

## Electronic Supplementary information

# Highly Efficient Red Iridium(III) Complexes Cyclometalated by 4-Phenylthieno[3,2-c]quinoline Ligands for Phosphorescent OLEDs with External Quantum Efficiencies over 20%

Bei Jiang,<sup>a</sup> Xiaowen Ning,<sup>a</sup> Shaolong Gong,<sup>a</sup> Nan Jiang,<sup>\*b</sup> Cheng Zhong,<sup>a</sup> Zheng-Hong  
Lu<sup>\*b</sup> and Chuluo Yang<sup>\*a</sup>

<sup>a</sup> Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials,  
Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of  
Chemistry, Wuhan University, Wuhan 430072, P. R. China

\*E-mail: [clyang@whu.edu.cn](mailto:clyang@whu.edu.cn)

<sup>b</sup> Yunnan Key Laboratory for Micro/Nano Materials and Technology, Department of  
Physics, Yunnan University, Kunming 650091, P. R. China

\*E-mail: [jiangnan@ynu.edu.cn](mailto:jiangnan@ynu.edu.cn); [zhenghong.lu@utoronto.ca](mailto:zhenghong.lu@utoronto.ca)

## Experimental Section

**General information:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a MERCURY-VX300 spectrometer using  $\text{CDCl}_3$  as solvent. Mass spectra were acquired on a thermo DSQ II mass spectrometer and a Varian 450 GC & Varian 320 mass spectrophotometer. Elemental analysis was performed on a Vario EL III microanalyzer. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Shimadzu UV-2700 spectrophotometer. Photoluminescence (PL) spectra were obtained on a Hitachi F-4600 fluorescence spectrophotometer. The solid state PLQYs were measured on a Quantaaurus-QY measurement system (C9920-02, Hamamatsu Photonics) in the host of CBP (4 wt%). PL decay lifetimes were measured by time-correlated single-photon counting (TCSPC) option on FLS920 spectrometer and the Edinburgh Instruments picoseconds pulsed diode laser (Model: EPL-375) as the light source. Thermogravimetric analysis (TGA) was undertaken with a NEZSCH STA 449C instrument under nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from  $25\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$ . Cyclic voltammetry (CV) was performed on a CHI voltammetric analyzer. The measurements were carried out in  $\text{CH}_2\text{Cl}_2$  solution ( $\sim 1\text{ mM}$ ) for anodic sweeping and in DMF solution ( $\sim 1\text{ mM}$ ) for cathodic sweeping at scan rate of  $100\text{ mV s}^{-1}$  at room temperature by using a three-electrode configuration, which consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode. The ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple was employed as the internal standard. The supporting electrolyte was tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) ( $0.1\text{ M}$ ). The HOMO and LUMO levels were calculated

according to the formula  $\text{HOMO} = -e [4.8 \text{ V} + E_{ox}]$  and  $\text{LUMO} = -e [4.8 \text{ V} + E_{red}]$ , respectively, where  $E_{ox}$  and  $E_{red}$  were taken from the onsets of the oxidation and reduction potentials (vs Fc/Fc<sup>+</sup>). Quantum chemical calculations based on density functional theory (DFT) were performed. The geometry optimization were performed by B3LYP methods with the 6-31G(d) basis set for light atoms and LanL2DZ basis set for Ir atom. TD-DFT calculation were performed at B3LYP/def2-TZVP on the optimized geometry of (ptq)<sub>2</sub>Ir(acac).

**Device Fabrication and Measurement:** Patterned indium tin-oxide (ITO)-coated glass substrates were cleaned with a standard regiment of deionized water, acetone, and methanol inside an ultrasonic bath. After UV ozone treatment, the substrates were transferred to the vacuum chamber at a bass pressure of 10<sup>-5</sup> pa. Hole-injecting material MoO<sub>3</sub> (1 nm) and hole-transporting material CBP (35 nm) were gradually deposited onto the ITO substrates, followed by an emissive layer (15 nm), and electron-transporting material TPBi (65 nm). Finally, a cathode composed of LiF (1 nm) and Al (100 nm) was sequentially deposited. The current density-voltage-luminance (*J-V-L*) characteristics were measured using a HP4140B picoammeter and a Minolta LS-110 luminance meter. The EL spectra were collected by an USB2000-UV-vis Miniature Fiber Optic Spectrometer. All measurements were carried out in an ambient atmosphere and at room temperature.

**Synthesis of materials:** All reagents were purchased from commercial sources and used as received without further purification unless otherwise stated. Solvents were purified according to the standard procedures before usage. Chromatographic

separations were carried out by using silica gel (200-300 nm).

**Synthesis of 4-phenylthieno[3,2-*c*]quinoline (ptq):** A mixture of 2-(thiophen-2-yl)aniline (5.3 g, 30 mmol), benzaldehyde (5.3 g, 50 mmol) in 10 mL of trifluoroacetic acid (TFA) and 100 mL of toluene was refluxed for 3 days at 130 °C. After cooled to room temperature, the mixture was neutralized by NaOH (aq) and extracted with ethyl acetate. The product was obtained by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent to give a white solid with the yield of 54%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.30 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.91-7.70 (m, 2H), 7.68-7.52 (m, 5H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 155.79, 146.34, 143.95, 140.13, 132.19, 130.39, 129.33, 129.15, 128.71, 126.91, 125.83, 125.30, 123.61, 123.23; MS (EI, *m/z*): [M<sup>+</sup>] calcd for C<sub>17</sub>H<sub>11</sub>NS 261.06, found 260.10; Anal. calcd for C<sub>17</sub>H<sub>11</sub>NS (%): C 78.13, H 4.24, N 5.36; found: C 78.19, H 4.31, N 5.31.

**Synthesis of 4-(*p*-tolyl)thieno[3,2-*c*]quinoline (ttq):** It was prepared in a similar procedure to ptq except using 4-methylbenzaldehyde to replace benzaldehyde. Yield: 47%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.28 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 5.4 Hz, 2H), 7.60-7.54 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 155.81, 143.92, 139.13, 137.24, 132.20, 130.30, 129.72, 129.37, 129.26, 129.08, 128.67, 128.42, 126.75, 125.69, 125.40, 123.53, 123.19, 21.46; MS (EI, *m/z*): [M<sup>+</sup>] calcd for C<sub>18</sub>H<sub>13</sub>NS 275.08, found 274.08; Anal. calcd for C<sub>18</sub>H<sub>13</sub>NS (%): C 78.51, H 4.76, N 5.09; found: C 78.72, H 4.74, N 5.23.

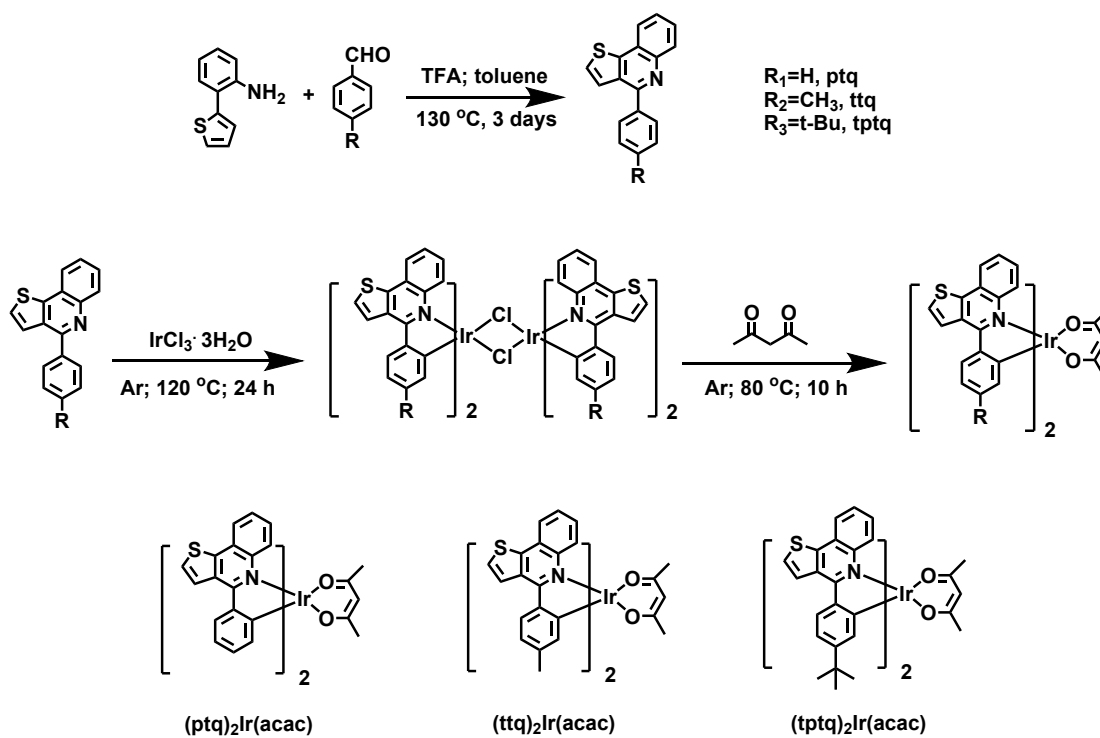
**Synthesis of 4-(4-(*tert*-butyl)phenyl)thieno[3,2-*c*]quinoline (tptq):** It was prepared in a similar procedure to ptq except using 4-(*tert*-butyl)benzaldehyde to replace benzaldehyde. Yield: 53%;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28 (d,  $J = 8.1$  Hz, 1H), 8.15 (d,  $J = 7.8$  Hz, 1H), 7.88 (d,  $J = 8.1$  Hz, 2H), 7.75-7.71 (m, 2H), 7.63-7.54 (m, 4H); 1.40 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.71, 152.14, 146.14, 143.88, 137.18, 132.08, 130.23, 128.89, 128.54, 126.62, 125.58, 125.35, 123.41, 123.09, 34.72, 31.28; MS (EI,  $m/z$ ):  $[\text{M}^+]$  calcd for  $\text{C}_{21}\text{H}_{19}\text{NS}$  317.45, found 317.13; Anal. calcd for  $\text{C}_{21}\text{H}_{19}\text{NS}$  (%): C 79.45, H 6.03, N 4.41; found: C 79.07, H 6.07, N 4.60.

**Synthesis of (ptq) $_2$ Ir(acac):** A mixture of ptq (650 mg, 2.5 mmol),  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (350 mg, 1 mmol), 15 mL of 2-ethoxyethanol, and 5 mL of  $\text{H}_2\text{O}$  was refluxed at 120 °C for 24 h under argon atmosphere. The resulting mixture was cooled and filtered, washed by water, ethanol and diethyl ether to obtain the chloride-bridged dimer. Without further purification, a mixture of the dimer (600 mg, 0.4 mmol),  $\text{Na}_2\text{CO}_3$  (210 mg, 2 mmol) and pentane-2,4-dione (200 mg, 2 mmol) was added into 20 mL of 2-ethoxyethanol. The reaction was refluxed at 90 °C for 12 h under argon atmosphere. The reaction was quenched with water, extracted with  $\text{CH}_2\text{Cl}_2$ . The product was purified by column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent to give a red solid with the yield of 30%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.52 (d,  $J = 5.1$  Hz, 2H), 8.44 (d,  $J = 9.0$  Hz, 2H), 8.35 (d,  $J = 7.8$  Hz, 2H), 8.08 (d,  $J = 7.5$  Hz, 2H), 7.73 (d,  $J = 5.7$  Hz, 2H), 7.53 (t,  $J = 7.2$  Hz, 2H), 7.40 (t,  $J = 8.1$  Hz, 2H), 7.05 (t,  $J = 7.5$  Hz, 2H), 6.75 (d,  $J = 7.8$  Hz, 2H), 6.68

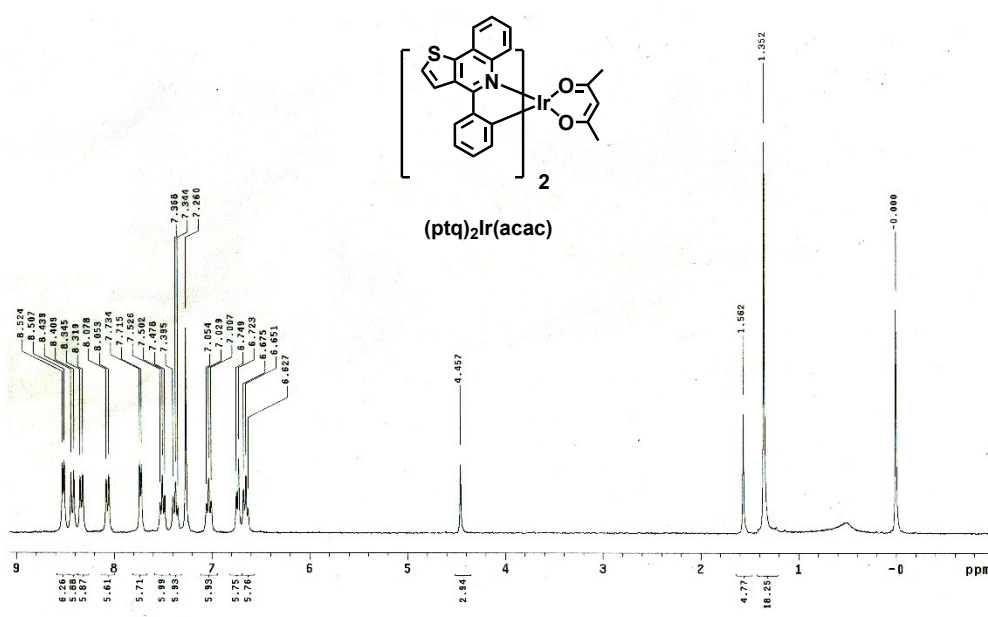
(t,  $J = 7.2$  Hz, 2H), 4.46 (s, 1H), 1.35 (s, 6H); MS (EI,  $m/z$ ):  $[M^+]$  calcd for  $C_{39}H_{27}IrN_2O_2S_2$  812.11, found 812.50; Anal. calcd for  $C_{39}H_{27}IrN_2O_2S_2$  (%): C 57.69, H 3.35, N 3.45; found: C 57.72, H 3.33, N 3.42.

**Synthesis of (ttq)<sub>2</sub>Ir(acac):** According to the procedure for (ptq)<sub>2</sub>Ir(acac), (ttq)<sub>2</sub>Ir(acac) was prepared from ttq (685 mg, 2.5 mmol) and IrCl<sub>3</sub>·3H<sub>2</sub>O (350 mg, 1 mmol) as red solid with the yield of 38%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.51 (d,  $J = 5.1$  Hz, 2H), 8.40 (d,  $J = 8.7$  Hz, 2H), 8.23 (d,  $J = 8.1$  Hz, 2H), 8.06 (d,  $J = 8.1$  Hz, 2H), 7.71 (d,  $J = 5.7$  Hz, 2H), 7.50 (t,  $J = 7.2$  Hz, 2H), 7.38 (t,  $J = 7.5$  Hz, 2H), 6.86 (d,  $J = 6.6$  Hz, 2H), 6.58 (s, 2H), 4.42 (s, 1H), 1.99 (s, 6H), 1.32 (s, 6H); MS (EI,  $m/z$ ):  $[M^+]$  calcd for  $C_{41}H_{31}IrN_2O_2S_2$  840.15, found 840.60; Anal. calcd for  $C_{41}H_{31}IrN_2O_2S_2$  (%): C 58.62, H 3.72, N 3.33; found: C 58.53, H 3.98, N 3.51.

**Synthesis of (tptq)<sub>2</sub>Ir(acac):** According to the procedure for (ptq)<sub>2</sub>Ir(acac), (tptq)<sub>2</sub>Ir(acac) was prepared from tptq (790 mg, 2.5 mmol) and IrCl<sub>3</sub>·3H<sub>2</sub>O (350 mg, 1 mmol) as red solid with the yield of 38%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.53 (d,  $J = 6.0$  Hz, 2H), 8.45 (d,  $J = 9.0$  Hz, 2H), 8.27 (d,  $J = 8.7$  Hz, 2H), 8.05 (d,  $J = 6.9$  Hz, 2H), 7.72 (d,  $J = 5.1$  Hz, 2H), 7.48 (t,  $J = 6.9$  Hz, 2H), 7.33 (d,  $J = 7.2$  Hz, 2H), 7.08 (d,  $J = 8.1$  Hz, 2H), 6.73 (s, 2H), 4.49 (s, 1H), 1.37 (s, 6H), 0.91 (s, 18H); MS (EI,  $m/z$ ):  $[M^+]$  calcd for  $C_{47}H_{43}IrN_2O_2S_2$  924.24, found 924.04; Anal. calcd for  $C_{47}H_{43}IrN_2O_2S_2$  (%): C 61.08, H 4.69, N 3.03; found: C 61.03, H 4.27, N 3.03.



**Scheme S1.** Synthetic routes and chemical structures of the iridium complexes.



**Fig. S1**  $^1\text{H}$  NMR spectrum of  $(\text{ptq})_2\text{Ir}(\text{acac})$ .

Spectrum 1A Plot - 3/12/2016 8:39 AM

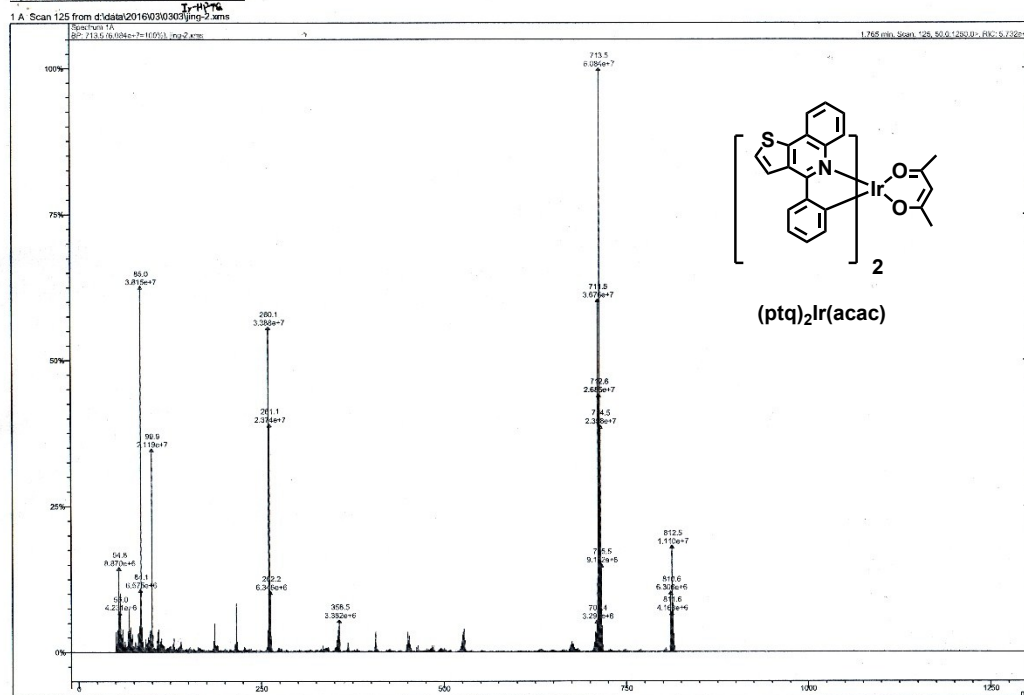


Fig. S2 GC-MS spectrum of (ptq)<sub>2</sub>Ir(acac).

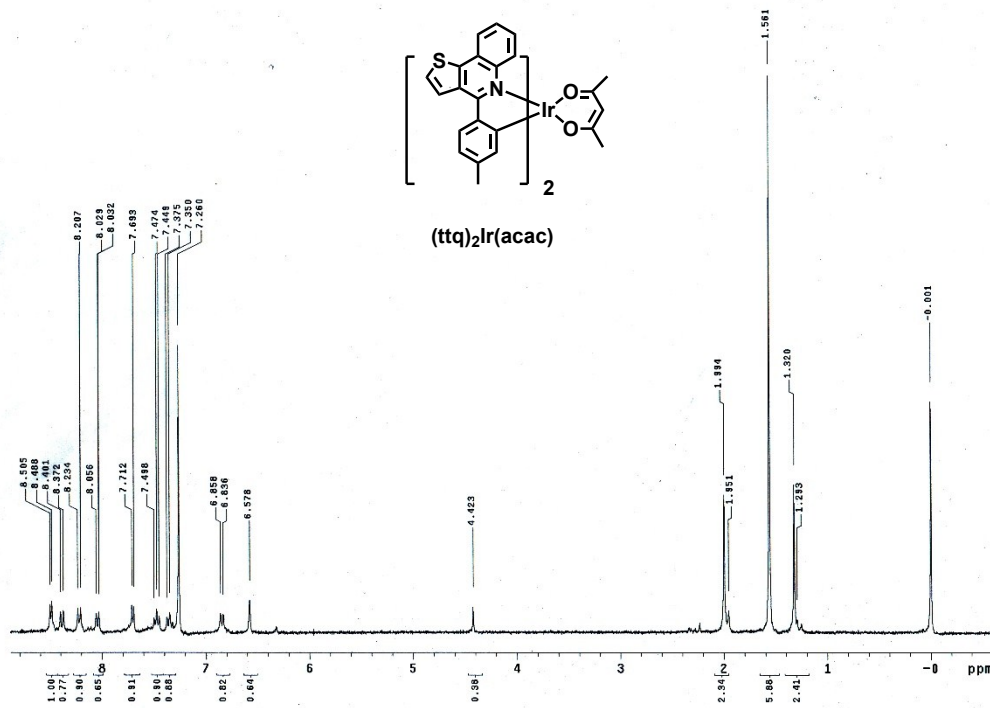


Fig. S3 <sup>1</sup>H NMR spectrum of (ttq)<sub>2</sub>Ir(acac).



JIANG-4 #115 RT: 3.73 AV: 1 SB: 122 0.04-3.28 , 4.35-5.00 NL: 2.92E4  
T: + c Full ms [40.00-1000.00]

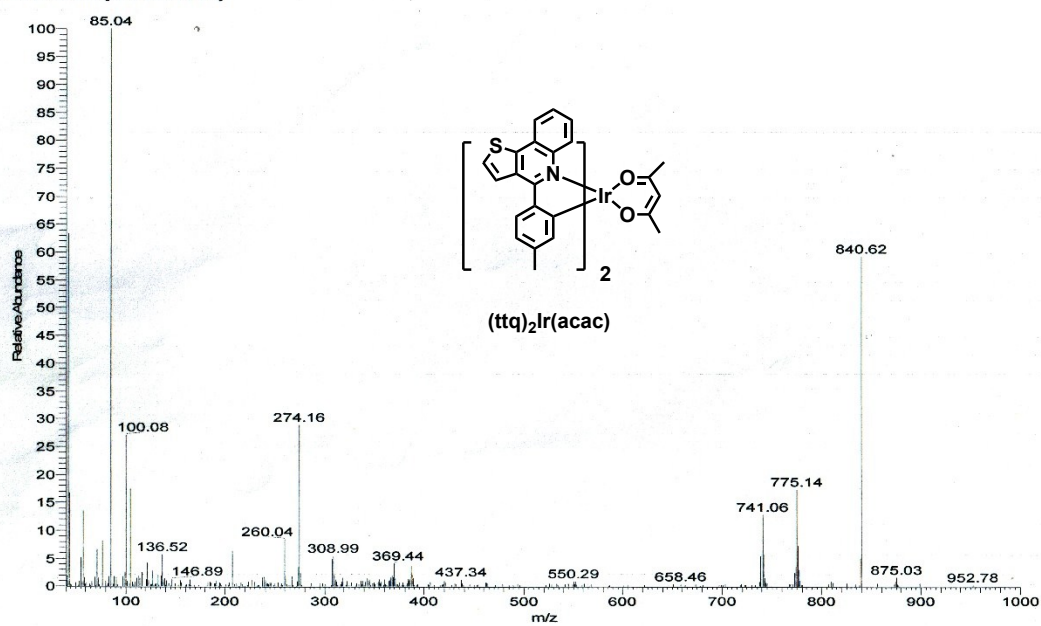


Fig. S4 GC-MS spectrum of  $(ttq)_2Ir(acac)$ .

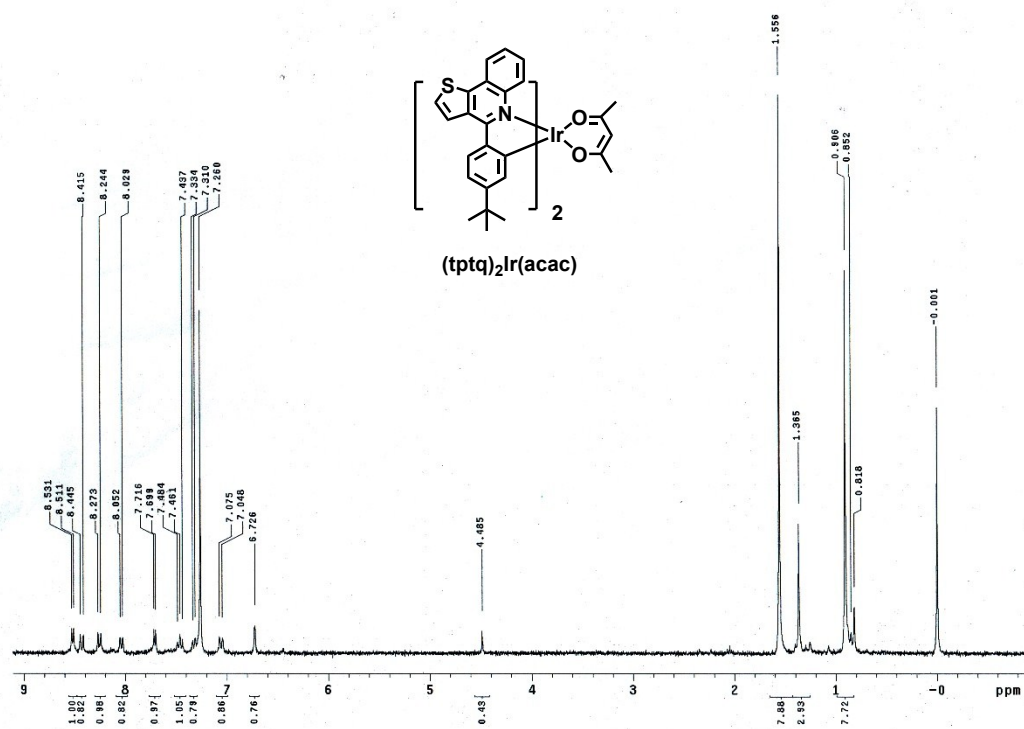


Fig. S5  $^1H$  NMR spectrum of  $(tptq)_2Ir(acac)$ .

JIANG-6 #122 RT: 3.96 AV: 1 SB: 80 1.69-3.77, 4.46-4.91 NL: 3.40E4  
T: + c Full ms [40.00-1000.00]

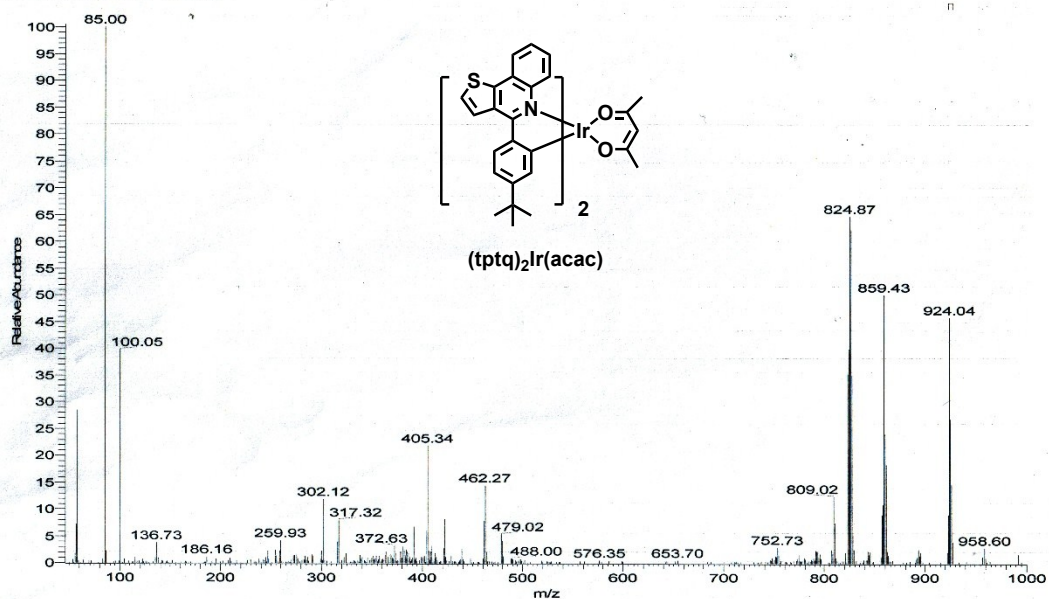


Fig. S6 GC-MS spectrum of  $(tptq)_2Ir(acac)$ .

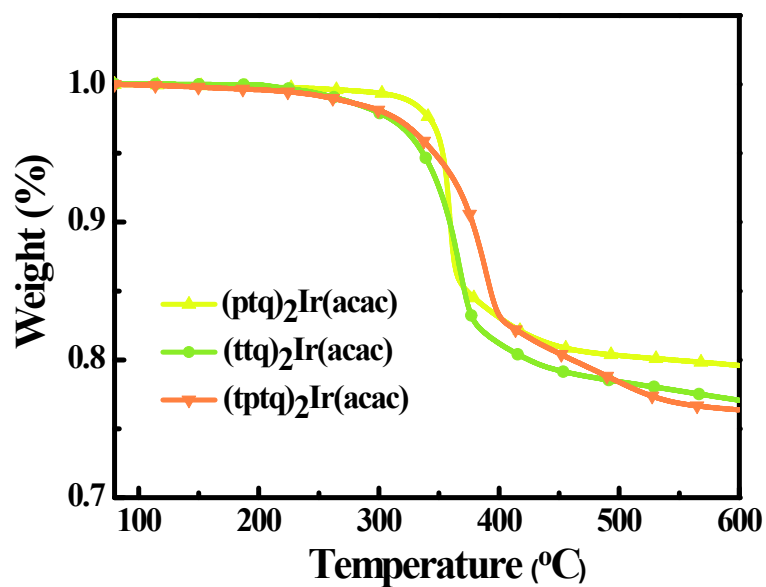
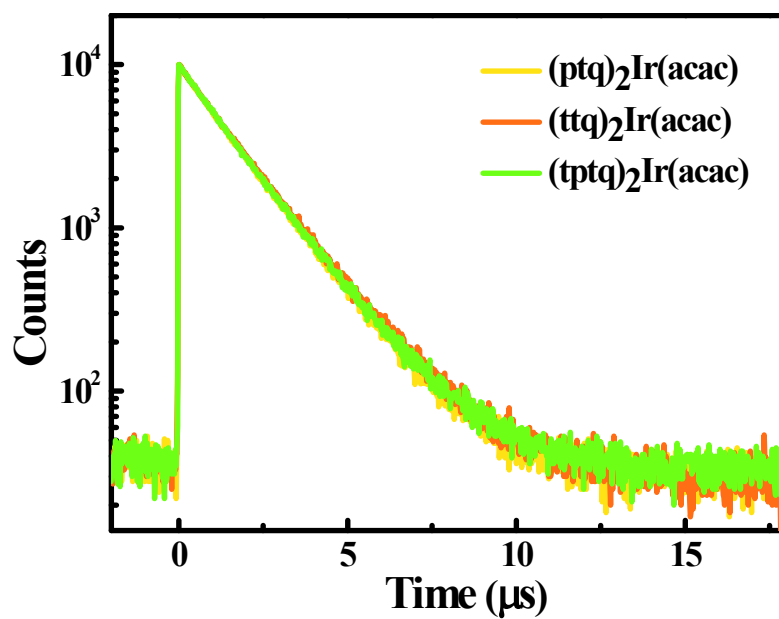
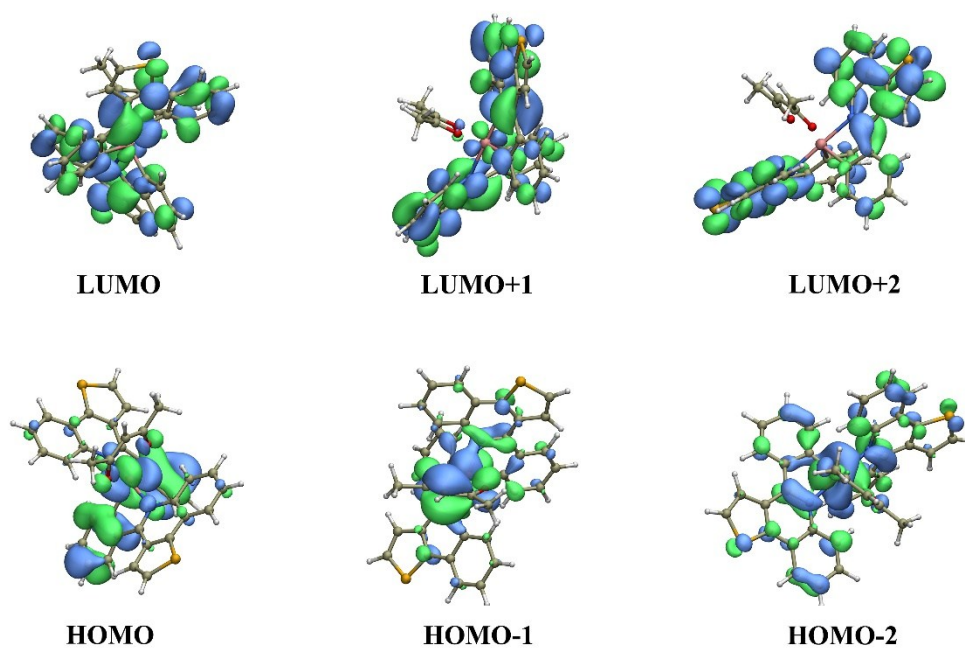


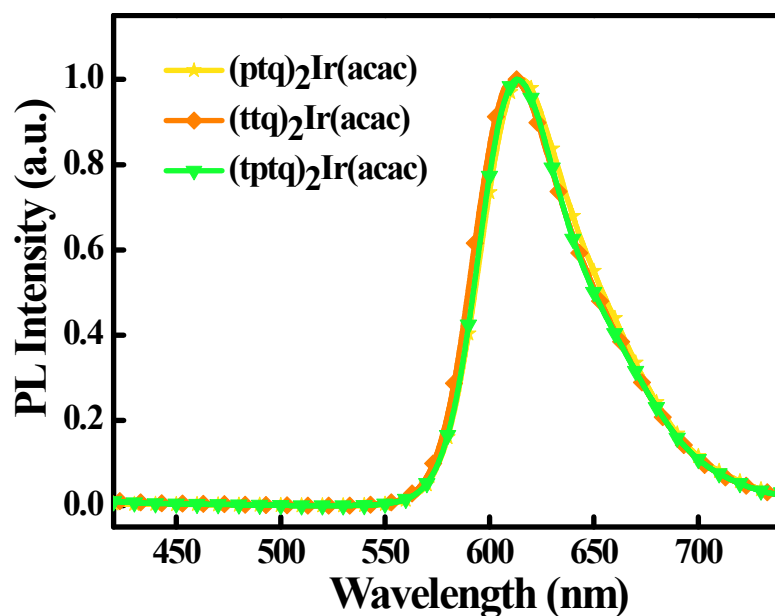
Fig. S7 TGA curves for  $(ptq)_2Ir(acac)$ ,  $(ttq)_2Ir(acac)$  and  $(tptq)_2Ir(acac)$ .



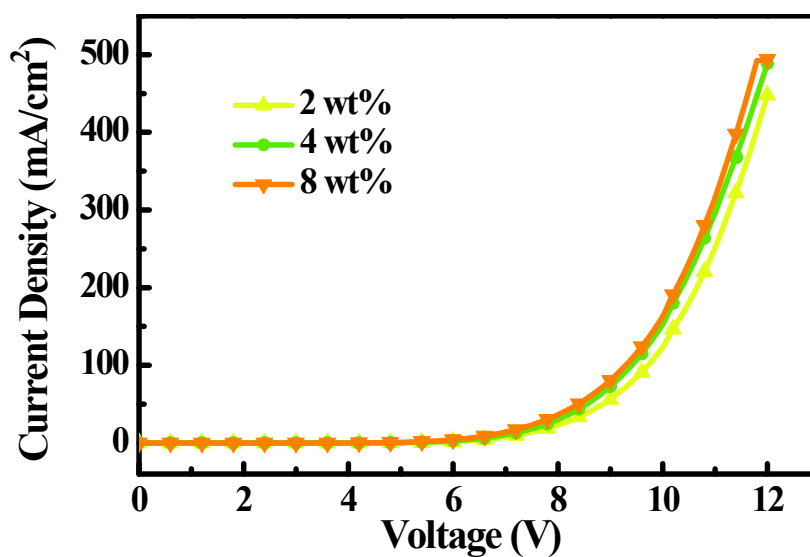
**Fig. S8** Transient PL decay curves of  $(\text{ptq})_2\text{Ir}(\text{acac})$ ,  $(\text{ttq})_2\text{Ir}(\text{acac})$  and  $(\text{tptq})_2\text{Ir}(\text{acac})$  in deaerated  $\text{CH}_2\text{Cl}_2$  solution at room temperature (excited at 377 nm).



**Fig. S9** Spatial plots of selected frontier molecular orbitals of  $(\text{ptq})_2\text{Ir}(\text{acac})$  obtained from TD-DFT calculation.



**Fig. S10** PL spectra of (ptq)<sub>2</sub>Ir(acac), (ttq)<sub>2</sub>Ir(acac) and (tptq)<sub>2</sub>Ir(acac) in 4 wt% doped CBP films.



**Fig. S11** Current density versus voltage characteristics with a function of doping concentration for devices with the structure of ITO/MoO<sub>3</sub>/CBP/CBP:*x* wt% (ptq)<sub>2</sub>Ir(acac)/TPBi/LiF/Al, where *x* = 2, 4, and 8.

**Table S1.** The summary of vacuum-deposited red PhOLEDs based on cyclometalated iridium complexes with EQEs of over than 20%.

Compounds	$\lambda_{\max}$ (nm)	EQE (%)	CIE (x, y)	Reference
(phq) <sub>2</sub> Ir(acac)	597	21.0	(0.62, 0.37)	<i>Org. Electron.</i> , 2009, 10, 240-246 <sup>1</sup>
(piq) <sub>2</sub> Ir(acac)	620	21.6	(0.68, 0.32)	<i>J. Mater. Chem.</i> , 2010, 20, 1759-1765 <sup>2</sup>
(mphmq) <sub>2</sub> Ir(tmd)	600	24.6	(0.65, 0.35)	<i>Adv. Mater.</i> 2011, 23, 2721-2726 <sup>3</sup>
(tmq) <sub>2</sub> Ir(acac)	611	25.9	(0.67, 0.33)	<i>Adv. Mater.</i> , 2011, 23, 2981-2985 <sup>4</sup>
(mpmi) <sub>2</sub> Ir(priq)	599	24.9	(0.60, 0.39)	<i>Adv. Mater.</i> , 2011, 23, 4933-4937 <sup>5</sup>
Ir(piq) <sub>3</sub>	620	21.4	(0.67, 0.33)	<i>J. Mater. Chem. C.</i> , 2014, 2, 6183-6191 <sup>6</sup>
(piq) <sub>2</sub> Ir(acac)	620	23.6	(0.67, 0.33)	<i>J. Mater. Chem. C.</i> , 2015, 3, 1491-1496 <sup>7</sup>
Ir(mimb)(L3)	593	27.4	(0.63, 0.38)	<i>Adv. Mater.</i> , 2016, 28, 2795-2800 <sup>8</sup>
(ptq) <sub>2</sub> Ir(acac)	612	22.9	(0.61, 0.36)	This work
(ttq) <sub>2</sub> Ir(acac)	614	22.5	(0.62, 0.36)	This work
(tptq) <sub>2</sub> Ir(acac)	617	20.2	(0.63, 0.35)	This work

**Table S2.** The top eight excited states of (ptq)<sub>2</sub>Ir(acac) computed by TD-DFT at the optimized ground-state geometries.

No.	Excitation <sup>a</sup>	Orbital Composition <sup>b</sup> (%)	Orbital distribution	L <sup>c</sup> (nm)	<i>f</i> <sup>d</sup>
1	H-1 → L	95.0	acac π+ Ir d → ptq π*	458	0.08
2	H-5 → L; H-1 → L+3	80.8 13.2	ptq π+ Ir d → ptq π*	351	0.08

3	H-2 → L+2; H-4 → L+1	74.1 11.5	Ir d → ptq π*	318	0.11
4	H-3 → L+3; H-7 → L+1	61.4 11.8	ptq π → ptq π*	309	0.20
5	H-3 → L+2; H-6 → L+1	42.9 21.5	ptq π → ptq π*	308	0.06
6	H → L+7 H-6 → L+3	41.6 19.4	ptq π+ Ir d → ptq π*	276	0.17
7	H-7 → L+2; H-11 → L	33.4 20.3	ptq π → ptq π*	267	0.14
8	H-1 → L+5; H-1 → L+13	34.9 12.4	acac π+ Ir d → ptq π*	263	0.14

a The orbitals involved in the excitation (H = HOMO and L = LUMO).

b The orbital pair contribution (%) to excited states.

c Vertical excitation energy.

d Oscillator strengths.

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