

## **Supporting Information**

### **Solution-Processable Highly Efficient Deep-Red and Orange Organic Light-Emitting Diodes Based on Multi-functional Ir(III) complexes.**

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## Device fabrication and measurements

Patterned indium tin oxide (ITO) glass substrate with a sheet resistance of 10  $\Omega$  per square was washed with a cleaning detergent (Sigma-Aldrich, Micro-90 concentrated cleaning solution) followed by deionized water, acetone, and isopropyl alcohol in ultrasonic bath at 50 °C. Shortly after this cleaning cycle, the ITO glass was treated in UV-ozone chamber for 20 min. Firstly, deep-red PhOLEDs were fabricated by the following method. A 40 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) [PEDOT:PSS (Clevios P VP AI4083)] was coated onto the substrate and baked at 150 °C for 20 min on a hot plate in air. In case of the devices consisting of gradient hole injection layer (GraHIL), GraHIL was coated onto the substrate and baked in air at 150 °C for 30 min, with 40 nm thick film.<sup>1-3</sup> Chlorobenzene (CB) was used as the solvent for processing of the emitting layer (EML). The EML, which is a mixed solution of TCTA:TPBi (weight ratio, 1:1)<sup>4</sup> doped with 10 wt% of the Ir(III) complex, was spin-coated onto the PEDOT:PSS or GraHIL coated substrate. Here, the Ir(III) complexes that were evaluated as dopants for the deep-red PhOLEDs are TPQIr-HT, TPQIr, and TPQIr-ET with the configuration of ITO/PEDOT:PSS or GraHIL (40 nm)/EML (40 nm)/TmPyPB (20 nm)/LiF (1 nm)/Al (100 nm). The EML was then annealed at 80 °C for 30 min in glove box. A 20 nm thickness of TmPyPB was evaporated in vacuum at pressure  $5 \times 10^{-6}$  Torr. The deposition rate of electron transport layer (ETL) was 1 Å/s. Finally, lithium fluoride (LiF) and aluminium (Al) were evaporated under  $5 \times 10^{-6}$  Torr in a vacuum chamber at deposition rates of 0.1 Å/s and 5 Å/s, respectively. The emitting area of PhOLED device was 9 mm<sup>2</sup> for all the samples.

The orange PhOLEDs were fabricated by the following method. A 40 nm thick layer of PEDOT:PSS was coated onto the substrate and baked at 150 °C for 20 min on a hot plate. CB was used as the solvent for processing of the EML. The EML, which is a mixed solution of

TAPC:26DCzPPy (weight ratio, 2:3) doped with 10 wt% of the Ir(III) complex, was spin-coated onto the PEDOT:PSS coated substrate. Here, the Ir(III) complexes that were evaluated as dopants for the orange PhOLEDs are *m*-CF<sub>3</sub>DPQIr, *m*-CF<sub>3</sub>DPQIr-HT, and *m*-CF<sub>3</sub>DPQIr-ET with the configuration of ITO/PEDOT:PSS (40 nm)/EML (40 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm). The EML was then annealed at 100 °C for 30 min in glove box. A 50 nm thickness of TmPyPB was evaporated in vacuum at pressure  $5 \times 10^{-6}$  Torr. The deposition rate of ETL was 1 Å/s. Finally, LiF and Al were evaporated under  $5 \times 10^{-6}$  Torr in a vacuum chamber at deposition rates of 0.1 Å/s and 5 Å/s, respectively. The emitting area of PhOLED device was 9 mm<sup>2</sup> for all the samples.

All measurements were carried out under ambient condition at room temperature. The thickness of each layer was measured by an Alpha-step IQ surface profiler (KLA Tencor, San Jose, CA). The current density and voltage were controlled with a measurement unit (Keithley, model 236) power source. The luminance, current efficiency, external quantum efficiency, Commission International de L'Eclairage (CIE) coordinates (x, y), current density characteristics, and electroluminescence spectra were measured by a spectra scan CS-2000 photometer (Minolta).

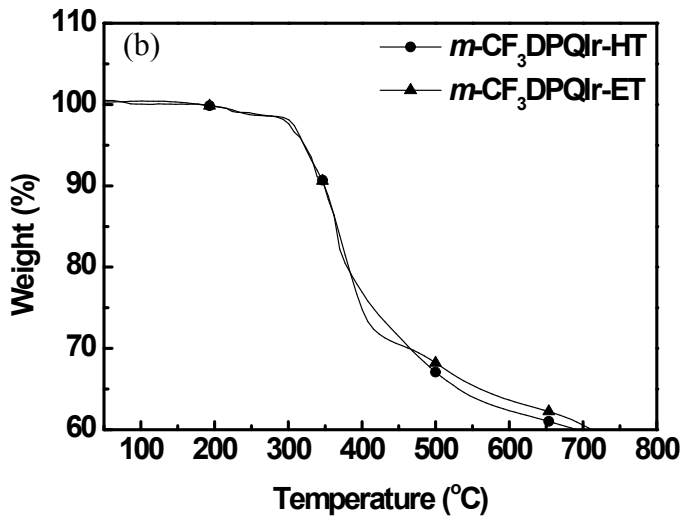
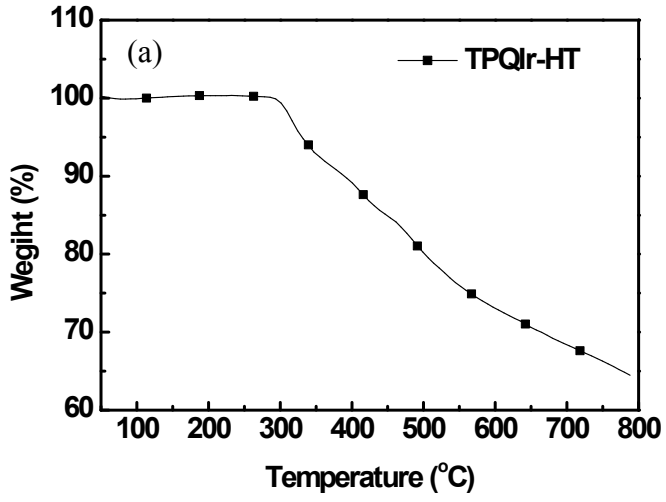
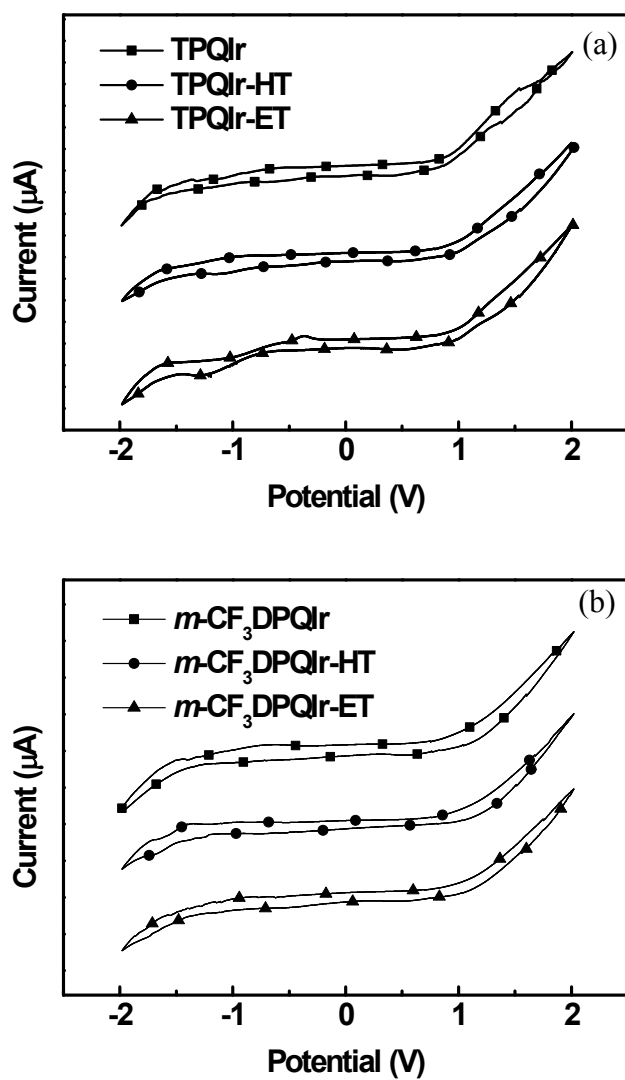
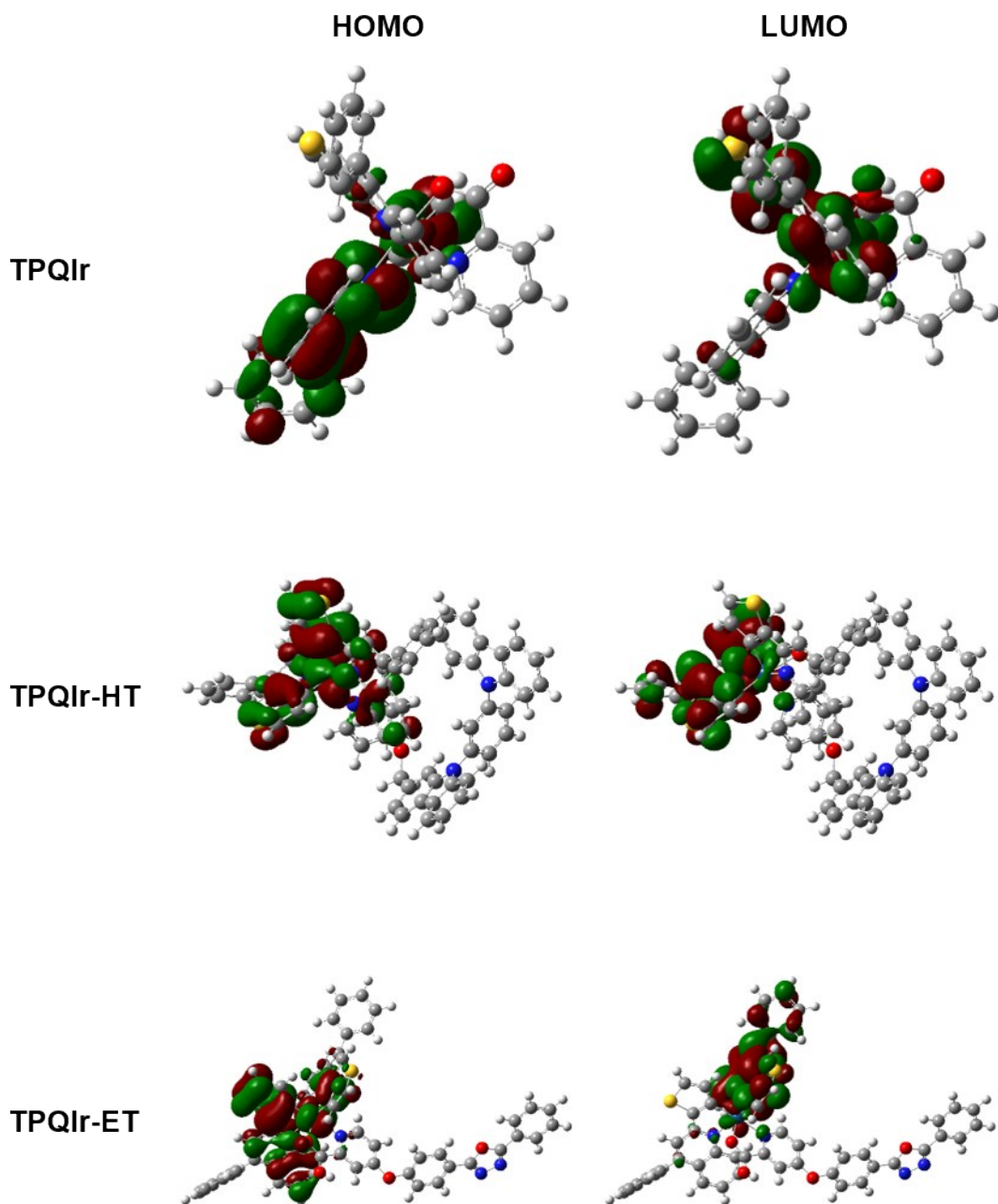


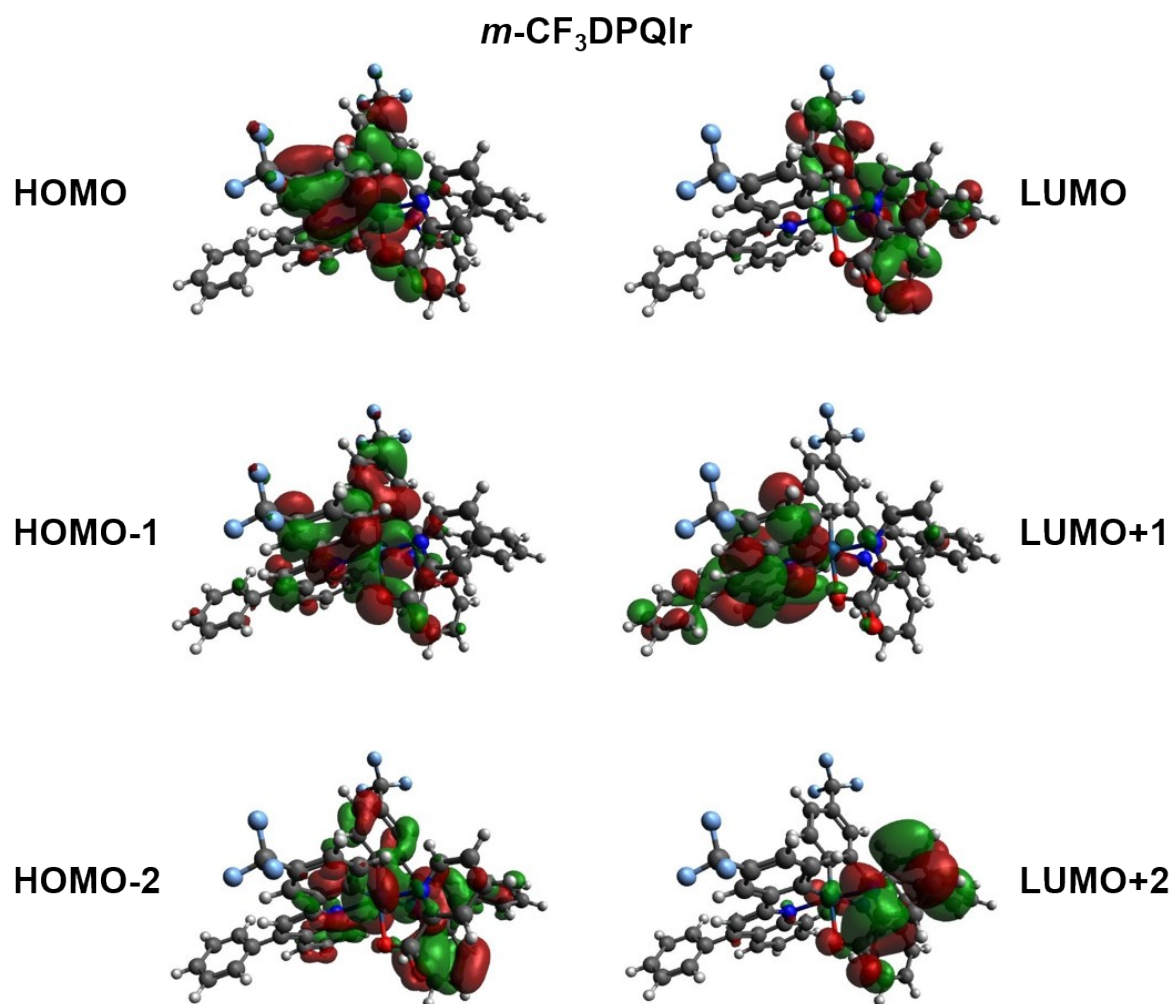
Fig. S1. (a) TGA curve of TPQIr-HT and (b) TAG curve of  $m$ -CF<sub>3</sub>DPQIr-HT and  $m$ -CF<sub>3</sub>DPQIr-ET measured at a scan rate of 10 °C/min under a N<sub>2</sub> atmosphere.



**Fig. S2.** (a) Cyclic voltammograms (CV) of TPQIr, TPQIr-HT and TPQIr-ET and (b) CV of *m*-CF<sub>3</sub>DPQIr, *m*-CF<sub>3</sub>DPQIr-HT and *m*-CF<sub>3</sub>DPQIr-ET measured in CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 100 mV/s.

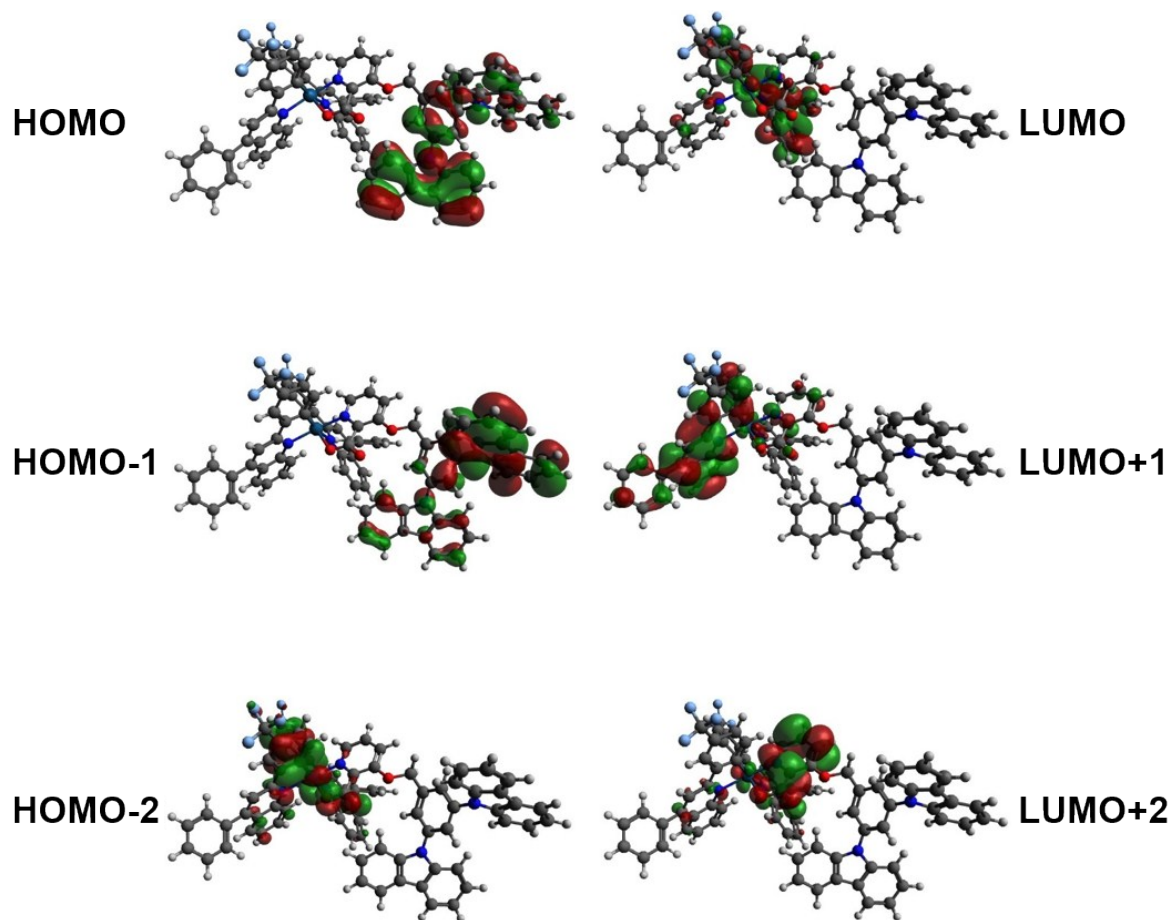


**Fig. S3.** HOMOs and LUMOs of the optimized geometries of deep-red Ir(III) Complexes from DFT calculation.



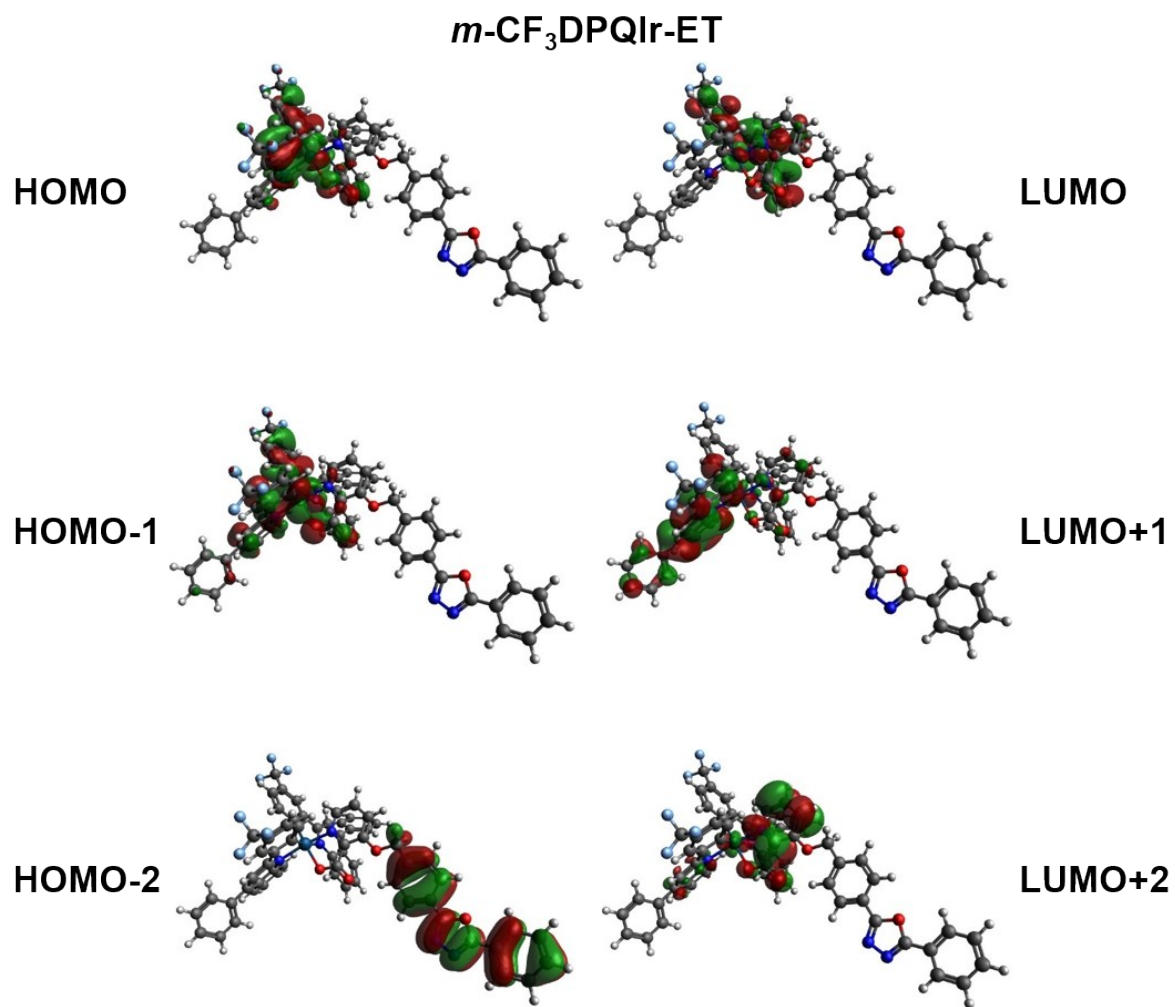
**Fig. S4.** Contour plots of HOMO to HOMO-2 and LUMO to LUMO+2 for *m*-CF<sub>3</sub>DPQIr from DFT.

*m*-CF<sub>3</sub>DPQIr-HT

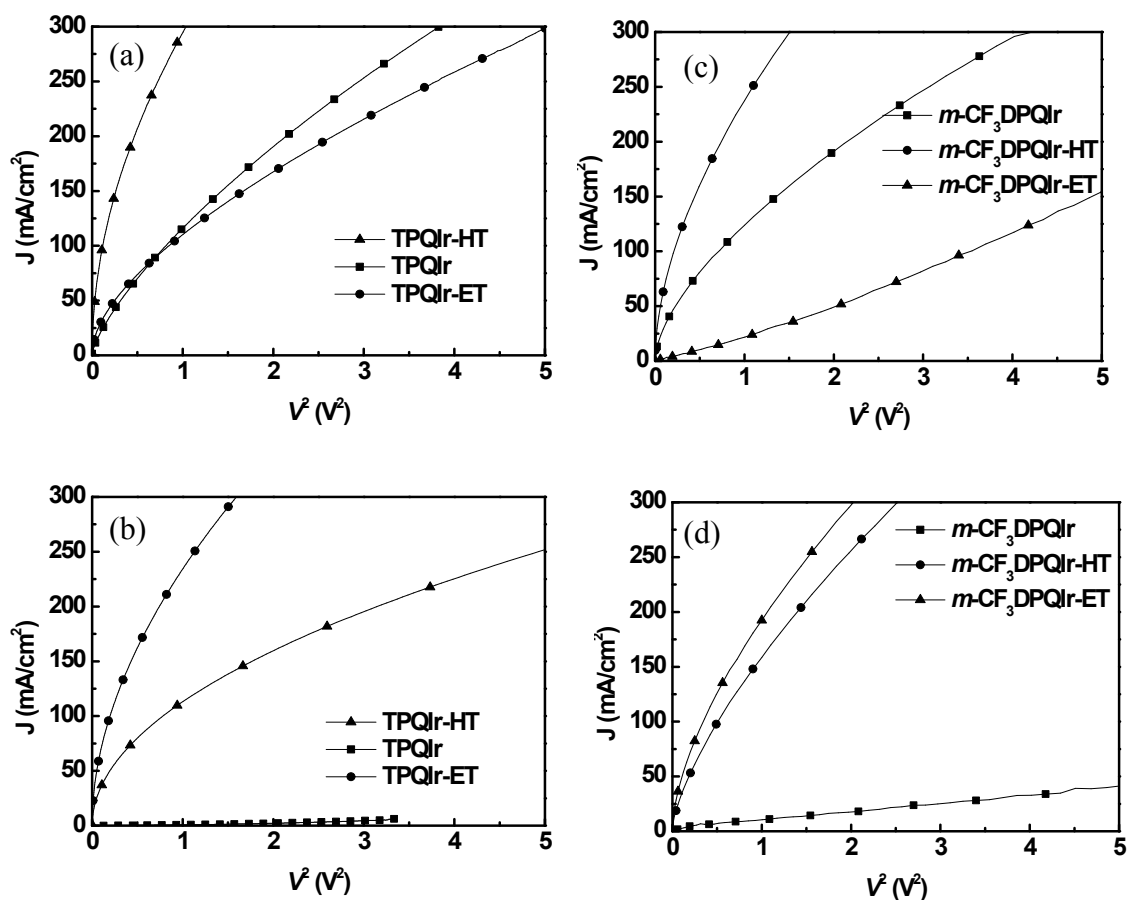


**Fig. S5.** Contour plots of HOMO to HOMO-2 and LUMO to LUMO+2 for *m*-CF<sub>3</sub>DPQIr-HT from DFT.

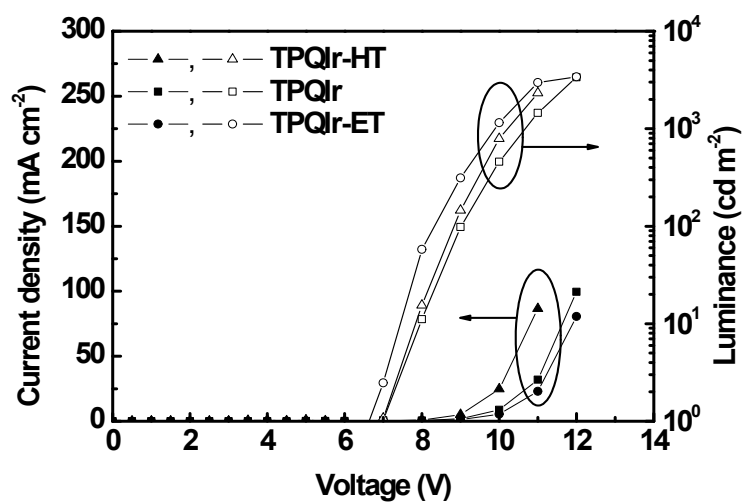




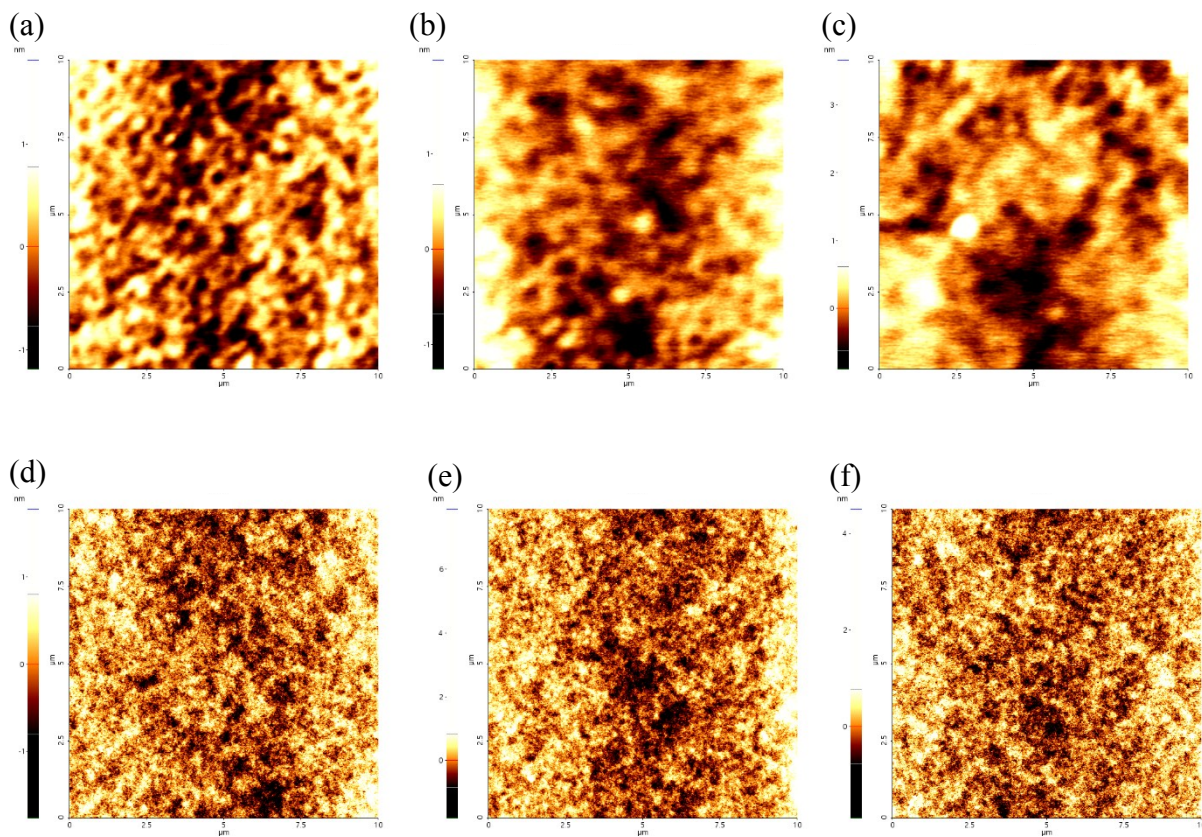
**Fig. S6.** Contour plots of HOMO to HOMO-2 and LUMO to LUMO+2 for *m*-CF<sub>3</sub>DPQIr-ET from DFT.



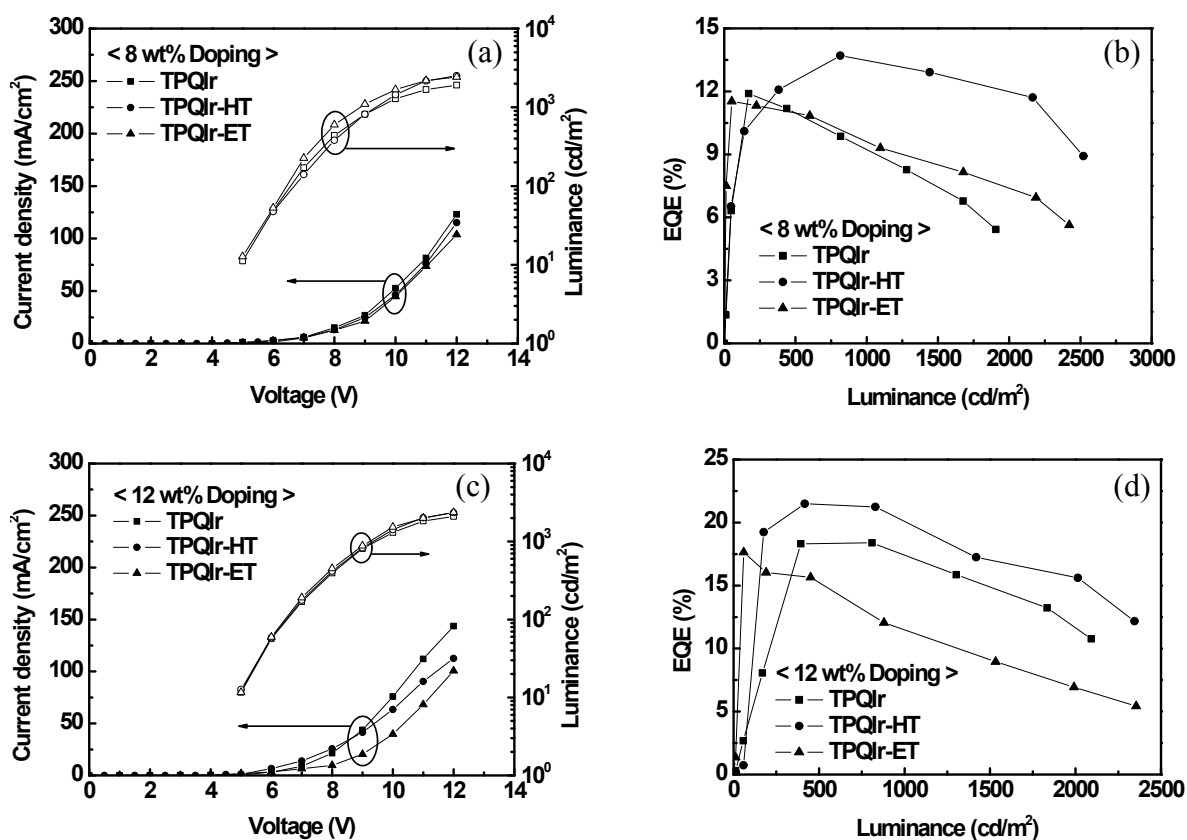
**Fig. S7.** (a), (c) Hole only device and (b), (d) electron only device of  $J$ - $V^2$  characteristics [ITO/LiF (10 nm)/Ir(III) complex (100 nm)/LiF (1 nm)/Al (100 nm) for electron-only device and ITO/PEDOT:PSS (40 nm)/Ir(III) complex (100 nm)/MoO<sub>3</sub> (5 nm)/Al (100 nm) for hole-only device].



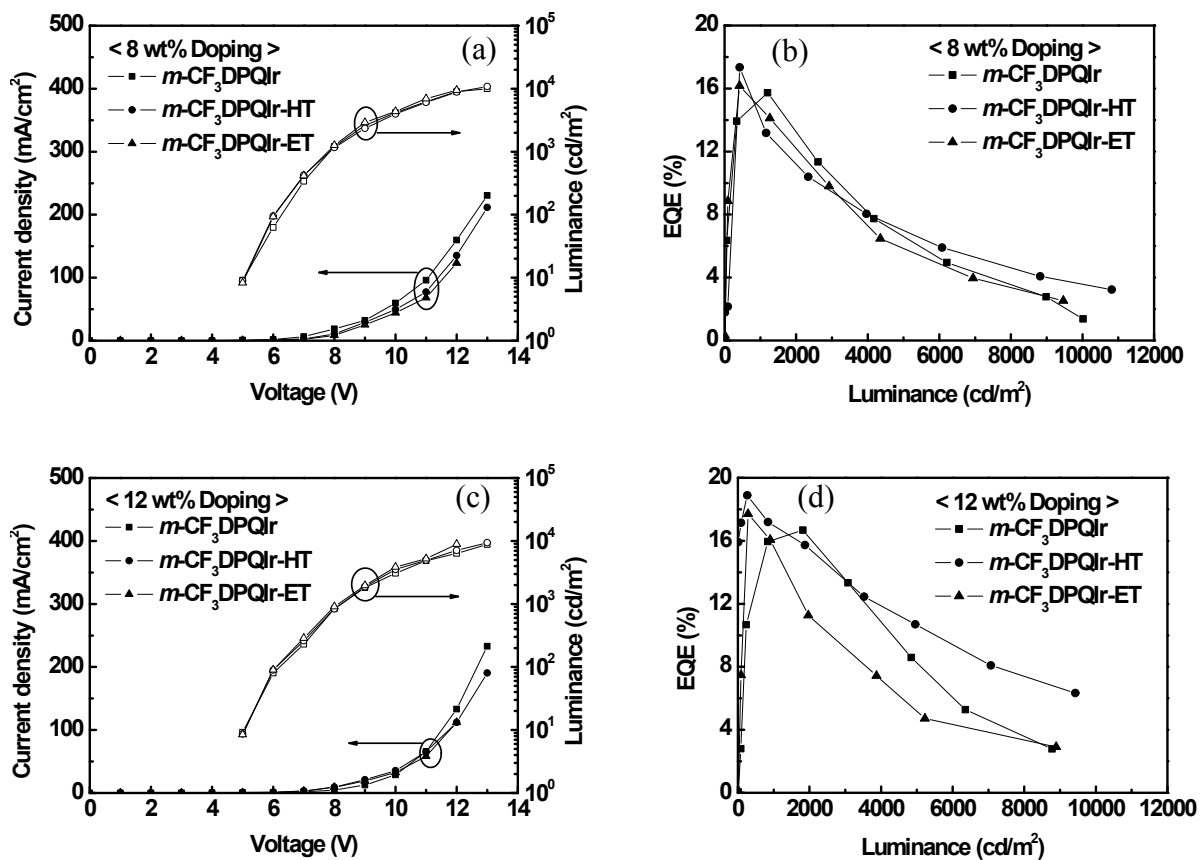
**Fig. S8.** Current density-voltage-luminance (J-V-L) characteristics of the deep-red PhOLEDs using PEDOT:PSS as HIL.



**Fig. S9.** (a) AFM topographic images of TCTA:TPBi:TPQIr (b) TCTA:TPBi:TPQIr-HT (c) TCTA:TPBi:TPQIr-ET films formed by the spin-coating process and (d) AFM topographic images of TAPC:26DCzPPy:*m*-CF<sub>3</sub>DPQIr (e) TAPC:26DCzPPy:*m*-CF<sub>3</sub>DPQIr-HT (f) TAPC:26DCzPPy:*m*-CF<sub>3</sub>DPQIr-ET films formed by the spin-coating process



**Fig. S10.** (a) Energy level diagram (b) EQE vs Luminance of the PhOLED of deep-red Ir(III) complexes at doping concentration of 8 wt% and (c) Energy level diagram (d) EQE vs Luminance of the PhOLED of deep-red Ir(III) complexes at doping concentration of 12 wt%.



**Fig. S11.** (a) Energy level diagram (b) EQE vs Luminance of the PhOLED of orange Ir(III) complexes at doping concentration of 8 wt% and (c) Energy level diagram (d) EQE vs Luminance of the PhOLED of orange Ir(III) complexes at doping concentration of 12 wt%.

**Table S1.** Frontier molecular orbital energies [eV] of the orange Ir(III) complexes from DFT

Molecular Orbital	<i>m</i> -CF <sub>3</sub> DPQIr [eV]	<i>m</i> -CF <sub>3</sub> DPQIr-HT [eV]	<i>m</i> -CF <sub>3</sub> DPQIr-ET [eV]
LUMO+2	1.75	1.88	1.83
LUMO+1	2.11	2.14	2.11
LUMO	2.15	2.16	2.13
HOMO	5.52	5.26	5.49
HOMO-1	5.75	5.44	5.70
HOMO-2	6.18	5.53	5.99

**Table S2.** Mobility data for TPQIr-HT in comparison with TPQIr & TPQIr-ET.

Ir(III) complex	Hole mobility (cm <sup>2</sup> /V s)	Electron mobility (cm <sup>2</sup> /V s)
TPQIr	1.28 x 10 <sup>-4</sup>	5.42 x 10 <sup>-6</sup>
TPQIr-HT	2.84 x 10 <sup>-4</sup>	8.72 x 10 <sup>-5</sup>
TPQIr-ET	7.35 x 10 <sup>-5</sup>	5.42 x 10 <sup>-4</sup>
<i>m</i> -CF <sub>3</sub> DPQIr	1.64 x 10 <sup>-4</sup>	3.22 x 10 <sup>-5</sup>
<i>m</i> -CF <sub>3</sub> DPQIr-HT	6.02 x 10 <sup>-4</sup>	1.75 x 10 <sup>-4</sup>
<i>m</i> -CF <sub>3</sub> DPQIr-ET	8.32 x 10 <sup>-5</sup>	5.03 x 10 <sup>-4</sup>



Device	Dopant	HIL	Turn on <sup>a</sup> (V)	EQE <sup>b</sup> (%)	CE <sup>b</sup> (cd/A)	PE <sup>b</sup> (lm/W)	L <sub>max</sub> <sup>b</sup> (cd/m <sup>2</sup> )	CIE at 10 cd/m <sup>2</sup> (x, y)	CIE at 100 cd/m <sup>2</sup> (x, y)
I	TPQIr-HT	PEDOT:PSS	6.99	15.88	14.30	4.08	2325	(0.67, 0.32)	(0.67, 0.32)
II	TPQIr	PEDOT:PSS	7.01	11.90	10.41	3.22	3368	(0.67, 0.32)	(0.67, 0.32)
III	TPQIr-ET	PEDOT:PSS	6.70	19.68	17.34	4.95	3404	(0.67, 0.32)	(0.67, 0.32)

**Table S3.** Device performances of the PhOLEDs with the Ir(III) complexes as dopants.

<sup>a</sup> At 1 cd/m<sup>2</sup>. <sup>b</sup> Maximum efficiency.

**Table S4.** Summary of the state-of-the-art device performances of solution-processed red/deep-red PhOLEDs.

Year	Previous literature	CIE coordinates (x, y)	LE, PE	EQE
2007	Ref. [5]	(0.65, 0.33)	12.7 cd/A, -	15.1%
2008	Ref. [6]	(0.64, 0.36)	4.6 cd/A, 0.67 lm/W	-
2010	Ref. [7]	(0.61, 0.38)	4.2 cd/A, -	3.2%
2010	Ref. [8]	(0.59, 0.39)	21 cd/A, 11 lm/W	14.2%
2011	Ref. [9]	(0.64, 0.36)	13.3 cd/A, 8.6 lm/W	10.2%
2012	Ref. [10]	(0.65, 0.35)	12 cd/A, 7.9 lm/W	10.8%
2014	Ref. [11]	(0.64, 0.34)	26 cd/A, 12.6 lm/W	21%
2014	Ref. [12]	(0.67, 0.32)	17.20 cd/A, 6.72 lm/W	20.59%
2015	Ref. [13]	(0.68, 0.31)	5.8 cd/A, 6.5 lm/W	8.2%
2016	Ref. [14]	(0.64, 0.36)	32.4 cd/A, 44.5 lm/W	19.3%
2017	Our work	(0.67, 0.32)	19.70 cd/A, 5.62 lm/W	21.48%

**Table S5.** Summary of the state-of-the-art device performances of solution-processed orange PhOLEDs.

Year	Previous literature	CIE coordinates (x, y)	CE, PE	EQE
2007	Ref. [15]	(0.52, 0.47)	11.19 cd/A, 2.69 lm/W	3.94%
2008	Ref. [16]	(0.50, 0.36)	3.8 cd/A, 0.44 lm/W	-
2009	Ref. [17]	(0.60, 0.38)	7.70 cd/A, 3.26 lm/W	4.45%
		(0.60, 0.38)	6.51 cd/A, 2.37 lm/W	3.80%
2010	Ref. [18]	(0.58–0.59, 0.41)	20.0 cd/A, 16.8 lm/W	10.8%
2012	Ref. [19]	(0.60, 0.40)	14.49 cd/A, 7.38 lm/W	8.73%
2012	Ref. [20]	(0.531, 0.466)	49.7 cd/A, 43.9 lm/W	17.6%
2013	Ref. [21]	(0.53, 0.46)	20.18 cd/A, -	7.81%
2013	Ref.[22]	(0.526, 0.469)	18.5 cd/A, 6.9 lm/W	7.0%
		(0.600, 0.397)	26.9 cd/A, 12.1 lm/W	14.2%
2014	Ref. [23]	(0.57, 0.42)	12.4 cd/A, 6.6 lm/W	8.8%
2015	Ref [24]	(0.52, 0.47)	73.4 cd/A, 97.2 lm/W	25.2%
2016	Ref. [25]	(0.53, 0.46)	43.90 cd/A, 22.98 lm/W	17.14 %
2017	Our work	(0.54, 0.46)	52.16 cd/A, 24.56 lm/W	21.64%

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