

## Electronic Supplementary Information

# High performance solution-processed yellow organic light-emitting device and fluoride ion sensor based on a versatile phosphorescent Ir(III) complex

Xiaolong Yang,<sup>a</sup> Zhao Feng,<sup>a</sup> Jingshuang Dang,<sup>b</sup> Yuanhui Sun,<sup>a</sup> Guijiang Zhou<sup>\*a</sup> and Wai-Yeung Wong<sup>\*c</sup>

<sup>a</sup> Department of Chemistry, School of Science, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, China. E-mail: zhougj@mail.xjtu.edu.cn

<sup>b</sup> School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China.

<sup>c</sup> Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China. E-mail: wai-yeung.wong@polyu.edu.hk

## Experimental Section

**General information** Commercially available starting reactants were used directly without further purification. The solvents were distilled prior to use.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in  $\text{CDCl}_3$ . Chemical shifts were recorded in ppm scale and referenced to the solvent residual peak. The thermal gravimetric analysis (TGA) was recorded on a NETZSCH STA 409C instrument under  $\text{N}_2$  with the heating rate of  $20\text{ K min}^{-1}$ . UV-vis spectra were measured at room temperature on a Shimadzu UV-2250 spectrophotometer. Emission spectra and lifetimes of the complex in solution and film were measured using an Edinburgh Instruments Ltd (FLSP920) fluorescence spectrophotometer. The solution PLQY was determined in THF solution at room temperature against *fac*- $[\text{Ir}(\text{ppy})_3]$  (PLQY = 0.40). The PLQY of the doped film was measured using an integrating sphere. The cyclic voltammetry was tested on the Princeton Applied Research (PARSTAT<sup>®</sup> 2273, Advanced Electrochemical System) equipment in MeCN solution containing *n*- $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte with a scan rate of  $100\text{ mV s}^{-1}$ . The ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was used as the internal reference. The mass spectral measurement was performed on a micrOTOF-Q II mass spectroscopy. The the film morphology was recorded by a NT-MDT Atomic Force Microscope (NEXT).

**Computational details** Geometrical optimizations were conducted using the popular B3LYP functional theory. The basis set used for C, H, O, N, B, F and S atoms was 6-311G while effective core potentials with a LanL2DZ basis set were employed for Ir atoms. The energies of the excited states of the complexes were computed by time-dependent DFT (TD-DFT) based on all the ground-state geometries. The natural transition orbitals were calculated based on the optimized  $T_1$  geometry. All calculations were carried out by using the Gaussian 09 program.<sup>1</sup>

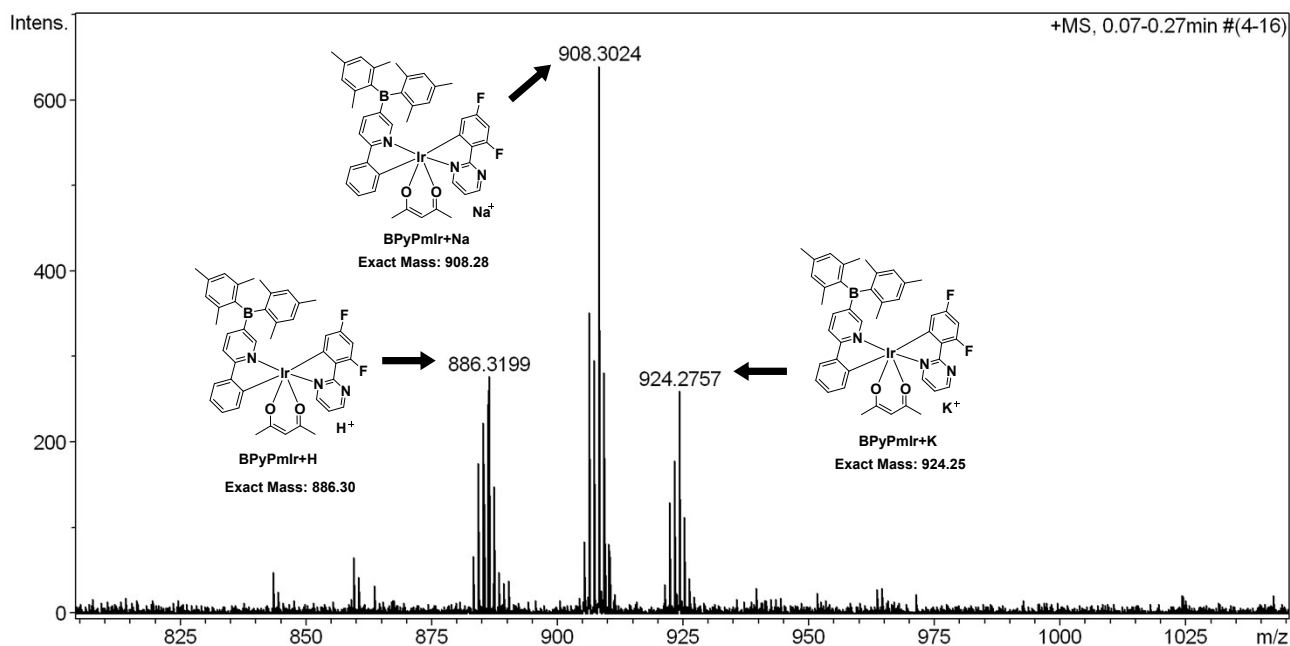
**OLED Fabrication and Measurements** The ITO glass substrates were pre-cleaned and exposed to ultraviolet-ozone for ca. 10 min. The PEDOT:PSS was spin-coated on the surface of ITO glass substrates to form a hole-injection layer and annealed at  $120\text{ }^\circ\text{C}$  for 30 min in the air. Then, the chlorobenzene solution containing the complex and TCTA was spin-coated on surface of PEDOT:PSS layer to form the emission layer. After drying at  $60\text{ }^\circ\text{C}$  for 10 min, the TPBI layer, LiF

and Al cathode was vacuum-deposited in deposition system. The EL spectra were measured with a PR650 spectra colorimeter. The driving voltages and efficiencies of the devices were measured with the Keithley 2602 and Source Meter. All the experiments and measurements were carried out under ambient conditions.

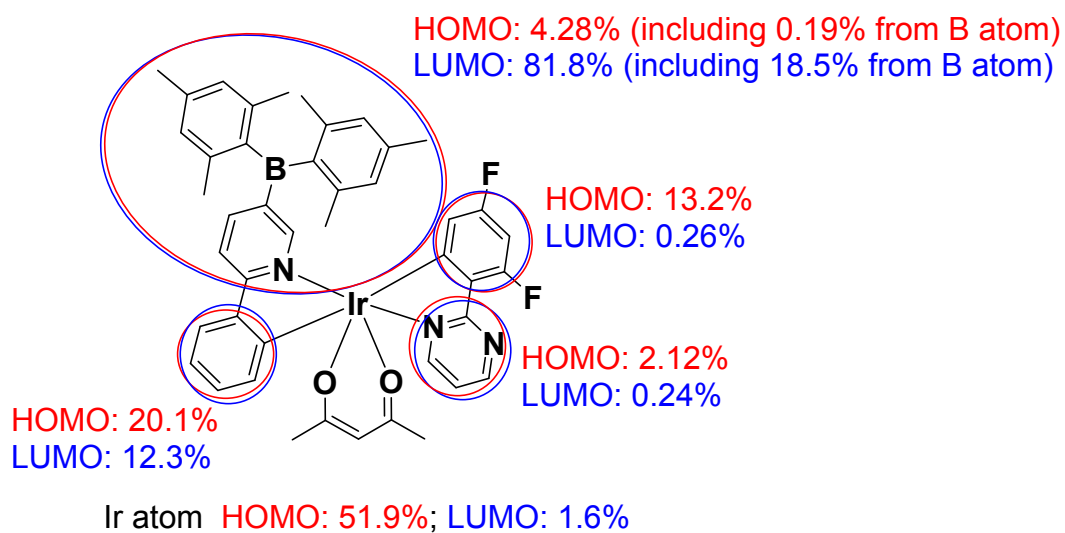
**Synthesis of 2-(2,4-difluorophenyl)pyrimidine (Pm):** Under a N<sub>2</sub> atmosphere, 2-chloropyrimidine (0.38 g, 3.3 mmol), (2, 4-difluorophenyl)boronic acid (0.51 g, 3.2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.17 g, 0.15 mmol) were added to a mixture of 1,2-dimethoxyethane (10 mL), ethanol (10 mL) and potassium carbonate solution (2M, 5 mL). The reaction mixture was heated to 90 °C and stirred for 12 h. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> several times. The organic layers were combined, dried over anhydrous sodium sulfate and concentrated. The residual was purified on a silica column using a mixture of petroleum ether and dichloromethane (v/v, 1:3) as eluent to give 0.53 g white solid in 86.2 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.50 (d, *J* = 4.8 Hz, 2H), 8.14–8.08 (m, 1H), 7.24 (t, *J* = 5.2 Hz, 1H), 7.02–6.92 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 165.42, 165.30, 162.96, 162.91, 162.84, 162.79, 162.71, 162.65, 160.39, 160.27, 159.76, 157.27, 133.21, 133.18, 133.11, 133.08, 122.80, 122.74, 119.14, 116.65, 111.72, 111.68, 111.51, 111.47, 105.31, 105.06, 104.80; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ): –106.76 (d, *J* = 11.3 Hz, 1F), –110.02 (d, *J* = 7.5 Hz, 1F).

**Synthesis of BPyPmIr:** Under a N<sub>2</sub> atmosphere, 5-(dimesitylboranyl)-2-phenylpyridine (BPy)<sup>2</sup> (0.28 g, 0.69 mmol), 2-(2,4-difluorophenyl)pyrimidine (Pm) (0.13 g, 0.68 mmol) and IrCl<sub>3</sub>•nH<sub>2</sub>O (0.22 g, 0.68 mmol) were added to a mixture of tetrahydrofuran and water (3:1, v/v) (30 mL). The reaction mixture was heated to 110 °C for 18 h with stirring. After cooling to room temperature, water (10 mL) was added to the reaction mixture. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> several times. The organic layers were combined, dried over anhydrous sodium sulfate and concentrated.

Without purification, together with thallium(I) acetylacetonate (0.2 g, 0.70 mmol), the residue were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) under a N<sub>2</sub> atmosphere. After stirring for 16 h at room temperature, the solvent was removed under reduced pressure and the residue was purified on preparative TLC plates to give the orange-red solid in 23.5 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.83 (d, *J* = 2.8 Hz, 1H), 8.66 (dd, *J* = 2.0 Hz, 5.6 Hz, 1H), 8.41 (s, 1H), 7.85–7.79 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 5.2 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 6.85 (s, 4H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.35–6.27 (m, 2H), 5.70 (dd, *J* = 2.0 Hz, 8.8 Hz, 1H), 5.13 (s, 1H), 2.30 (s, 6H), 2.07 (s, 12H), 1.78 (s, 3H), 1.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 185.50, 184.53, 175.02, 170.25, 157.12, 155.55, 154.94, 152.97, 147.82, 144.84, 144.05, 140.80, 140.37, 139.45, 138.30, 132.92, 129.95, 128.55, 127.78, 125.10, 121.64, 118.12, 116.88, 115.36, 115.20, 100.82, 98.02, 97.76, 97.50, 28.14, 28.01, 23.46, 21.23; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ): –105.85 (d, *J* = 11.3 Hz, 1F), –109.75 (d, *J* = 11.3 Hz, 1F); MS (*m/z*): 908.3 [M+Na]<sup>+</sup>.



**Fig. S1** The MS spectrum of **BPyPmIr**.



**Fig. S2** Contributions from each fragments in **BPyPmIr** to HOMO and LUMO.

**Table S1** Theoretical calculation results for **BPYPmIr** based on the optimized  $S_0$  geometry

Complex	Stat	$\lambda^{\text{cal.}}$	$f$	Composition	Assignment
	e				
<b>BPYPmIr</b>	$S_1$	501 nm	0.0763	HOMO→LUMO (96.6%)	MLCT/LLCT/ $\pi\pi^*$
	$T_1$	550 nm	0.0000	HOMO→LUMO (88.7%)	MLCT/LLCT/ $\pi\pi^*$

**Table S2** NTO results for **BPYPmIr** and **BPYPThIr** based on optimized  $T_1$  geometries

Complexes	NTOs	Contribution from metal center orbitals and ligand orbitals to NTOs (%)			
		<b>Ir</b>	<b>BPY</b>	<b>Pm</b>	<b>acac</b>
<b>BPYPmIr</b>	Hole	40.80	46.51	8.10	4.59
	Particle	4.24	93.77	0.74	1.25
<b>BPYPThIr</b>	Hole	44.98	38.83	10.81	5.38
	Particle	4.13	93.65	0.99	1.23

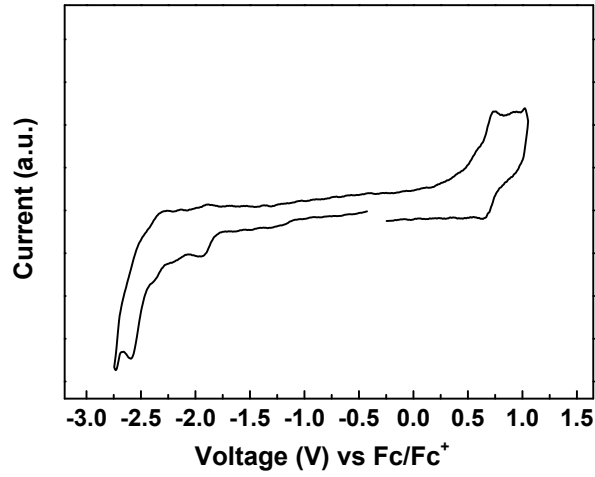


Fig. S3 The CV curve of BPyPmIr.

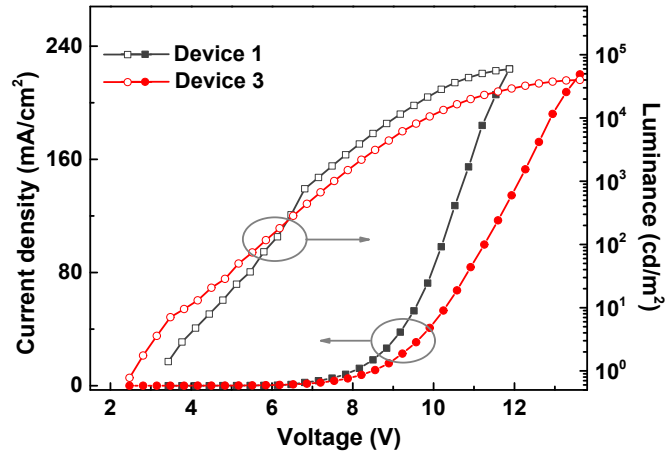


Fig. S4 The  $J$ - $V$ - $L$  curves of Device 1 and Device 3.

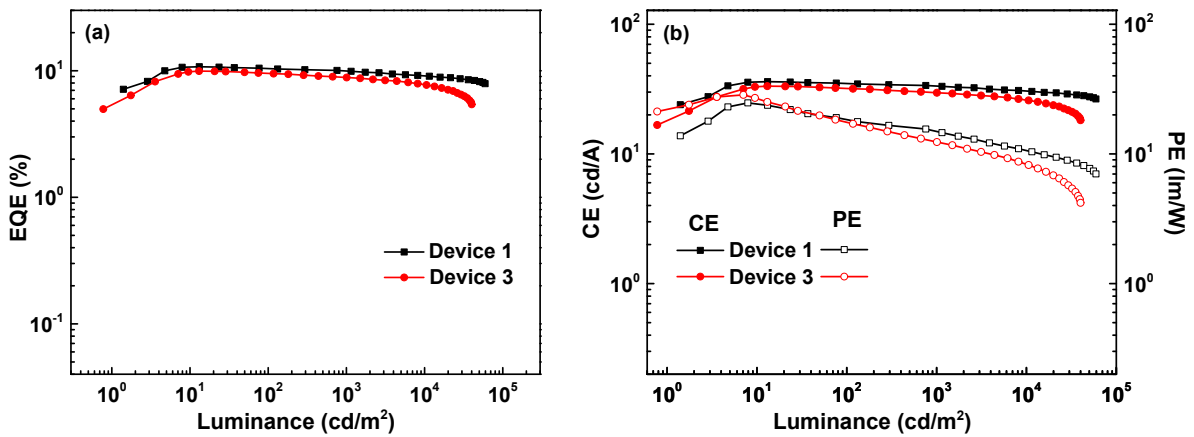
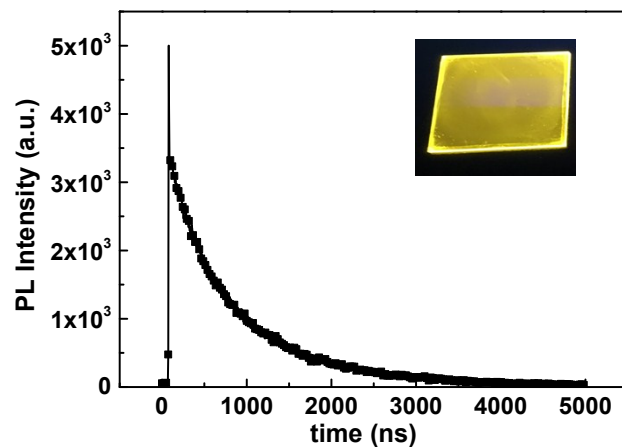
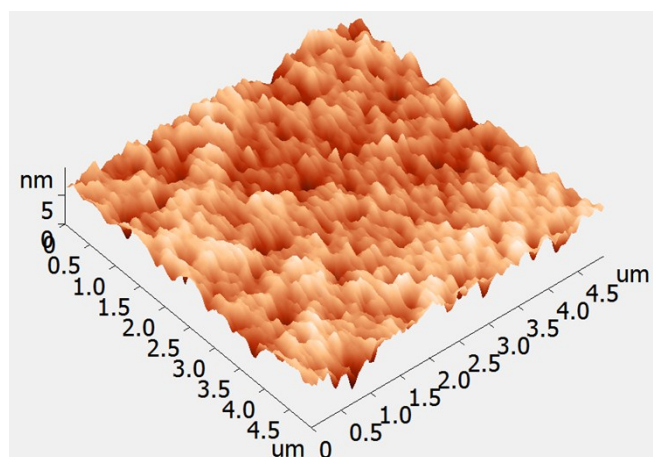


Fig. S5 The plots of (a) EQE and (b) CE and PE versus luminance for Device 1 and Device 3.

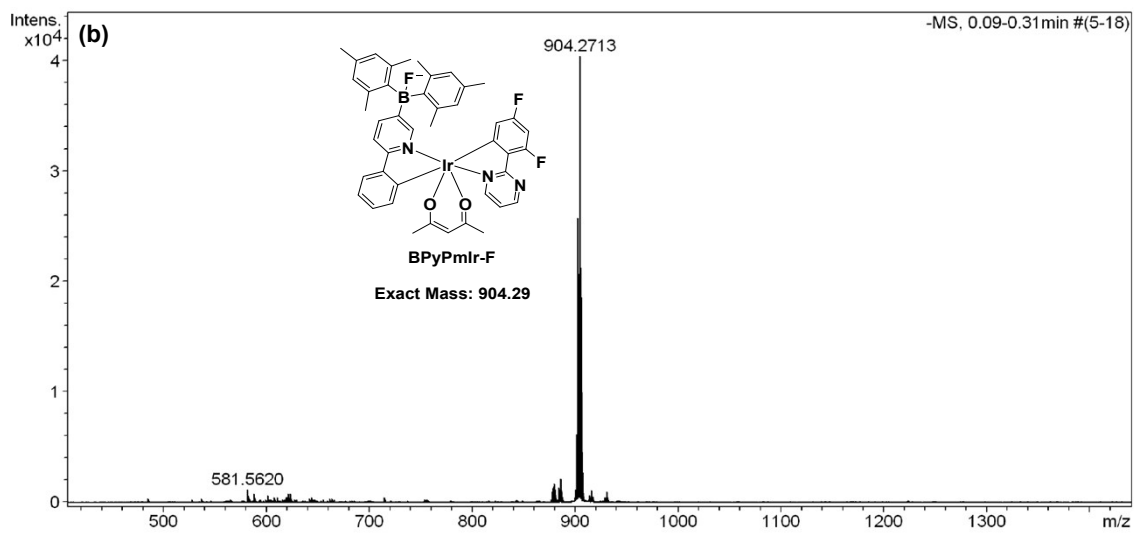
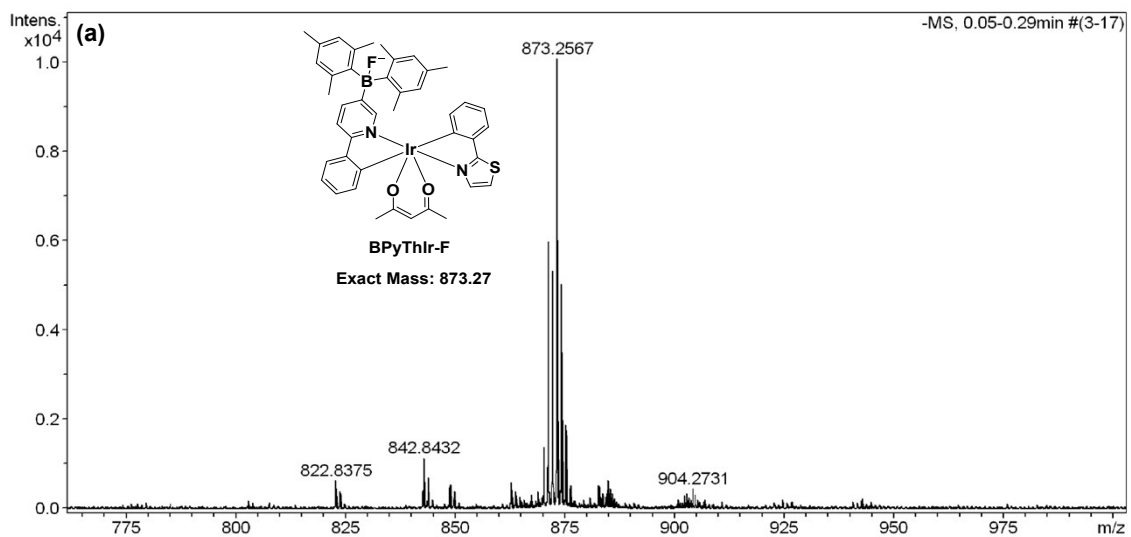


**Fig. S6** The decay curve of the TCTA film doped with 10 wt% **BPyPmIr** (The inset is a picture of this film irradiated under 365 nm).



**Fig. S7** The atomic force microscope (AFM) topographic image of 10 wt% **BPyPmIr** doped TCTA film ( $S_q = 1.17$  nm).





**Fig. S8** MS spectra of the adductions for (a) **BPyThIr-F** and (b) **BPyThIr-F**.

**Table S3** Contribution from metal center orbitals and ligand orbitals to HOMO and LUMO of **BPYPmIr-F**

and **BPYPhIr-F** based on optimized  $S_0$  geometries

Complexes	MOs	Contribution from metal center orbitals and ligand orbitals to HOMO and LUMO (%)			
		Ir	BPY-F	Pm	acac
<b>BPYPmIr-F</b>	HOMO	30.61	58.08	7.11	4.20
	LUMO	6.31	1.53	90.15	2.01
<b>BPYThIr-F</b>	HOMO	45.95	36.08	13.03	4.94
	LUMO	3.85	1.19	93.85	1.11

**Table S4** Theoretical calculation results for **BPYPmIr-F** and **BPYPhIr-F** based on the optimized  $S_0$ 

geometry

Complex	Stat	$\lambda^{\text{cal.}}$	$f$	Composition
<b>BPYPmIr-F</b>	$S_1$	499 nm	0.0042	HOMO $\rightarrow$ LUMO (67.6%)
				HOMO-1 $\rightarrow$ LUMO (27.3%)
	$T_1$	528 nm	0.0000	HOMO $\rightarrow$ LUMO (61.3%)
				HOMO-1 $\rightarrow$ LUMO (26.9%)
<b>BPYThIr-F</b>	$S_1$	510 nm	0.0244	HOMO $\rightarrow$ LUMO (94.3%)
	$T_1$	568 nm	0.0000	HOMO $\rightarrow$ LUMO (81.0%)

**Table S5** NTO results for **BPYPmIr-F** and **BPYPThIr-F** based on optimized  $T_1$  geometries

Complexes	NTOs	Contribution from metal center orbitals and ligand orbitals to NTOs (%)			
		Ir	BPY-F	Pm	acac
<b>BPYPmIr-F</b>	Hole	51.82	18.39	21.48	8.31
	Particle	8.45	1.88	86.80	2.87
<b>BPYPThIr-F</b>	Hole	39.79	8.75	48.40	3.06
	Particle	5.94	1.05	91.52	1.49

## References

- 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox. *Gaussian 09, Revision A.01*, Gaussian, Inc.: Wallingford CT, 2009.

- 2 X. Yang, N. Sun, J. Dang, Z. Huang, C. Yao, X. Xu, C.-L. Ho, G. Zhou, D. Ma, X. Zhao and W.-Y. Wong, *J. Mater. Chem. C*, 2013, **1**, 3317-3326.