Supplementary Information for

A simple and efficient approach toward deep-red to near-infrared-emitting iridium(III) complexes for organic light-emitting diodes with external quantum efficiencies of over 10%

Zhao Chen*, Hongyang Zhang, Dawei Wen, Wenhai Wu, Qingguang Zeng, Shuming Chen* and Wai-Yeung Wong*

Dr. Z. Chen, Dr. D. Wen, W. Wu, Prof. Q. Zeng
School of Applied Physics and Materials, Wuyi University, Jiangmen, 529020, P. R. China
E-mail: chenzhao2006@163.com
Dr. H. Zhang and Prof. W.-Y. Wong
Department of Applied Biology and Chemical Technology, the Hong Kong Polytechnic University, Hung Hom, Hong Kong, P. R. China; The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen, 518057, P. R. China
E-mail: wai-yeung.wong@polyu.edu.hk
Dr. S. Chen
Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen, 518055, P. R. China
E-mail: chen.sm@sustc.edu.cn

Instrument: ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ solvent at room temperature on a Bruker Avance 400 MHz spectrometer by using tetramethyl silane (TMS) signal as internal standards. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) was conducted on a Bruker Autoflex to obtain the mass spectra for **CNIr** and **TCNIr**. By using the operation mode of the positive ion mode, the Thermo Scientific Q Exactive HF Orbitrap-FTMS was used to record the electrospray ionization (ESI) mass spectrometry for the ligands (**L1** and **L2**). The UV-vis spectra were obtained on a HP-8453 diode array spectrophotometer at room temperature. During the absorption measurement, a quartz cuvette with the length of 1 cm was used as the holder. The concentration of phosphor was around 10^{-4} M in tetrahydrofuran (THF) solution. The steady- and transient-state PL spectra at room temperature or 77 K were recorded from an Edinburgh Instruments Spectrometer FS5. The THF solutions consisting of phosphors (10^{-5} to 10^{-4} M) and thin films fabricated by doping these phosphors into CBP were used to obtain the PL spectra, absolute PLQYs and lifetimes of excited states. Meanwhile, the absolute PLQYs were measured on a Hamamatsu Quantaurus-QY Plus C13534-12 by using the excitation at 450 nm for solutions and 300 nm for the doped films. The PLQY values were calculated by using equation (1):

$$PLQY = \frac{Number\ of\ photons\ emitted\ from\ the\ sample}{Number\ of\ photons\ absorbed\ by\ the\ sample} \quad (1).$$

During the time-resolved fluorescence measurements, a laser at 375 nm was used as an excitation source. The PL decay curves at room temperature and 77 K were fitted by using a single-exponential function $I(t) = A\exp(-t/\tau)$, where $I(t)$ is the intensity of light at time t, t is the time and τ is the luminescence lifetime of the species. Electrochemical measurements were made by using a Princeton Applied Research model 273 A potentiostat as a scan rate of 100 mV s^{-1}. A conventional three-electrode configuration consisting of a glassy carbon (working electrode), platinum wire (counter electrode) and Ag/AgCl in saturated potassium chloride solution (reference electrode) was used. The supporting electrolyte was 0.1 M $[Bu_4N]PF_6$ in dichloromethane. Ferrocene was used as a calibrant during each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium (Fc/Fc^+) couple (taken as $E_{1/2}$ = +0.27 V relative to the reference electrode). The oxidation (E_{ox}) potentials were used to determine the HOMO energy levels by using the equation $E_{HOMO} = -(E_{ox} + 4.8)$, in which –4.8 eV is the HOMO of the internal standard ferrocene with respect to the vacuum level.[1] Meanwhile, the LUMO energy levels of phosphors were estimated by using the equation $E_{LUMO} = E_{HOMO} + E_g$, where E_g is the band gaps of the phosphors and estimated from the absorption edge of UV-visible spectra. Thermal analyses were performed with Perkin-Elmer TGA thermal analyzer with a heating rate of 10 °C/min in the region from room temperature (25 °C) to 800 °C. For DFT calculations, the structures of these Ir(III) complexes were optimized by using density functional theory (DFT) with the PBE0 functional and 6-31G(d)/LanL2DZ basis set. The LanL2DZ basis set was used to treat the iridium atom and the 6-31G(d) basis set was used to treat all other atoms. All the calculations were performed using Gaussian 09 software package.[2]

Device fabrication and measurement: By using the architecture of ITO/HATCN (20 nm)/TAPC (40 nm)/mCP (5 nm)/x wt% **CNIr** or **TCNIr** doped in host materials (30 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100), the devices were fabricated by depositing these functional materials layer-by-layer on pre-cleaned ITO glass substrates at a pressure of less than 10^{-6} Torr. The concentrations of emitters were 5-20% and TcTa, TPBi, CBP and CDBP were used as the host materials. The sublimation rates for organics, LiF and Al were around 1, 0.3 and 10 Å/s. The active area of device was 2 mm × 2 mm. The EL spectra of devices were measured by fiber optic spectrometer (Ocean Optics USB 2000) in the normal direction. The J–V–L curves were investigated by a dual-channel Keithley 2614B source measure unit and a PIN-25D silicon photodiode. A PR-670 spectrometer (Photo Research) was used to record the EL spectra of **D7** at different applied voltages. All the measurements were conducted at room temperature under ambient condition.

References:

[1] R. S. Ashraf, M. Shahid, E. Klemm, M. Al-Ibrahim, S. Sensfuss, *Macromol. Rapid Comm.,* 2006, **27**, 1454

[2] Z. Chen, L. Wang, C.-L. Ho, S. Chen, S. Suramitr, A. Plucksacholatarn, N. Zhu, S. Hannongbua, W.-Y. Wong, *Adv. Optical Mater.*, 2018, **6**, 1800824.

Figures:

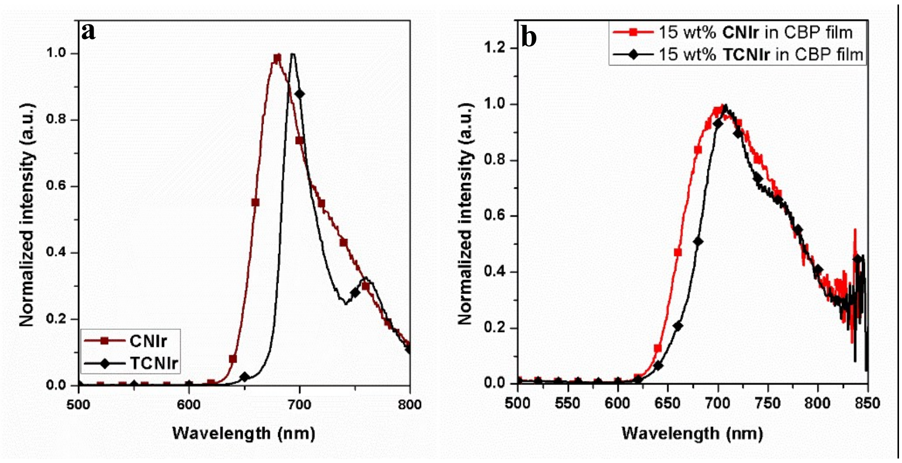


Figure S1. The photoluminescence spectra of **CNIr** and **TCNIr**: a) measured at 77 K in tetrahydrofuran solution, b) measured at room temperature in their doped films.

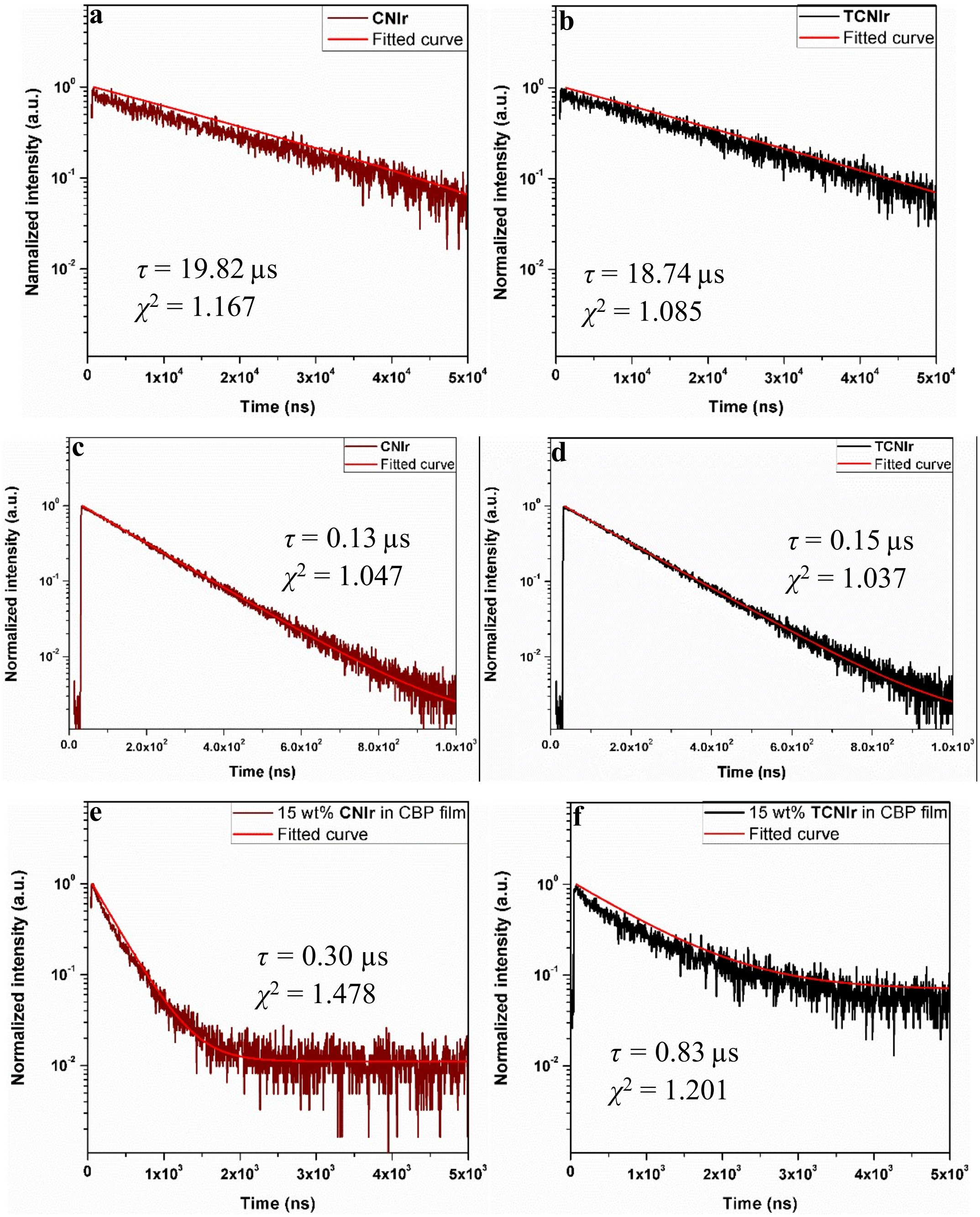


Figure S2. The photoluminescence decay curves of excited states for **CNIr** and **TCNIr**: a) and b) measured at 77 K in tetrahydrofuran solution, c) and d) measured at room temperature in tetrahydrofuran solution, e) and f) measured at room temperature in their doped films.

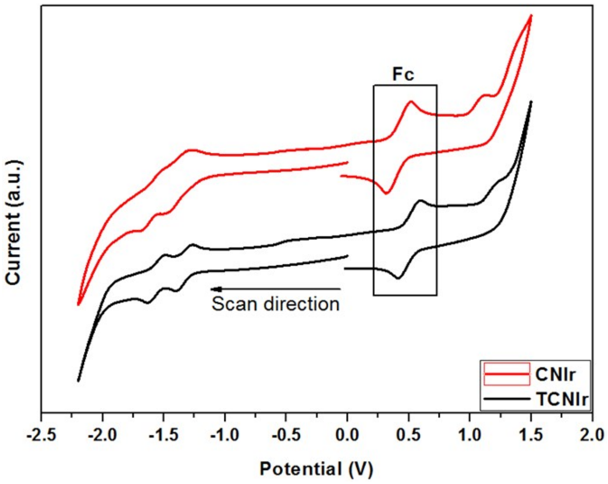


Figure S3. Cyclic voltammetry (CV) curves of the **CNIr** and **TCNIr** by referring to the standard ferrocene (Fc).

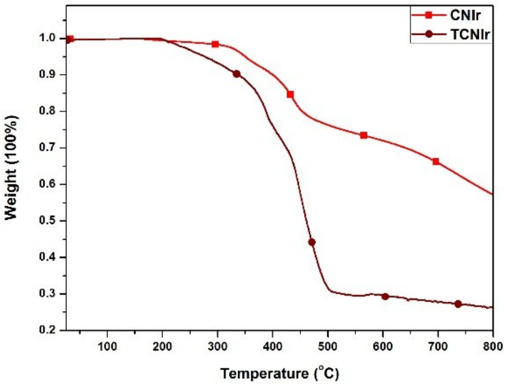


Figure S4. Thermogravimetric analysis (TGA) curves of the NIR-emitting **CNIr** and **TCNIr**.

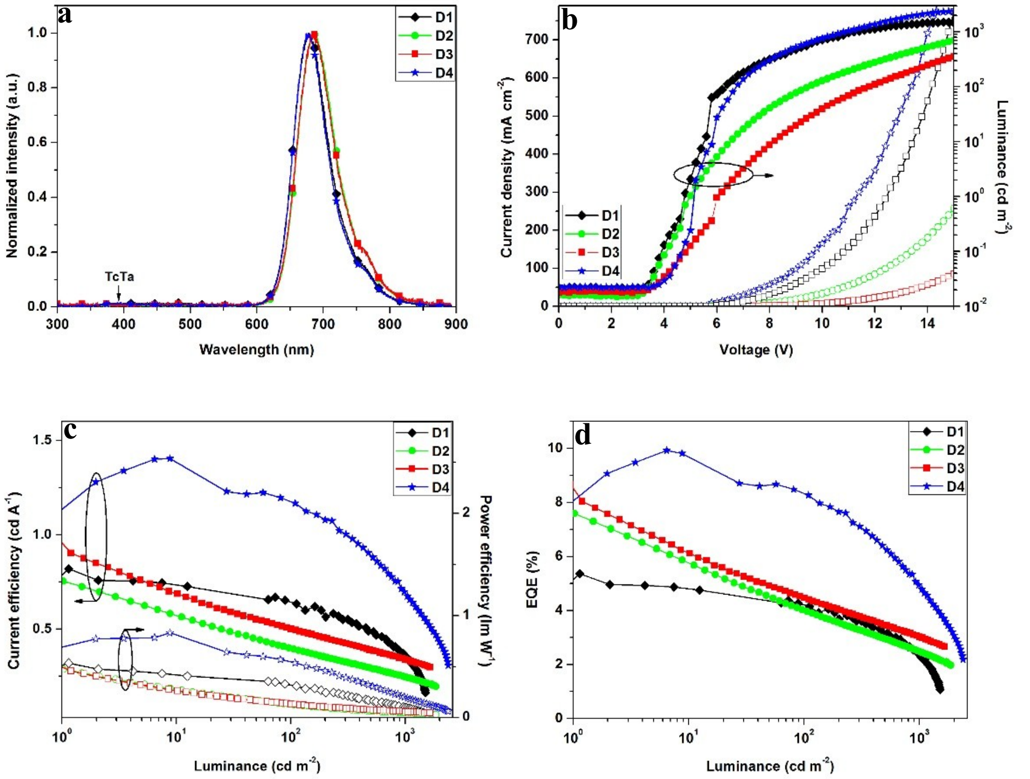


Figure S5. The performance of **D1−D4**: a) electroluminescence spectra; b) current density-voltage-luminance (*J*-*V*-*L*) curves; c) current efficiency (CE) and power efficiency (PE) *vs* *L* curves and d) EQE *vs* *L* curves.

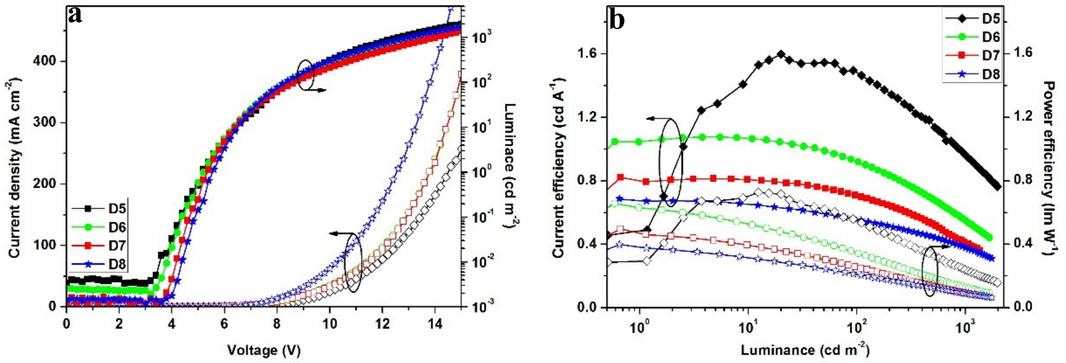


Figure S6. The *J*-*V*-*L* currves a) and CE/PE *vs* *L* curves b) of **D5−D8**.

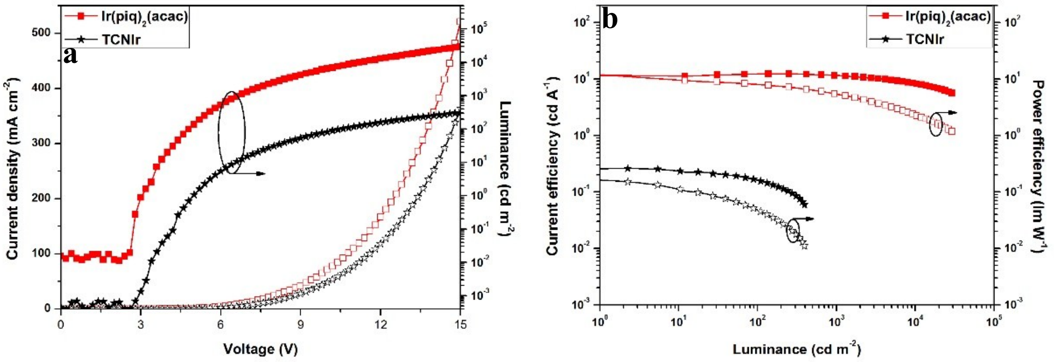


Figure S7. The *J*-*V*-*L* currves a) and CE/PE *vs* *L* curves b) of **D9** (made by **TCNIr**) and **D10** (made by **Ir(piq)$_2$(acac)**).

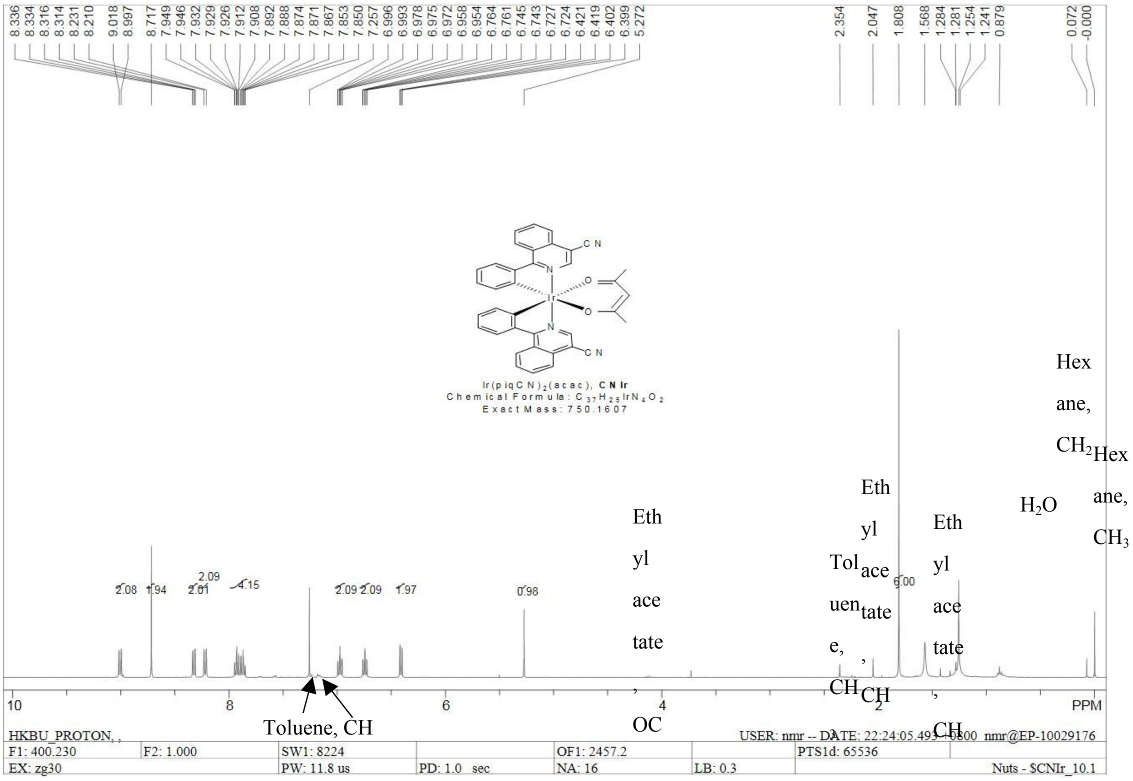


Figure S8. The ^{1}H NMR spectrum of **CNIr**.

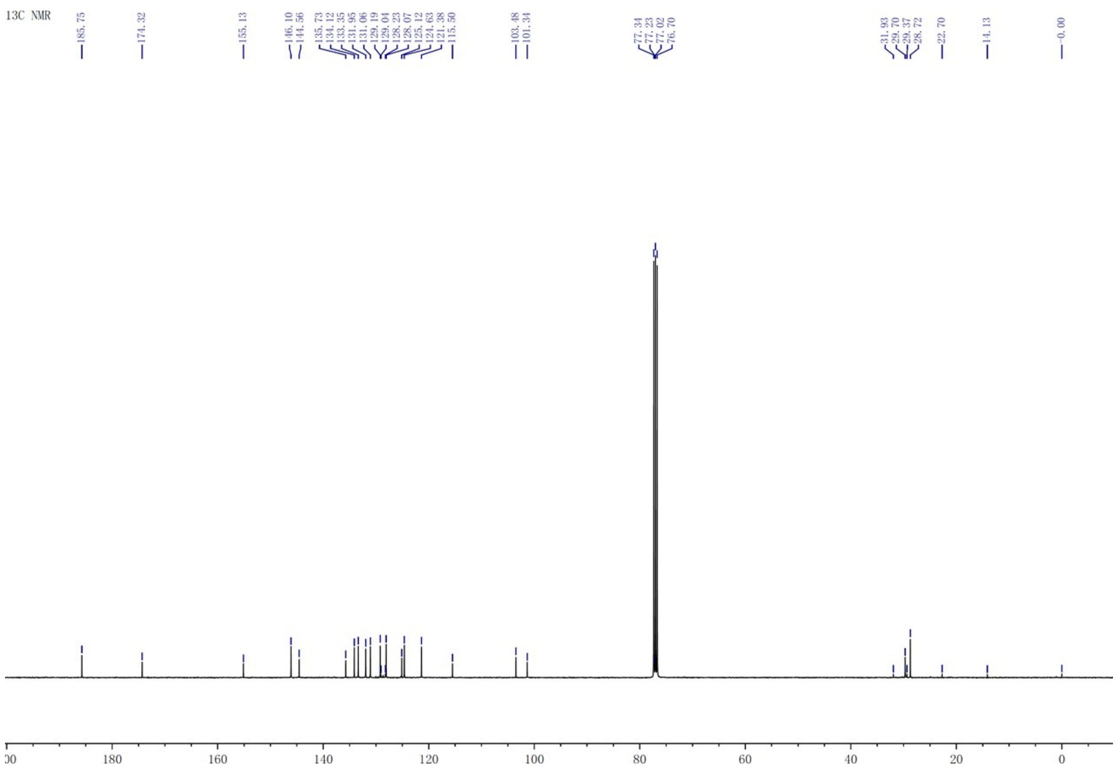
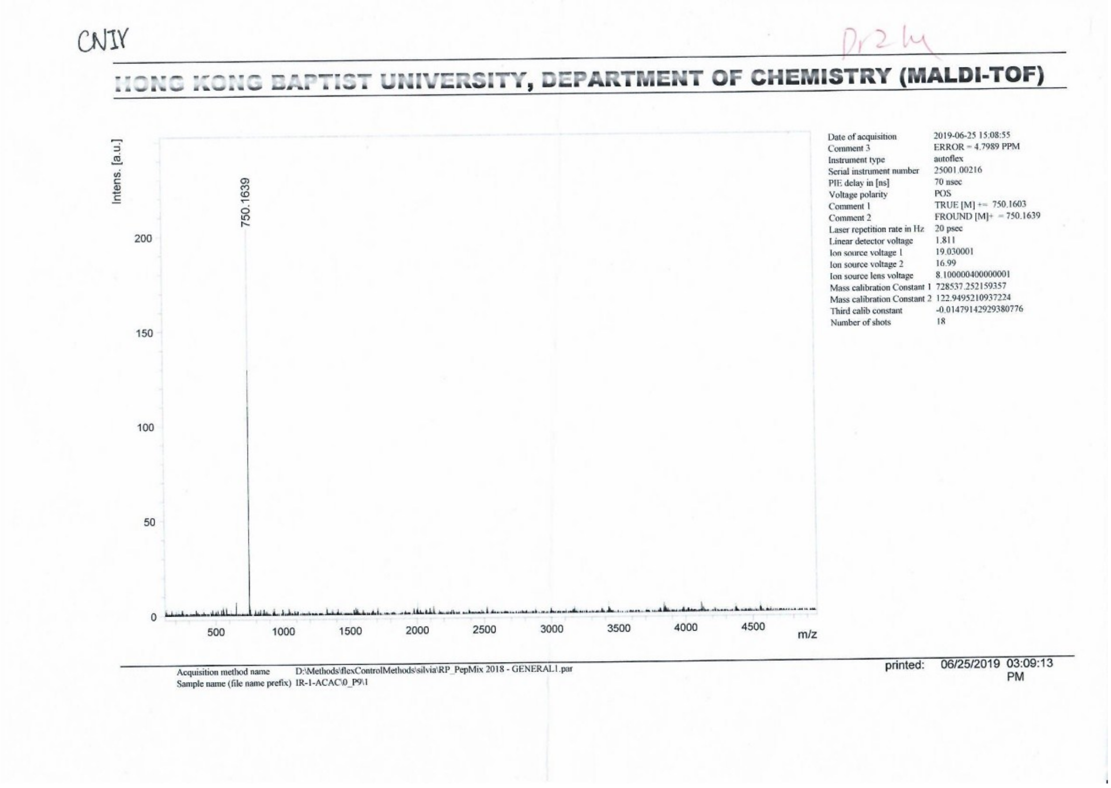


Figure S9. The ^{13}C NMR spectrum of **CNIr**.



CNIr

Dr2h

HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

Date of acquisition	2019-06-25 15:08:55
Comment 3	ERROR = 4.7989 PPM
Instrument type	autoflex
Serial instrument number	25001.00216
PIE delay in [ns]	70 nsec
Voltage polarity	POS
Comment 1	TRUE [M] += 750.1603
Comment 2	FROUND [M]+ = 750.1639
Laser repetition rate in Hz	20 psec
Linear detector voltage	1.811
Ion source voltage 1	19.030001
Ion source voltage 2	16.99
Ion source lens voltage	8.100000400000001
Mass calibration Constant 1	728537.252159357
Mass calibration Constant 2	122.9495210937224
Third calib constant	-0.01479142929380776
Number of shots	18

Acquisition method name	D:\Methods\flexControlMethods\silvia\RP_PepMix 2018 - GENERAL1.par
Sample name (file name prefix)	IR-1-ACAC\0_P9\1

printed: 06/25/2019 03:09:13 PM

Figure S10. The mass spectrum of **CNIr**.

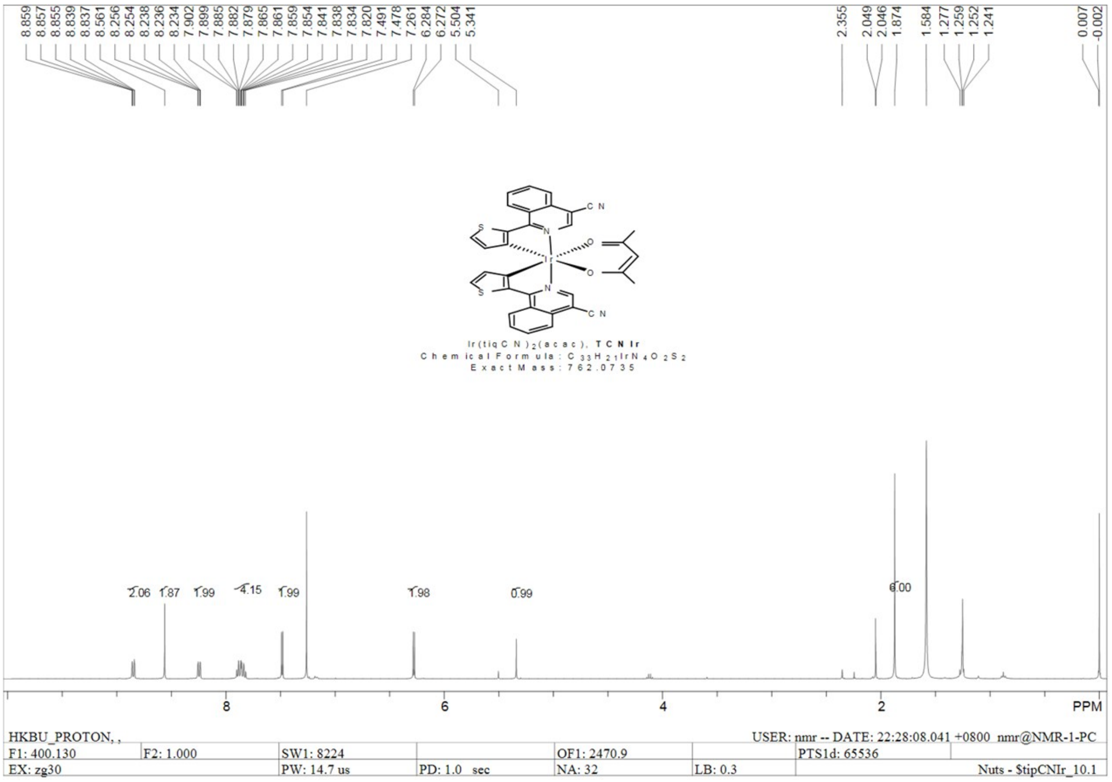


Figure S11. The ^{1}H NMR spectrum of **TCNIr**.

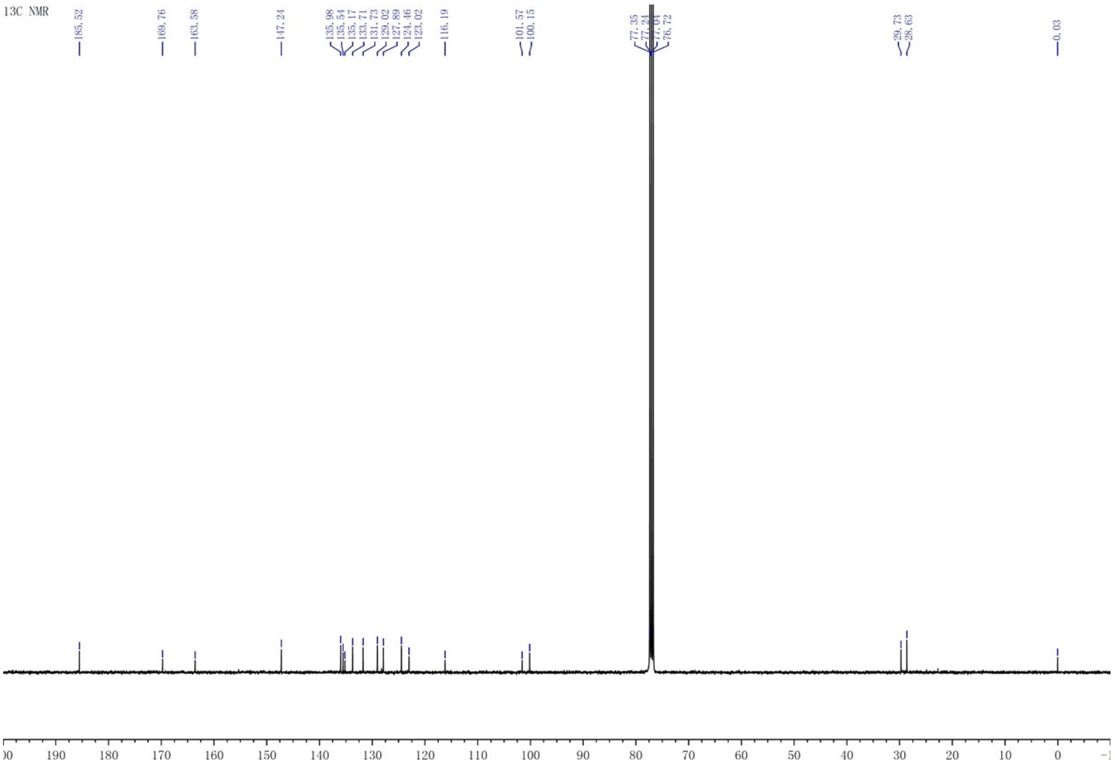
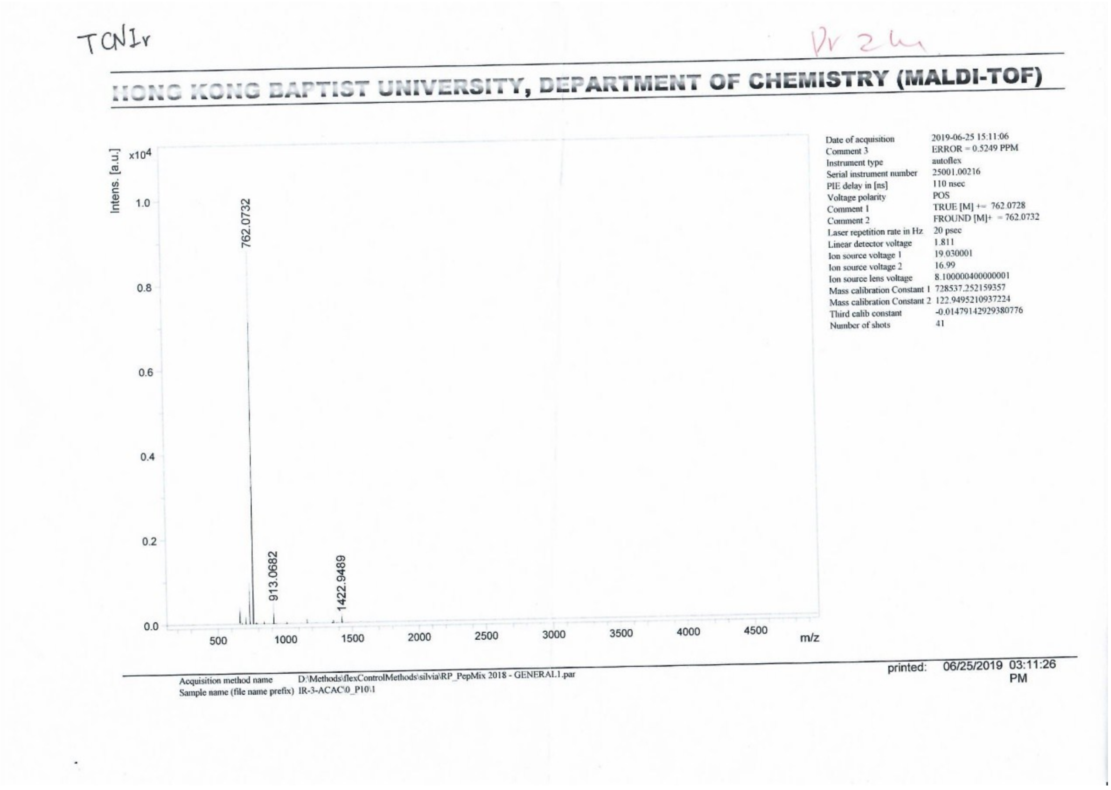


Figure S12. The ^{13}C NMR spectrum of **TCNIr**.



TCNIr

Dr Zhu

HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

Date of acquisition	2019-06-25 15:11:06
Comment 3	ERROR = 0.5249 PPM
Instrument type	autoflex
Serial instrument number	25001.00216
PIE delay in [ns]	110 nsec
Voltage polarity	POS
Comment 1	TRUE [M] += 762.0728
Comment 2	FROUND [M]+ = 762.0732
Laser repetition rate in Hz	20 psec
Linear detector voltage	1.811
Ion source voltage 1	19.030001
Ion source voltage 2	16.99
Ion source lens voltage	8.100000400000001
Mass calibration Constant 1	728537.252159357
Mass calibration Constant 2	122.9495210937224
Third calib constant	-0.01479142929380776
Number of shots	41

Acquisition method name D:\Methods\flexControlMethods\silvia\RP_PepMix 2018 - GENERAL1.par
Sample name (file name prefix) IR-3-ACAC\0_P10\1

printed: 06/25/2019 03:11:26 PM

Figure S13. The mass spectrum of **TCNIr**.