Supporting Information

Novel furo[3,2-c]pyridine based iridium complex for highperformance organic light-emitting diodes with over 30% external quantum efficiency

Zhimin Yan,^{a,b} Yanping Wang,^c Jiaxiu Wang,^b Yue Wang,^{*,a} Junqiao Ding,^{*,b} Lixiang Wang^{*,b}

a. State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China
*E-mail: yuewang@jlu.edu.cn

 b. State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China
 *E-mail: junqiaod@ciac.ac.cn, lixiang@ciac.ac.cn

c. School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, P. R. China

Experimental

Measurements and Characterization: ¹H NMR spectra were recorded by Bruker Avance NMR spectrometer. The elemental analysis was performed using a Bio-Rad elemental analysis system. MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT) with 2-[(2E)-3-(4-tert-butylphenyl)-2methylprop-2-enylidene] malononitrile (DCTB) as the matrix. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a flow of nitrogen using a Perkin-Elmer-TGA 7 and Perkin-Elmer-DSC 7 system, respectively. The UV-Vis absorption and photoluminescence (PL) spectra were measured by a Perkin-Elmer Lambda 35 UV/Vis spectrometer and a Perkin–Elmer LS 50B spectrofluorometer, respectively. The PL quantum yield was measured in N₂-saturated toluene with a typical green phosphor Ir(ppy)₃ ($\Phi_{PL} = 0.97$) as the reference.¹ The transient PL spectra were measured in N₂ atmosphere excited by 355 nm pulse with ca. 3 ns width from a Quanty-Ray DCR-2 pulsed Nd:YAG laser. The radiative rate (k_r) and nonradiative rate (k_{nr}) were calculated according to the equations: $\tau = 1/(k_r + k_{nr})$ and $\Phi = k_r/(k_r + k_{nr})$.² Cyclic voltammetry (CV) experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The measurements were carried out in dichloromethane for anodic sweeping and in N,N-dimethylformamide for cathodic sweeping with a conventional three-electrode system consisting of a platinum working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (n-Bu₄NClO₄). All potentials were calibrated against the ferrocene/ferrocenium couple (Fc/Fc⁺). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were determined by the equations HOMO = $-e(E_{ox, onset} + 4.8 \text{ V})$ and LUMO = $-e(E_{red, onset} + 4.8 \text{ V})$, where $E_{ox, onset}$ and $E_{red, onset}$ were the potential onset obtained from the first oxidation and reduction waves, respectively. DFT calculations were performed on Gauss09 program on the basis of the geometries from the X-ray diffraction data using the B3LYP hybrid functional. The "double-5" basis set LANL2DZ was employed for Ir atom and 6-31G(d) basis sets for H, C, N, O and S atoms.

The single crystal X-ray diffraction experiments were carried out using a Bruker Smart APEX diffractometer with CCD detector and graphite monochromator, Mo K α radiation (λ =0.71073 Å). The intensity data were recorded with ω scan mode. Lorentz, polarization factors were made for the

intensity data and absorption corrections were performed using SADABS program. The crystal structure was determined using the SHELXTL program and refined using full matrix least squares. All non-hydrogen atoms were assigned with anisotropic displacement parameters, whereas hydrogen atoms were placed at calculated positions theoretically and included in the final cycles of refinement in a riding model along with the attached carbons. Crystallographic data for the structural analyses have been deposited with Cambridge Crystallographic Data center (CCDC). CCDC referance number for (pthpy)₂Ir(acac) and (pfupy)₂Ir(acac) are 1541442 and 1541443, respectively. 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).

Device fabrication and testing: All the devices were fabricated on glass substrates pre-coated with 180 nm indium tin oxide (ITO) with a sheet resistance of 10 Ω /sq. The ITO substrates were degreased in ultrasonic solvent bath and then dried at 120 °C for 30 min. Before loaded into the vacuum deposition chamber, the ITO surface was treated with UV-ozone for 15 min. Then 10 nm of MoO₃ was firstly deposited on the top of ITO substrates, followed by 60 nm TAPC, 5 nm TCTA, 20 nm emissive layer, and 35 nm BmPyPB. Finally, 1 nm thickness of LiF and 120 nm thickness of Al was sequentially deposited to form the cathode. All the layers were grown by thermal evaporation in a high-vacuum system with a pressure of less than 5×10⁻⁴ Pa without breaking vacuum. The organic materials were evaporated at the rate in a range of 1-2 Å/s while the evaporation rate of LiF layer is 0.1 Å/s, and the metal Al was evaporated at the rate of 8-10 Å/s. The overlap between ITO and Al electrodes was 4 mm × 4 mm, which is the active emissive area of the OLED devices. The current-voltage-brightness characteristics were measured by using a set of Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The electroluminescence (EL) spectra were measured by a Spectrascan PR650 spectrophotometer. All the measurements were carried out in ambient atmosphere at room temperature.

Synthesis: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures.



Scheme S1. Synthetic route for the furan-containing complex $(pfupy)_2Ir(acac)$. Reagents and conditions: i) CH₂(COOH)₂, piridine, pyridine, 100 °C; ii) Et₃N, isobutyl chloroformate; then NaN₃/H₂O; iii) Bu₃N, Dowtherm[®] A, 220 °C; iv) POCl₃, reflux; v) benzeneboronic acid, Pd(PPh₃)₄, Na₂CO₃ (a.q.), THF, reflux; vi) IrCl₃·H₂O, 2-ethoxyethanol, H₂O 110 °C; then Na₂CO₃, Hacac, 2-ethoxyethanol, 80 °C.

Synthesis of 3-(furan-2-yl)acrylic acid (1)

A mixture of propanedioic acid (2.59 g, 24.8 mmol), pyridine (9.5 mL) and piperidine (0.18 mL) was heated at 100 °C. Then furfural (1.5 mL, 18 mmol) was added dropwise. After being stirred for 12 h, the solution was cooled to room temperature, poured into water (100 mL) and then acidified with 2 M HCl (100 mL). The resulting off-white precipitate was collected by filtration and recrystallized from ethanol-water (1:1) to afford a needle-like product **1** (2.06 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.59 - 7.45 (m, 2H), 6.67 (d, *J* = 3.2 Hz, 1H), 6.49 (d, *J* = 1.7 Hz, 1H), 6.32 (dt, *J* = 15.7, 3.1 Hz, 1H).

Synthesis of (E)-3-(furan-2-yl)acryloylazide (2)

A 100 mL round bottom flask was charged with **1** (2.06 g, 15.0 mmol), acetone (30 mL), and Et₃N (2.3 mL, 16 mmol). With the dropwise addition of isobutyl chloroformate (3.8 mL, 30 mmol), white precipitate was produced. After stirring for 8 h, a solution of Na₃N (1.94 g, 29.8 mmol) in water (5 mL) was added. The resulting mixture was stirred at 0 °C for another 5 h, and then poured into water. The precipitate was collected by filtration and further desiccated by Na₂SO₄ after

redissolved into dichloromethane. The solvent of the dry solution was removed below 40 $^{\circ}$ C to avoid the decomposition. A white solid **2** (2.00 g) was obtained without further purification for next step.

Synthesis of furo[3,2-c]pyridine-4-ol (3)

Dowtherm[®] A (10 mL) and tributylamine (3.7 mL, 15 mmol) were added into a 100 mL round bottom flask and stirred at 220 °C in argon atmosphere. To this solution was added dropwise a solution of the crude intermediate **2** in Dowtherm[®] A (30 mL). The reaction mixture was stirred at 220 °C for 5 h. After cooled to room temperature, a pie-like crystal was generated. Then a simple filtration and washing with petroleum lead to the pure cyclized product **3** (1.30 g, 65%) ¹H NMR (400 MHz, CDCl₃) δ 12.31 (s, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 1.7 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 1H).

Synthesis of 4-chlorofuro[3,2-c]pyridine (4)

The above-obtained **3** (1.30 g, 9.63 mmol) was added to a 50 mL round bottom flask, followed by the addition of POCl₃ in argon atmosphere. The solution was then heated to 100 °C and stirred for 8 h. After cooled to room temperature, the mixture was poured into ice-water and neutralized with aqueous Na₂CO₃. The resulting white solid was collected by filtration. Further purification was operated by column chromatography to give a white solid **4** (1.23 g, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 5.7 Hz, 1H), 7.70 (d, *J* = 2.2 Hz, 1H), 7.41 (d, *J* = 5.7 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H).

Synthesis of 4-phenylfuro[3,2-c]pyridine (5)

A round bottom flask was charged with 4 (1.20 g, 7.81 mmol), phenylboronic acid (1.90 g, 15.6 mmol), Pd(PPh₃)₄ (0.27 g, 0.23 mmol) and THF (60 mL) in argon atmosphere. Then 11.7 mL aqueous Na₂CO₃ (2 M) was added into the mixture, and refluxed for 8 h. After cooling, the mixture was extracted with ethyl acetate, dried over Na₂SO₄, filtered, concentrated and purified by column chromatography to giving a white solid **5** (1.40 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 5.7 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 5.8 Hz, 1H), 7.09 (d, *J* = 1.1 Hz, 1H).

Synthesis of (pfupy)₂Ir(acac)

The furan-based C^N ligand **5** (1.30 g, 6.66 mmol), $IrCl_3 \cdot 3H_2O$ (1.12 g, 3.17 mmol), 2ethoxyethanol (72 mL) and H₂O (24 mL) were added to a 250 mL round bottom flask. The mixture was then stirred at 110 °C in argon atmosphere for 48 h. After cooling, the mixture was directly filtered and washed with water and ethanol. The obtained yellow dimer was dried in vacuum at 65 °C.

A 100 mL round bottom flask was charged with the above dimer (1.10 g, 0.890 mmol), 2,4pentanedione (0.46 mL, 4.5 mmol) and Na₂CO₃ (0.47 g, 4.5 mmol). After heated at 80 °C in argon atmosphere for 24 h, the mixture was cooled and poured into the saturated aqueous NaCl solution. The resulting yellow solid was collected by filtration and washed with water. Further purification was operated by column chromatography to give a yellow solid (0.88 g, 39%). ¹H NMR (400 MHz, DMSO) δ 8.41 - 8.31 (m, 4H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.94 (s, 2H), 7.76 (d, *J* = 6.5 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 2H), 6.57 (t, *J* = 7.5 Hz, 2H), 6.06 (d, *J* = 7.6 Hz, 2H), 5.25 (s, 1H), 1.69 (s, 6H). MALDI-TOF MS: 680.1 [M⁺]. Anal. calcd for C₃₁H₂₃IrN₂O₄: C 54.78, H 3.41, N 4.12. Found: C 54.58, H 3.46, N 3.99.

References:

- T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard and M. E. Thompson, J. Am. Chem. Soc., 2009, 131, 9813.
- J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, 44, 1713.



Figure S1. ¹H NMR (a) and MALDI-TOF MS spectra (b) of (pfupy)₂Ir(acac).



Figure S2. TGA curves of (pthpy)₂Ir(acac) and (pfupy)₂Ir(acac). Inset: DSC curves.



Figure S3. The intermolecular packing in the crystal of the furan-containing complex $(pfupy)_2Ir(acac)$.



Figure S4. The intermolecular packing in the crystal of the thiophene-containing complex (pthpy)₂Ir(acac).



Figure S5. CV curves of (pthpy)₂Ir(acac) and (pfupy)₂Ir(acac).



Figure S6. Transition PL spectra of $(pthpy)_2Ir(acac)$ and $(pfupy)_2Ir(acac)$ in N₂-saturated toluene solutions.



Figure S7. Energy level diagram of the device and chemical structures of used materials.



Figure S8. Device performance for $(pfupy)_2Ir(acac)$: (a) current density-voltage-luminance characteristic; (b) luminance dependence on the current efficiency and power efficiency.



Figure S9. Device performance of the reference device based on 12 wt.% Ir(ppy)₃ doped into CBP: (a) current density-voltage-luminance characteristic; (b) luminance dependence on the external quantum efficiency (EQE) and current efficiency.

	(pfupy) ₂ Ir(acac) (pthpy) ₂ Ir(acac)		
Empirical formula	$C_{31}H_{23}IrN_2O_4 \bullet CH_2Cl_2$ $C_{31}H_{23}IrN_2O_2S_2$		
Formula weight	764.66	711.85	
Temperature (K)	293(2)	186(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Monoclinic	Monoclinic	
Space group	P21/c	$P 2_1/c$	
Unit cell dimensions:			
a (Å)	15.8143(10)	10.4155(5)	
b (Å)	17.4936(11)	17.9067(8)	
c (Å)	10.0825(6)	14.6999(7)	
α (°)	90	90	
β (°)	99.1900(10)	109.6850(10)	
γ (°)	90	90	
Volume (Å ³)	2753.5(3)	2581.4(2)	
Z	4	4	
Density (calculated) (Mg/m ³)	1.845	1.832	
Absorption coefficient (mm ⁻¹)	5.086	5.367	
F(000)	1496	1392	
Crystal size (mm ³)	0.180 x 0.140 x 0.110	0.25 x 0.18 x 0.11	
Theta range for data collection (°)	1.748 to 25.346	1.86 to 25.35	
Index ranges	-14<=h<=19	-12<=h<=8	
	-19<=k<=21	-21<=k<=21	
	-12<=1<=12	-14<=1<=17	
Reflections collected	17710	12948	
Independent reflections	5031 [R(int) = 0.0313]	4721 [R(int) = 0.0233]	
Completeness to theta 25.24°	99.9 %	100.00%	
(25.35° for (pthpy) ₂ Iracac)			
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	
Max. and min. transmission	0.670 and 0.527	0.5897 and 0.3472	
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	
Data / restraints / parameters	5031 / 0 / 372	4721 / 1 / 345	
Goodness-of-fit on F ²	1.048	1.07	
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.1001	R1 = 0.0234, wR2 = 0.0561	
R indices (all data)	R1 = 0.0422, wR2 = 0.1056	wR2 = 0.1056 $R1 = 0.0271$, $wR2 = 0.0578$	
Largest diff. peak and hole (e.Å ³)	1.816 and -1.421	1.206 and -0.791	

Table S1. Crystallographic data for (pfupy)₂Ir(acac) and (pthpy)₂Ir(acac).

Bond ler	ngths [Å]					
Ir(1)-C(14)	1.980(6)					
Ir(1)-C(1)	1.980(6)					
Ir(1)-N(2)	2.038(5)					
Ir(1)-N(1)	2.045(5)					
Ir(1)-O(4)	2.150(4)					
Ir(1)-O(3)	2.166(4)					
Bond Angles [°]						
C(1)-Ir(1)-N(1)	80.7(2)					
C(14)-Ir(1)-N(2)	80.5(2)					
O(4)-Ir(1)-O(3)	87.25(17)					
N(2)-Ir(1)-N(1)	175.52(18)					
C(1)-Ir(1)-O(4)	175.4(2)					
C(14)-Ir(1)-O(3)	172.4(2)					
Torsion Angles [°]						
N(1)-C(7)-C(6)-C(1)	-3.69					
N(2)-C(20)-C(19)-C(14)	3.48					

Table S2. Selected bond length, angle and torsion angle for (pfupy)₂Ir(acac).

Bond lengths [Å]						
Ir(1)-C(14)	1.982(4)					
Ir(1)-C(1)	1.976(3)					
Ir(1)-N(2)	2.030(3)					
Ir(1)-N(1)	2.037(3)					
Ir(1)-O(1)	2.152(2)					
Ir(1)-O(2)	2.147(2)					
Bond Angles [°]						
C(1)-Ir(1)-N(1)	80.25(12)					
C(14)-Ir(1)-N(2)	80.28(13)					
O(2)-Ir(1)-O(1)	87.32(10)					
N(2)-Ir(1)-N(1)	174.60(11)					
C(1)-Ir(1)-O(1)	176.25(11)					
C(14)-Ir(1)-O(2)	174.28(11)					
Torsion Angles [°]						
N(1)-C(7)-C(2)-C(1)	0.48					
N(2)-C(20)-C(15)-C(14)	-6.44					

Table S3. Selected bond length, angle and torsion angle for (pthpy)₂Ir(acac).

Doping Concentration	$V_{on}{}^a$	$\eta_c{}^b$	$\eta_p{}^b$	EQE ^b	CIE °
[wt.%]	[V]	[cd/A]	[lm/W]	[%]	[x, y]
4	3.2	101.1/95.0/88.6	98.8/48.1/33.1	28.1/26.4/24.6	(0.43, 0.55)
8	3.0	102.1/94.9/90.4	97.9/49.7/33.8	28.0/26.3/25.0	(0.44, 0.55)
12	2.8	110.5/96.4/92.7	124.0/54.1/37.3	30.5/26.6/25.6	(0.44, 0.55)
12 wt.% Ir(ppy)3 d	3.0	70.3/66.5/59.1	73.6/47.5/30.9	24.9/23.6/20.9	(0.28, 0.63)

Table S4. Device performance of (pfupy)₂Ir(acac) compared with Ir(ppy)₃.

^a Turn-on voltage at a brightness of 1 cd/m²; ^b maximum data, data at 1000 cd/m² and 5000 cd/m² for current efficiency (η_c), power efficiency (η_p) and external quantum efficiency (EQE), respectively; ^c CIE at 6 V; ^d reference device based on 12 wt.% Ir(ppy)₃ doped into CBP.