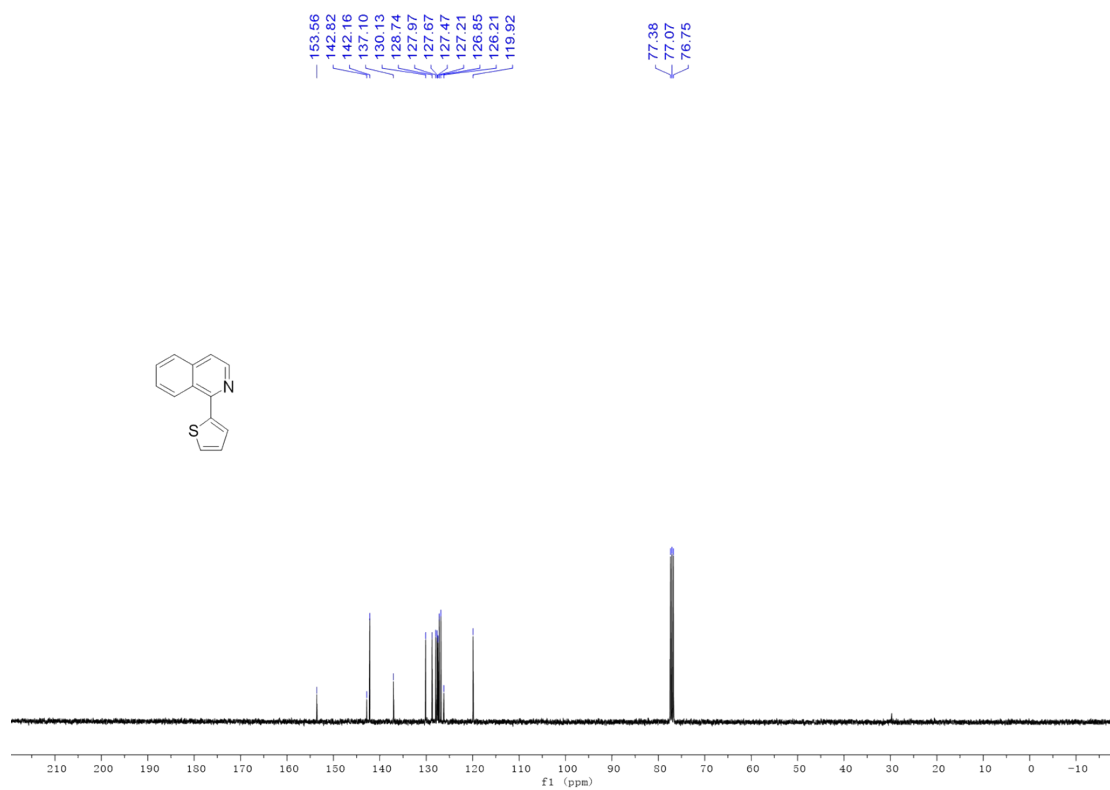


Figure S2. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-(thiophen-2-yl)isoquinoline.

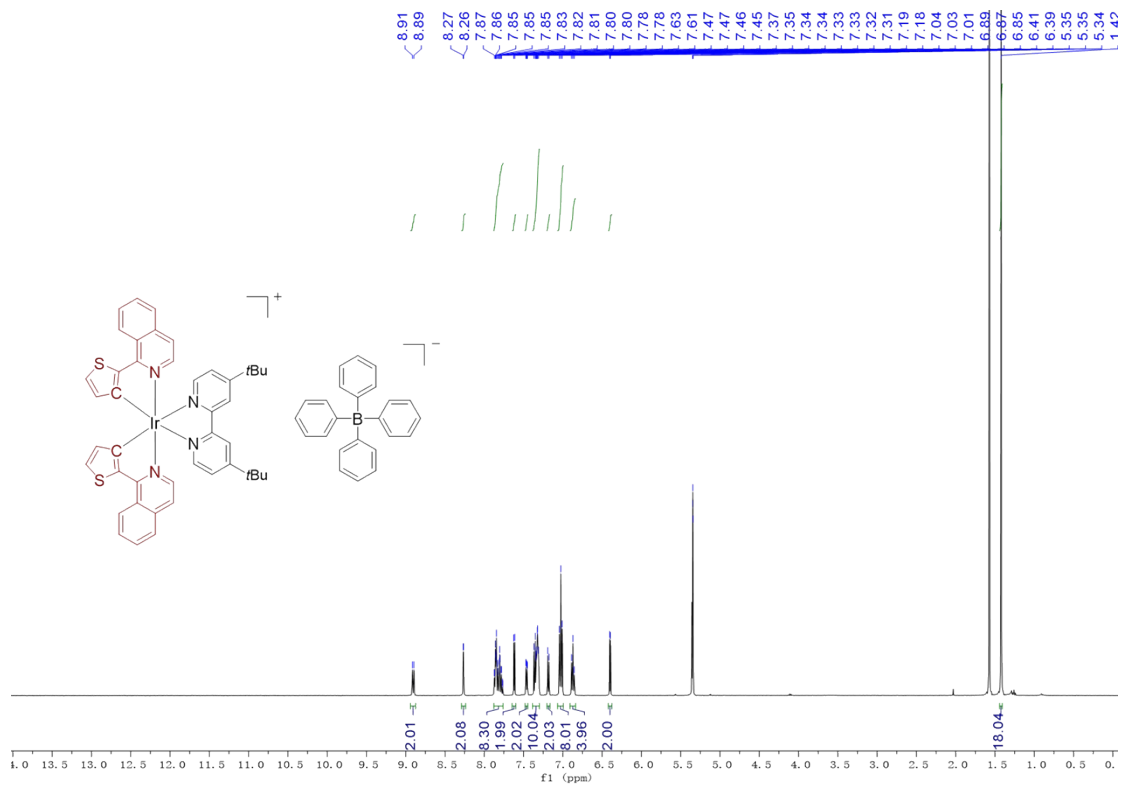


Figure S3. The 1H NMR spectrum of **Ira**.

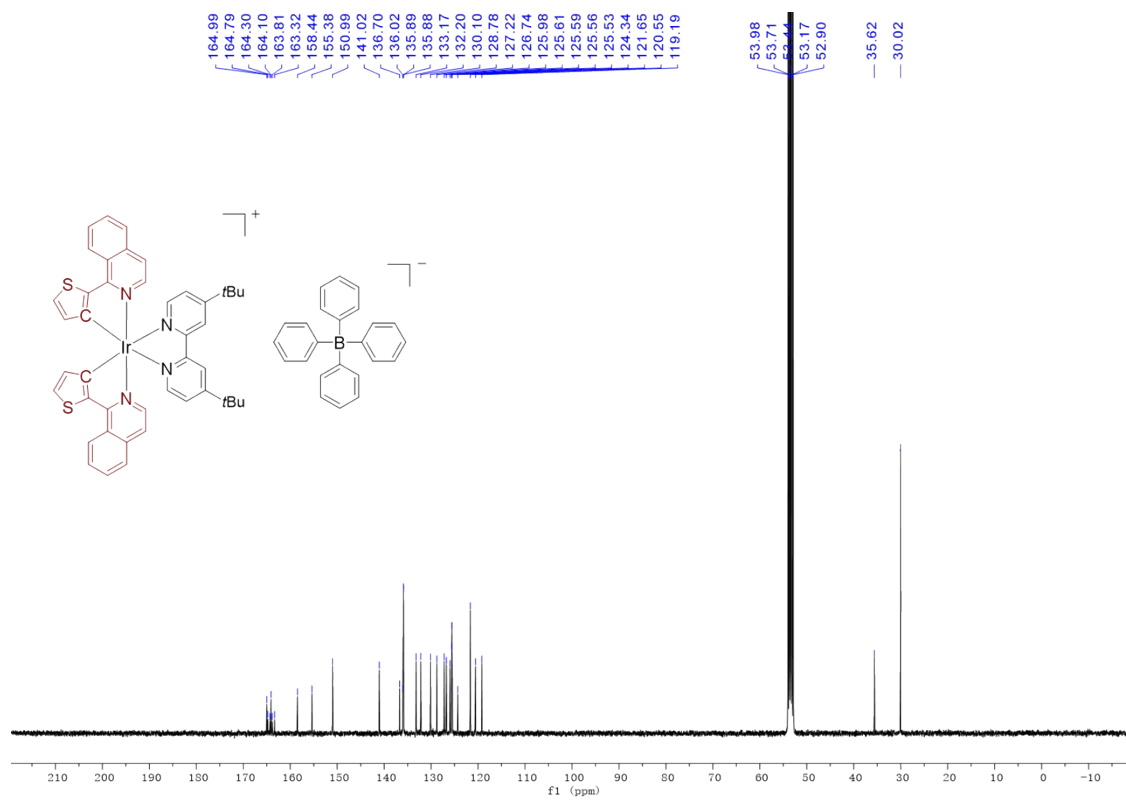


Figure S3. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Irb**.

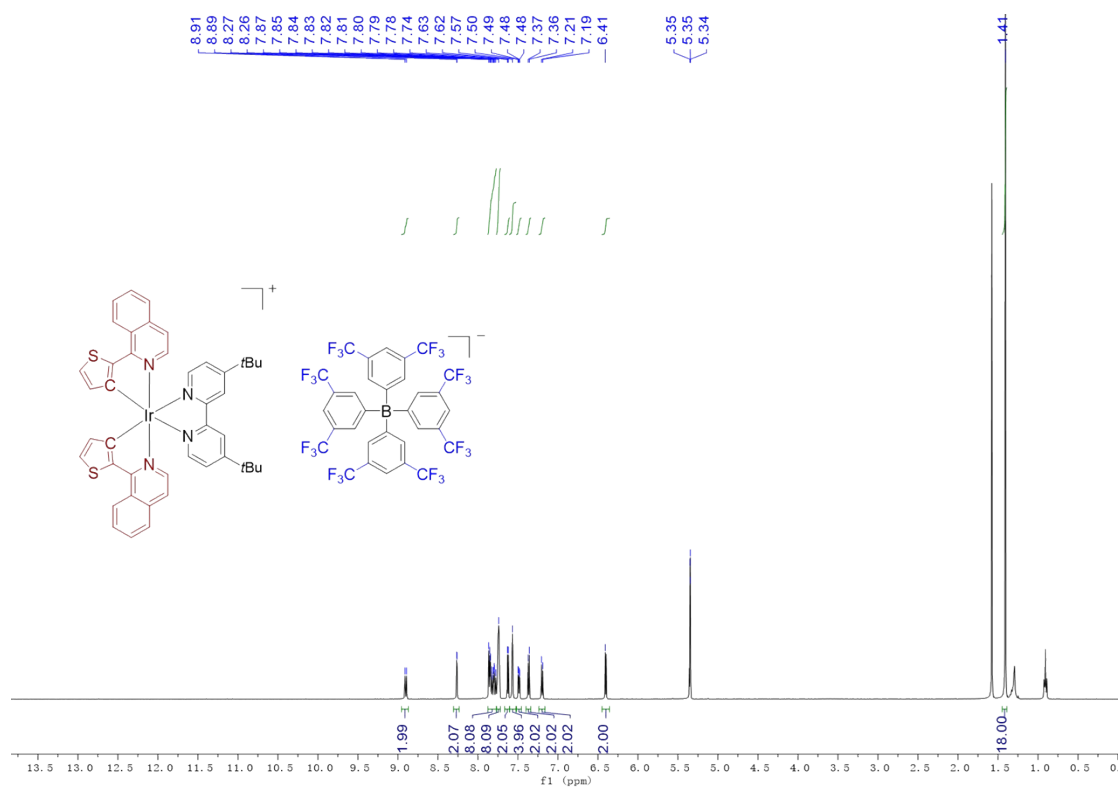


Figure S5. The ¹H NMR spectrum of **Irb**.

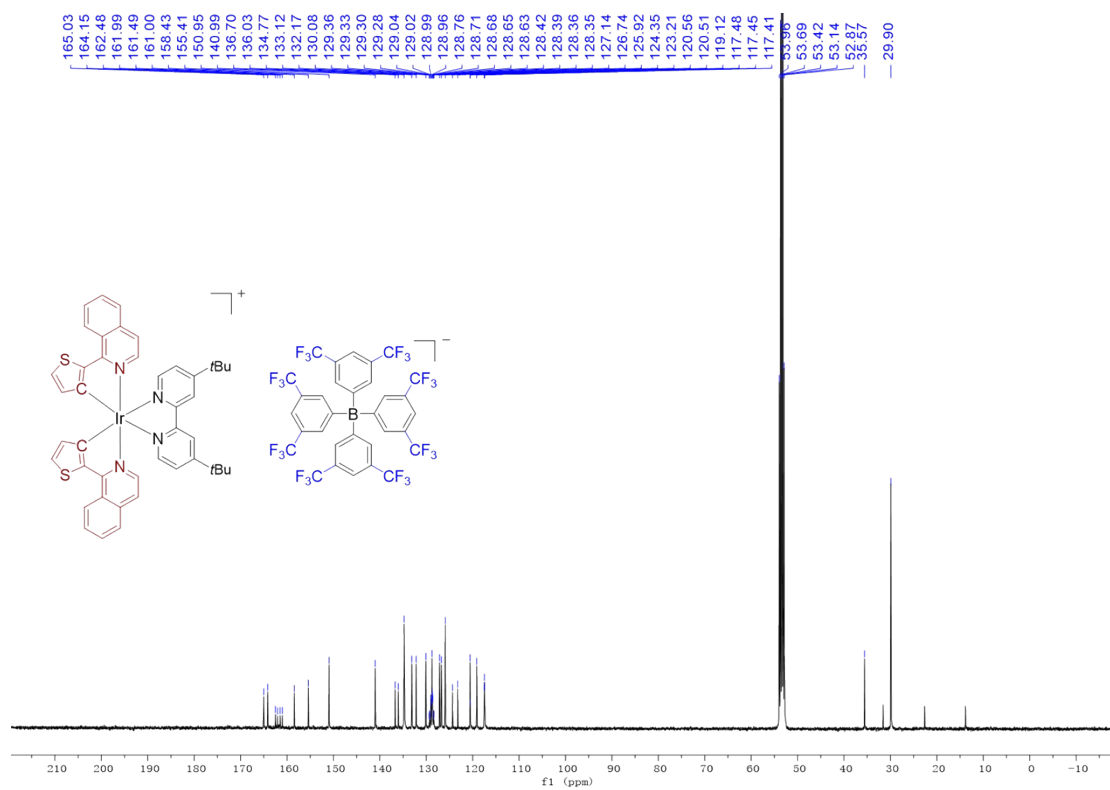


Figure S6. The $^{13}C\{^1H\}$ NMR spectrum of *Irb*.

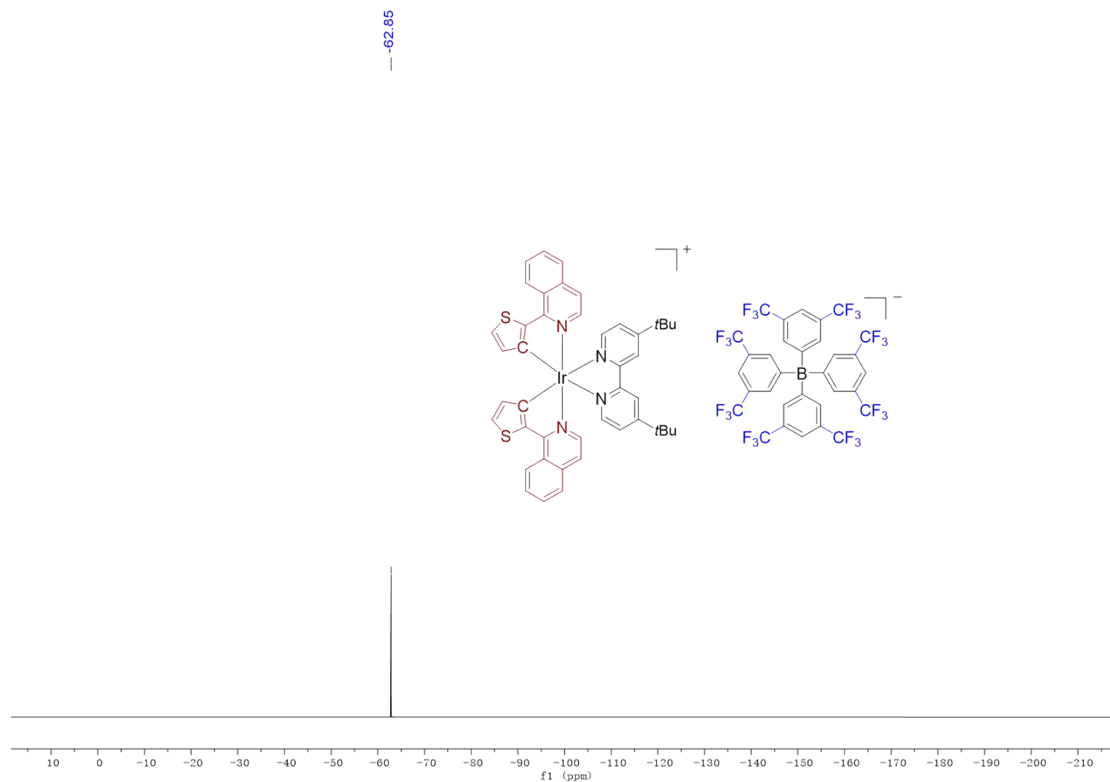


Figure S7. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **1rb**.

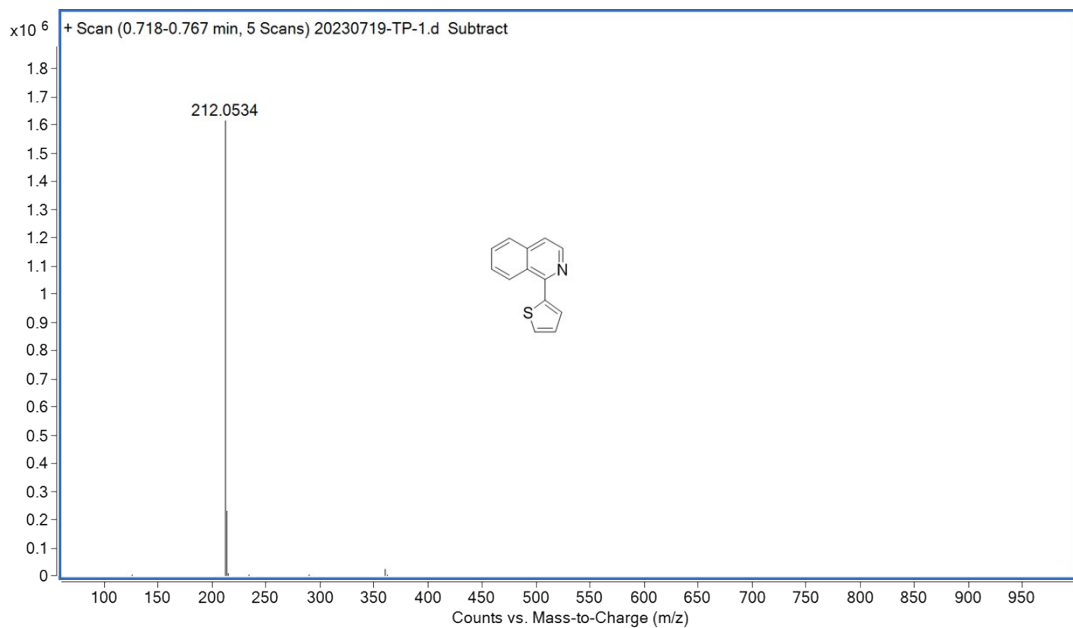


Figure S8. The ESI HR mass spectrum of 1-(thiophen-2-yl)isoquinoline.

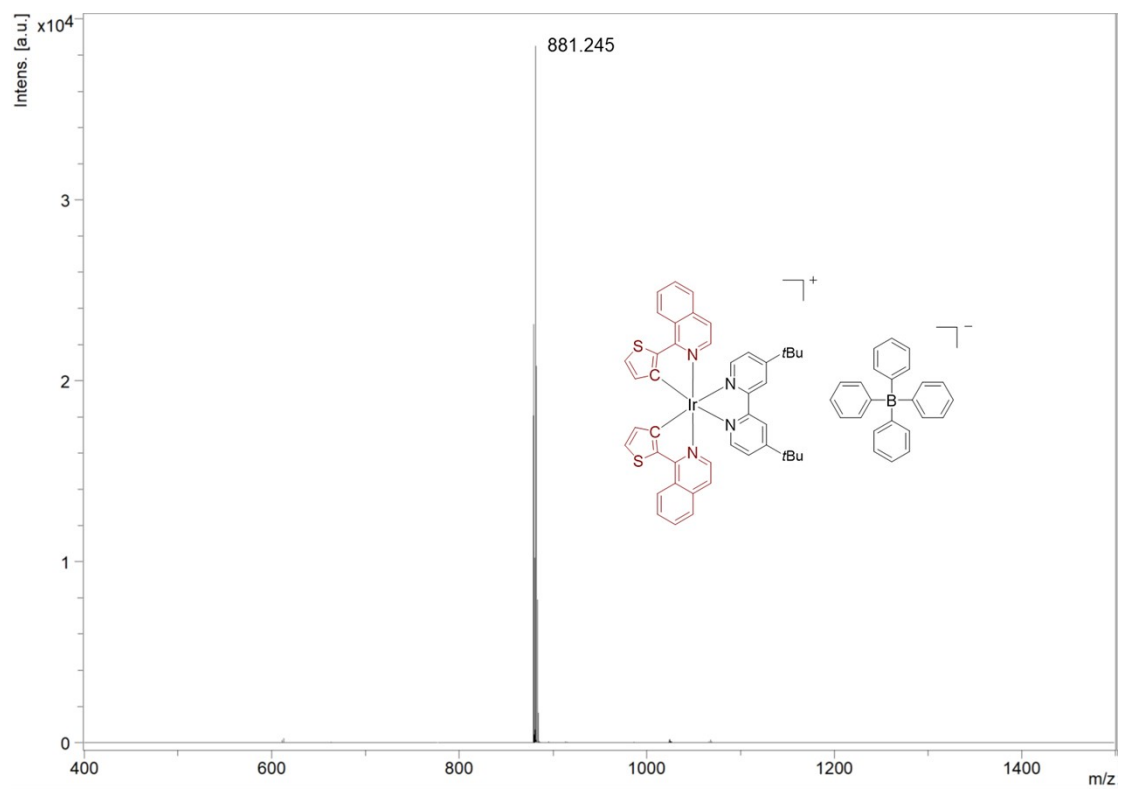


Figure S9. The MALDI-TOF mass spectrum of **Ira**.

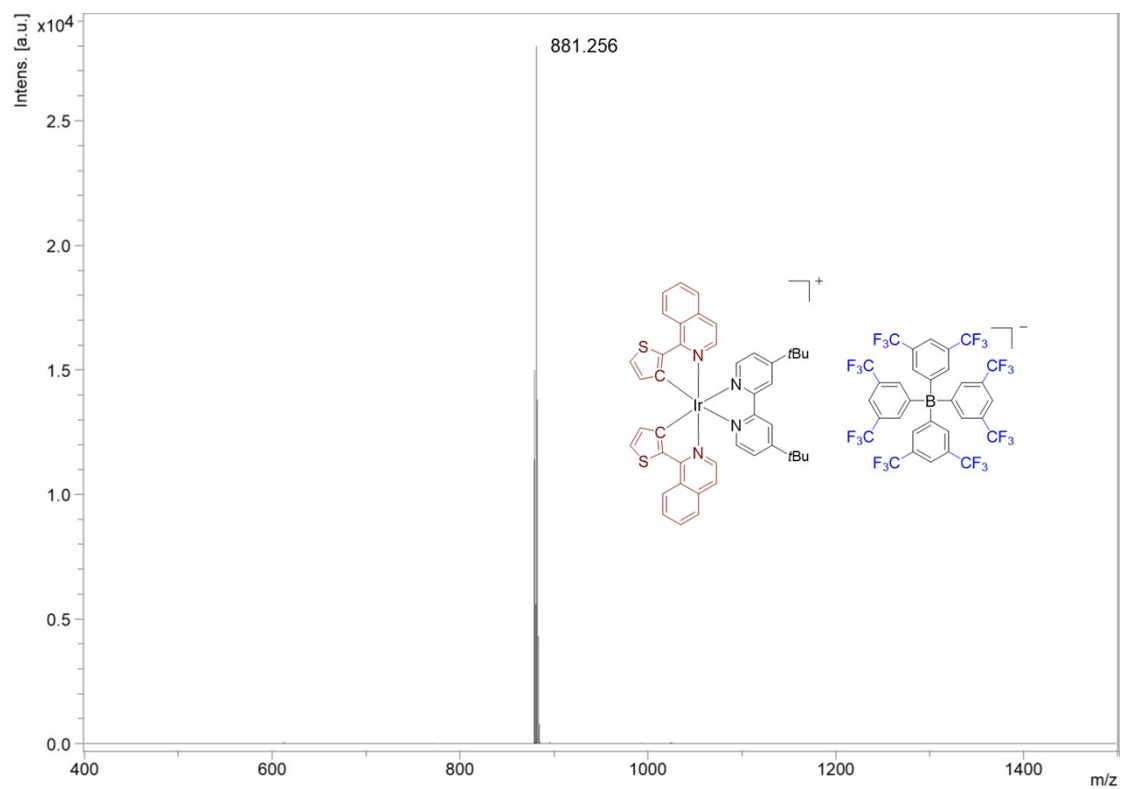


Figure S10. The MALDI-TOF mass spectrum of **Irb**.