Supporting Information

Saturated red iridium(III) complexes containing the unique four-membered Ir-S-C-N ring backbone: mild synthesis and application in OLEDs

Guangzhao Lu,^{a,b} Jingwen Yao,^c Zhanxiang Chen,^d Dongge Ma*,^c and Chuluo Yang*,^{a,d}

^aShenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China.

E-mail: clyang@whu.edu.cn

^bKey Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong

Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.

°State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic

Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.

E-mail: msdgma@scut.edu.cn

^dHubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan 430072, China.

Materials and Measurements.

All reagents and chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were recorded by Bruker Advanced II (400 MHz) spectrometers and MERCURYVX300 using CDCl3 as solvent and tetramethylsilane (TMS) as the internal standards. High resolution mass spectra (HRMS) were measured by Thermo Scientific LTQ Orbitrap XL mass spectrometer. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. Thermo gravimetric analyses (TGAs) were performed on a NETZSCH STA 449C instrument under nitrogen with a heating rate of 10 °C min⁻¹. Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. The decay lifetimes were measured with an Edinburgh Instruments FLS-920 fluorescence spectrometer in degassed CH₂Cl₂ solution at room temperature. The solution state absolute PLQYs were measured on a Quantaurus-QY measurement system (C9920-02,

Hamamatsu Photonics) equipped with a calibrated integrating sphere in the degassed CH_2Cl_2 and all the samples were excited at 360 nm.



Synthesis of thiourea derivatives ancillary ligands.

Scheme S1 The synthetic routes of the ligands and Ir(III) complexes: (a) $Pd(PPh_3)_4$, Na_2CO_3 , THF-H₂O, 70 °C, 12 h; (b) IrCl₃, EtOCH₂CH₂OH-H₂O, 115 °C, 12 h; (c) LDA, THF, 0 °C, 1 h; (d) CH₃OCH₂CH₂OCH₃, rt, 40 mins; (e) *n*-BuLi, 0 °C, 1 h.

Lithium 1,1,3-triisopropylthiourea (Li-tiptha). A solution of 2-isothiocyanatopropane (300 mg, 2.96 mmol) was dissolved in degassed THF (18 mL), then cooled to 0 °C and treated with LDA (1.8 mL, 3.55 mmol). After stirring for 1 h at 0 °C, the resulting product lithium 1,1,3-triisopropylthiourea was directly used for the synthesis of iridium complexes in the following step because of its sensitivity to air and water.

Lithium 1,1-diisopropyl-3-phenylthiourea (Li-phdiptha). A solution of isothiocyanatobenzene (399 mg, 2.96 mmol) was dissolved in degassed THF (18 mL), then cooled to 0 °C and treated with LDA (1.8 mL, 3.55 mmol). After stirring for 1 h at 0 °C, the resulting product lithium 1,1-diisopropyl-3-phenylthiourea was directly used for the synthesis of iridium complexes in the following step because of its sensitivity to air and water.

Lithium 3-(4-fluorophenyl)-1,1-diisopropylthiourea (Li-fphdiptha). A solution of 1-fluoro-4isothiocyanatobenzene (450 mg, 2.96 mmol) was dissolved in degassed THF (18 mL), then cooled to 0 °C and treated with LDA (1.8 mL, 3.55 mmol). After stirring for 1 h at 0 °C, the resulting product lithium 3-(4-fluorophenyl)-1,1-diisopropylthiourea was directly used for the synthesis of iridium complexes in the following step because of its sensitivity to air and water.

Lithium 3-isopropyl-1,1-diphenylthiourea (Li-ipdptha). A solution of diphenylamine (500 mg, 2.96 mmol) was dissolved in degassed THF (13 mL), then cooled to 0 °C and treated with *n*-BuLi (1.6 mL, 3.55 mmol). After stirring for 1 h at 0 °C, 2-isothiocyanatopropane in 5 ml degassed THF (298 mg, 2.96 mmol) was added. After stirring for another 1 h at 0 °C, the resulting product lithium 3-isopropyl-1,1-diphenylthiourea was directly used for the synthesis of iridium complexes in the following step because of its sensitivity to air and water.

Synthesis of iridium(III) complexes.

The IrCl₃ (0.64 g, 2.14 mmol) and 2.4 equivalent of cyclometalated ligand (5.14 mmol) were added in a 2-ethoxyethanol and water mixture. Then, the solution was heated for 16 h at 110 °C. After the addition of water, precipitated red powder of $[(C^N)_2 Ir(\mu-Cl)]_2$ chloride-bridged dimmer was filtered and reacted with thiourea derivatives without further purification for 40 minutes at room temperature. The solution was concentrated and the resulting residue was purified by silica gel column chromatography (CH₂Cl₂/petroleum ether 1:2 (v/v)) and vacuum sublimation gave red power.

(4tfmpiq)₂Ir(tiptha): Yield: 71.0%. ¹H NMR (400 MHz, CDCl₃) δ 10.03 (d, J = 6.44 Hz, 1H), 8.83 (dd, J = 18.88, 6.56 Hz, 3H), 8.25 (d, J = 8.27 Hz, 1H), 8.16 (d, J = 8.35 Hz, 1H), 8.01 (dd, J = 13.21, 7.76 Hz, 2H), 7.87 - 7.56 (m, 6H), 7.15 (d, J = 8.21 Hz, 1H), 7.02 (d, J = 8.57 Hz, 1H), 6.65 (s, 1H), 6.24 (s, 1H), 4.43 (dt, J = 12.74, 6.39 Hz, 1H), 3.50 (dt, J = 13.28, 6.59 Hz, 2H), 1.48 - 1.08 (m, 14H), 0.86 (t, J = 7.33 Hz, 4H). HR-MS, m/z: calcd for C₄₂H₄₀F₆IrN₄S⁺ (M+H)⁺ 939.2507, found 939.2503. Anal. Calcd for C₄₂H₃₉F₆IrN₄S: C, 53.78; H, 4.19; N, 5.97. Found: C, 53.46; H, 4.01; N, 5.73%.

(4tfmpiq)₂Ir(phdiptha): Yield: 72.0%. ¹H NMR (400 MHz, CDCl₃) δ 9.93 (d, *J* = 6.44 Hz, 1H), 9.16 (d, *J* = 6.40 Hz, 1H), 9.07 - 8.86 (m, 1H), 8.42 (d, *J* = 8.62 Hz, 1H), 8.30 (d, *J* = 8.34 Hz, 1H), 8.11-7.91 (m, 2H), 7.86 - 7.53 (m, 7H), 7.09 (d, *J* = 8.42 Hz, 1H), 6.93 (d, *J* = 8.00 Hz, 1H), 6.82 (s, 1H), 6.42 (dq, *J* = 14.35, 7.23 Hz, 4H), 5.91 (d, *J* = 7.58 Hz, 2H), 3.97 - 3.61 (m, 2H), 1.34 (d, *J* = 6.81 Hz, 6H), 1.13 (d, *J* = 6.73 Hz, 6H). HR-MS, m/z: calcd for C₄₅H₃₈F₆IrN₄S⁺ (M+H)⁺ 973.2351, found 973.2349. Anal. Calcd for C₄₅H₃₇F₆IrN₄S: C, 55.60; H, 3.84; N, 5.76. Found: C, 55.24; H, 3.62; N, 5.88%. (4tfmpiq)₂Ir(fphdiptha): Yield: 76.0%. ¹H NMR (400 MHz, CDCl₃) δ 9.89 (d, J = 6.45 Hz, 1H), 9.10 (d, J = 6.41 Hz, 1H), 8.96 (t, J = 7.82 Hz, 1H), 8.45 (d, J = 8.50 Hz, 1H), 8.30 (d, J = 8.37 Hz, 1H), 8.07 - 8.01 (m, 1H), 7.97 (d, J = 8.20 Hz, 1H), 7.83 - 7.57 (m, 7H), 7.09 (d, J = 9.04 Hz, 1H), 6.97 (d, J = 8.38 Hz, 1H), 6.83 (s, 1H), 6.40 (s, 1H), 6.08 (t, J = 8.65 Hz, 2H), 5.85 (dd, J = 8.65, 5.01 Hz, 2H), 3.93 - 3.71 (m, 2H), 1.35 (d, J = 6.87 Hz, 6H), 1.14 (d, J = 6.74 Hz, 6H). HR-MS, m/z: calcd for calcd for C₄₅H₃₇F₇IrN₄S⁺ (M+H)⁺ 991.2256, found 991.2258. Anal. Calcd for C₄₅H₃₆F₇IrN₄S: C, 54.59; H, 3.67; N, 5.66. Found: C, 54.33; H, 3.35; N, 5.82%.

(4tfmpiq)₂Ir(ipdptha): Yield: 73.0%. ¹H NMR (400 MHz, CDCl₃) δ 10.01 (d, J = 6.42 Hz, 1H), 8.95 - 8.74 (m, 3H), 8.33 - 7.97 (m, 4H), 7.90 - 7.71 (m, 6H), 7.33 (t, J = 7.82 Hz, 4H), 7.21 (d, J =7.52 Hz, 4H), 7.14 (t, J = 7.39 Hz, 3H), 7.06 - 7.01 (m, 1H), 6.67 (s, 1H), 6.27 (s, 1H), 4.05 (dt, J =12.73, 6.33 Hz, 1H), 0.50 (d, J = 6.34 Hz, 3H), -0.07 (d, J = 6.39 Hz, 3H). HR-MS, m/z: calcd for C₄₈H₃₆F₆IrN₄S⁺ (M+H)⁺ 1007.2188, found 1007.2184. Anal. Calcd for C₄₈H₃₅F₆IrN₄S: C, 57.30; H, 3.51; N, 5.57. Found: C, 57.44; H, 3.27; N, 5.85%.

X-ray Crystallography.

The single crystals of the three complexes were obtained from slow evaporation of methanol /CH₂Cl₂ solution at room temperature. And its X-ray-diffraction data were carried out on a Bruker APEX2 SMART CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. Crystal structures were solved by direct methods using the SHELXL-2014/7' software. None-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2 using SHELXL-2014/7', while the hydrogen atoms were directly introduced at calculated position and refined in the riding mode.^{S1}

Details of cyclic voltammetry measurements and theoretical calculations.

Cyclic voltammetry (CV) was measured on a CHI voltammetric analyzer at room temperature with the conventional three-electrode configuration, consisted of a platinum column working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo reference electrode. Cyclic voltammograms were recorded using tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) dissolved in dichloromethane (5 mL) as the supporting electrolyte, and ferrocenium-ferrocene

(Fc+/Fc) as the external standard, at the scan rate of 100 mV s⁻¹. The onset potential was determined from the intersection of two tangents of the rising and background current in cyclic voltammogram. We perform theoretical calculations employing Gaussian09 software with B3LYP function. The basis set of 6-31G(d, p) was used for C, H, N, O, and F atoms while the LanL2DZ basis set was employed for Ir atoms. The solvent effect of CH_2Cl_2 was taken into consideration using conductor like polarizable continuum model (C-PCM).^{S2}

OLEDs fabrication and measurement.

All the devices were grown on glass substrates pre-coated with a 180 nm thick layer of indium tin oxide (ITO) with a sheet resistance of 10 Ω per square. Before loading into the deposition system, the ITO substrates were pre-cleaned carefully and the surface was treated by oxygen plasma for 15 minutes. After UV ozone treatment, hole-injection material HATCN (6 nm) was firstly thermally deposited on, followed by the hole-transporting material TAPC (55 nm), emissive layer 1 (the phosphors doped in the host TCTA, 8 nm), emissive layer 2 (the phosphors doped in 2,6DCzPPy, 8 nm), and electron-transporting material TmPyPB (55 nm). Finally, a cathode composed of lithium fluoride (LiF, 1 nm)/aluminum (Al, 150 nm) was sequentially deposited onto the substrate in the vacuum of 10⁻⁶ Pa. The current density-voltage-luminance (*J-V-L*) characteristics were measured using a Keithey 2400 Source meter and a Keithey 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

 Table S1. The crystallographic data of (4tfmpiq)₂Ir(tiptha), (4tfmpiq)₂Ir(phdiptha) and

 (4tfmpiq)₂Ir(ipdptha).

	(4tfmpiq) ₂ Ir(tiptha)	(4tfmpiq) ₂ Ir(phdiptha)	(4tfmpiq) ₂ Ir(ipdptha)	
Formula	$C_{42}H_{39}F_6IrN_4S$	C ₄₅ H ₃₇ F ₆ IrN ₄ S	C ₄₈ H ₃₅ F ₆ IrN ₄ S	
Formula weight	938.03 972.04		1006.06	
T (K)	100.01(10)	100.00(10)	100.00(10)	
Wavelength (Å)	0.71073	0.71073	0.71073	
Crystal system	Triclinic	Triclinic	Triclinic	
Space group	P-1	P-1	P-1	
<i>a</i> (Å)	12.1968(5)	12.8780(5)	12.4517(4)	

<i>b</i> (Å)	12.2974(5)	12.9170(5)	13.3873(9)		
<i>c</i> (Å)	14.9668(6)	15.3252(6)	14.2244(7)		
a (deg)	95.331(3)	109.486(4)	69.304(5)		
β (deg)	97.300(3)	74.850(4)			
γ (deg)	118.359(4)	115.957(4)	66.706(5)		
$V(Å^3)$	1928.99(15)	2038.79(16)	2016.8(2)		
Z	2	2	2		
$\rho_{\rm calcd} ({ m g/cm^3})$	1.615	1.583	1.657		
μ (Mo K α) (mm ⁻¹)	3.580	3.390	3.431		
F (000)	932.0	964.0	996.0		
Range of transm	3.824-49.998	3.93-49.998	4.066-49.988		
Reflns collected	12875	20025	15717		
Unique(R _{int})	6797(0.0423)	7107(0.0366)	0.0459		
$R_{I}[I > 2s(I)]$	0.0379	0.0258	0.0327		
wR_2 (all data)	0.0782	0.0295 0.0606			
GOF on F^2	1.035	1.046	1.030		

 $R_1^{a} = \Sigma ||F_0| - |F_c|| / \Sigma F_0|$. w $R_2^{b} = [\Sigma w (F_0^{2} - F_c^{2})^2 / \Sigma w (F_0^{2})]^{1/2}$

Table S2. Selected bond lengths and angles of (4tfmpiq) ₂ Ir(tiptha), (4tfmpiq) ₂ Ir(phdiptha) and	nd
(4tfmpiq) ₂ Ir(ipdptha).	

Bond length	(4tfmpiq) ₂ Ir(tiptha)	(4tfmpiq) ₂ Ir(phdiptha)	(4tfmpiq) ₂ Ir(ipdptha)	
Selected	Bond length (Å)	Bond length (Å)	Bond length (Å)	
Ir-C(1)	2.002(4)	2.002(4) 1.972(3)		
Ir-C(2)	2.010(5) 2.009(3)		2.000(4)	
Ir-N(1)	2.034(4)	2.032(2)	2.038(3)	
Ir-N(2)	2.044(4)	2.052(2)	2.036(3)	
Ir-S(1)	2.4735(14)	2.4555(9)	2.4708(11)	
Ir-N(3)	2.196(4) 2.188(3)		2.194(3)	
S(1)-C(3)	1.764(5)	1.738(4)	1.739(4)	
C(3)-N(3)	1.285(6)	1.341(4)	1.305(5)	
Selected angles	(°)	(°)	(°)	
C(1)-Ir-N(1)	78.89(17)	79.14(12)	79.07(14)	
C(2)-Ir-N(2)	79.41(18)	79.43(11)	79.07(14)	
S(1)-Ir-N(3)	65.51(11)	66.09(8)	66.02(8)	

S(1)-C(3)-N(3)	111.7(4)	110.6(2)	113.2(3)
C(3)-N(3)-Ir	102.7(3)	101.8(2)	101.0(2)
C(3)-S(1)-Ir	80.04(18)	81.45(12)	79.81(14)

 Table S3. The electronic cloud density distribution.

Complex	Orbital	Energy/eVEnergy/eVComposition (%)				on (%)
		(Calculated)	(experiment)	Main ligands	Ir	Ancillary Ligands
(4tfmpiq) ₂ Ir(tiptha)	НОМО	-5.31	-5.25	24.88	39.53	35.58
	LUMO	-2.28	-3.30	94.31	3.14	2.55
(4tfmpiq) ₂ Ir(phdiptha)	НОМО	-5.21	-5.14	24.50	36.95	38.55
	LUMO	-2.20	-3.18	92.67	4.88	2.45
(4tfmpiq) ₂ Ir(fphdiptha)	НОМО	-5.18	-5.17	20.86	31.20	47.94
	LUMO	-2.20	-3.20	92.88	4.67	2.46
(4tfmpiq) ₂ Ir(ipdptha)	НОМО	-5.41	-5.32	25.37	39.08	35.55
	LUMO	-2.23	-3.33	93.11	4.38	2.50



Fig. S1. The TG curves of (4tfmpiq)₂Ir(tiptha), (4tfmpiq)₂Ir(phdiptha), (4tfmpiq)₂Ir(fphdiptha) and (4tfmpiq)₂Ir(ipdptha).



Fig. S2. Cyclic voltammograms of complexes four iridium(III) complexes.



Fig. S3. The PL spectra measured in 8 wt% doped TCTA films.



Fig. S4. The selected lifetime curves of four iridium(III) complexes in degassed CH₂Cl₂ solution.

References

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