

Supplementary Information for

Power-efficient solution-processed red organic light-emitting diodes based on exciplex host and novel phosphorescent iridium complex

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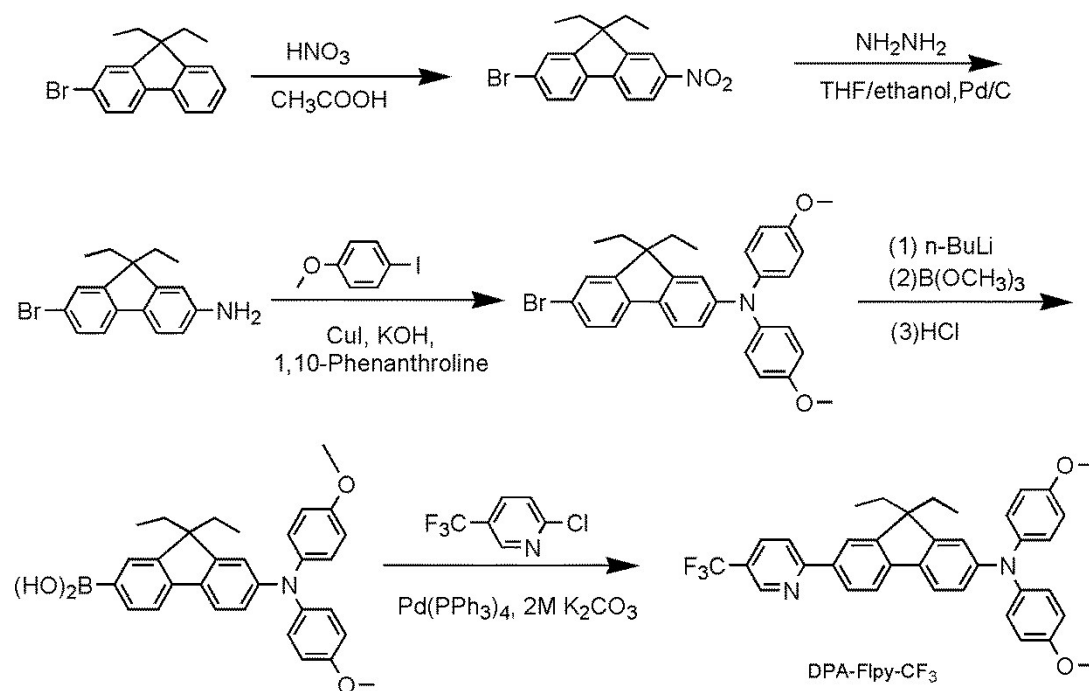


Figure S1. Synthesis of the organic ligand DPA-FIpy-CF₃ of the iridium complex.

Synthesis of 2-bromo-7-nitro-9,9-diethylfluorene:

2-Bromo-9,9-diethylfluorene (3.01g, 10.00mmol) was dissolved in glacial acetic acid (40 mL) in a round-bottom flask. The reaction mixture was chilled to 15°C in an ice/water bath and then fuming nitric acid (6mL) was added dropwise. After adding the nitric acid, the reaction mixture was allowed to room temperature and then it was stirred for 4 h. The mixture was poured into ice water, and then extracted with ethyl acetate (EA). The combined organic phase was washed with water. The organic phase was separated and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography eluting with CH₂Cl₂/hexane. The product was obtained as yellow solid. ¹HNMR (400 MHz, CDCl₃) δ [ppm] 8.27 (dd, 1H), 8.19 (d, 1H), 7.79 (t, 1H), 7.69 – 7.62 (m, 1H), 7.59 – 7.49 (m, 2H), 2.19 – 2.00 (m, 4H), 0.38 – 0.30 (t, 6H). ¹³CNMR (101 MHz, CDCl₃) δ [ppm]

152.58, 149.84, 146.42, 145.81, 137.10, 129.79, 125.67, 122.69, 122.49, 121.43, 118.91, 117.35, 56.02, 31.42, 7.36.

Synthesis of 2-amino-7-bromo-9,9-diethylfluorene:

A mixture of Palladium/activated carbon (300mg) and 2-bromo-7-nitro-9,9-diethylfluorene (1.50g, 4.33mmol) was suspended in ethanol/THF (50mL/50 mL). The mixture was heated to reflux. Hydrazine hydrate (10mL) in ethanol (50mL) was added dropwise, and then the mixture was refluxed overnight. After cooling to room temperature, the resulting mixture was filtered and extracted with EA. The combined organic phase was washed with water. The organic phase was separated and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography eluting with CH₂Cl₂/hexane. The pure product was obtained as a brown solid. ¹HNMR (400 MHz, CDCl₃) δ [ppm] 7.47 – 7.35 (m, 4H), 6.69 – 6.63 (m, 2H), 3.79 (dd, 2H), 2.01 – 1.86 (m, 4H), 0.30-0.36 (t, 6H). ¹³CNMR (101 MHz, CDCl₃) δ [ppm] 151.53, 151.28, 146.37, 141.10, 131.73, 129.77, 125.92, 120.63, 119.64, 119.05, 114.16, 109.67, 56.19, 32.88, 8.48.

Synthesis of (7-bromo-9,9-diethylfluoren-2-yl)di(p-methoxyphenyl)amine:

4-Iodoanisole (0.93g, 3.93mmol), 2-amino-7-bromo-9,9-diethylfluorene, 1,10-phenanthroline (0.5g, 1.58mmol), CuI (30mg,0.16mmol) and KOH (0.61g,10.87mmol) were added to the p-xylene (20mL) under argon atmosphere. The reaction mixture was stirred vigorously and refluxed for 36 h. After the solution cooled to room temperature, the mixture was poured into water and extracted with EA. Then the organic layer was washed with water three times and dried over MgSO₄. After the

solvent was evaporated, the crude product was purified by column chromatography using CH₂Cl₂/hexane as the eluent. The pure product was obtained as a white solid.

¹HNMR (400 MHz, CDCl₃) δ [ppm] 7.49 – 7.34 (m, 4H), 7.10 – 7.00 (m, 4H), 6.95 – 6.75 (m, 6H), 3.80 (s, 6H), 1.97 – 1.77 (m, 5H), 0.32-0.38 (t, 6H).

¹³CNMR (101 MHz, CDCl₃) δ [ppm] 155.66, 151.95, 150.84, 148.70, 141.39, 140.69, 133.62, 129.91, 126.10, 126.03, 120.63, 120.23, 120.07, 119.62, 116.09, 114.70, 56.29, 55.51, 32.62, 8.57.

Synthesis of ligand DPA-Flpy-CF₃:

Pd(PPh₃)₄ (40 mg) was added to a mixture of compound (9,9-diethylfluoren-2-yl)di(p-methoxyphenyl)amine boronic acid (2.83g, 5.73mmol)(synthesized from (7-bromo-9,9-diethylfluoren-2-yl)di(p-methoxyphenyl)amine, n-butyl lithium and trimethyl borate in a dry ice-acetone bath), and 2-chloro-5-(trifluoromethyl)pyridine (0.80 g, 4.41mmol) in toluene (40 mL) and 2 M aqueous K₂CO₃ (4mL) under an inert atmosphere of argon. The reaction was heated to 110°C for 24 h. After the mixture was cooled to room temperature, water was added and the solution mixture was extracted with EA. The combined organic layer was dried over MgSO₄ and was filtered and concentrated under reduced pressure. The residue was purified by column chromatography eluting with CH₂Cl₂/hexane. The title product was obtained as a yellowish-green solid. ¹HNMR (400 MHz, CDCl₃) δ [ppm] 9.03 – 8.87 (m, 1H), 7.98 (ddd, *J* = 7.8, 6.4, 3.6 Hz, 3H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.14 – 6.79 (m, 10H), 3.81 (s, 6H), 2.10 – 1.84 (m, 4H), 0.38 (t, *J* = 7.3 Hz, 6H). ¹³CNMR (101 MHz, CDCl₃) δ 161.04, 155.71, 152.00, 150.52, 149.00,

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146.40, 143.97, 141.30, 135.12, 133.87, 133.84, 133.70, 126.41, 126.20, 125.22,
124.39, 124.06, 122.51(CF₃), 121.48, 120.69, 120.45, 119.79, 119.04, 115.93,
114.68(Ar), 56.23(Quat. C), 55.50(OMe), 32.67, 8.63(Et).

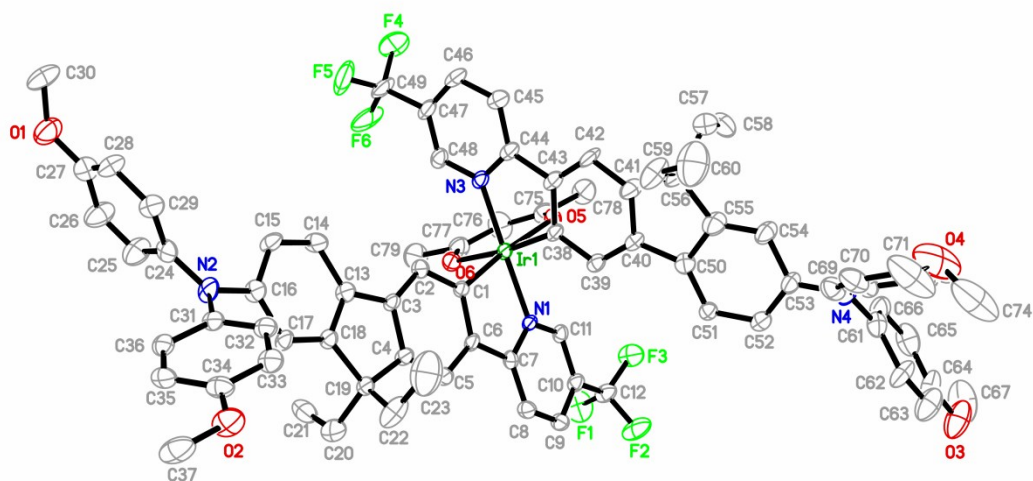


Figure S2. ORTEP diagram of the complex Ir(DTA-Flpy-CF₃)₂acac, solvent molecules removed for clarity.

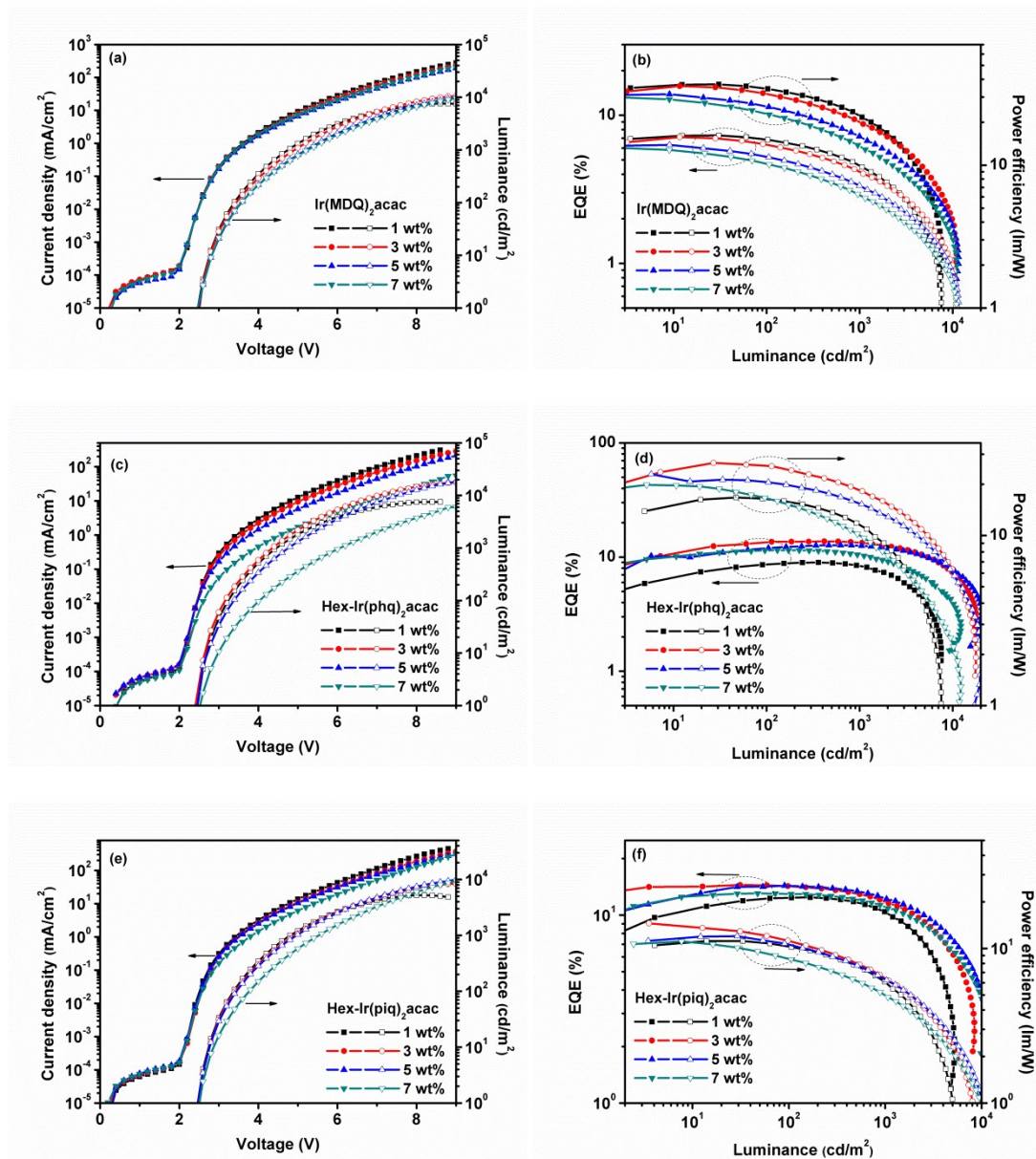


Figure S3. J-L-V and efficiency characteristics of the solution-processed red PhOLEDs with Ir(MDQ)₂acac (a, b), Hex-Ir(phq)₂acac (c, d) and Hex-Ir(piq)₂acac (e, f) as phosphorescent dopants, respectively.

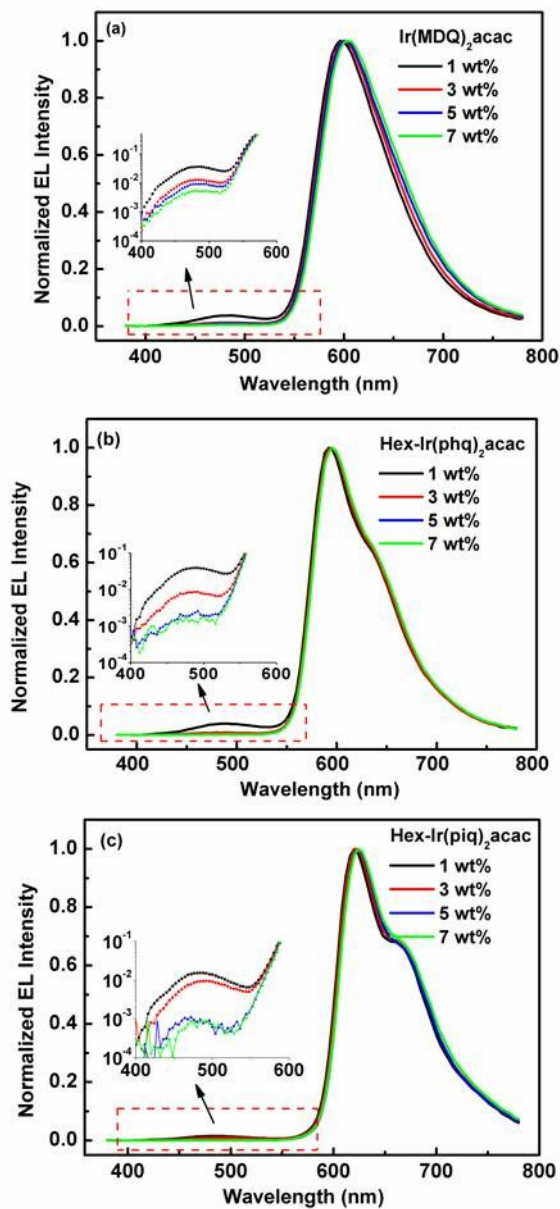


Figure S4. EL spectra of the red s-PhOLEDs (at a luminance of 100cd/m²) with Ir(MDQ)₂acac (a), Hex-Ir(phq)₂acac (b) and Hex-Ir(piq)₂acac (c) as phosphorescent dopants at different doping concentrations.

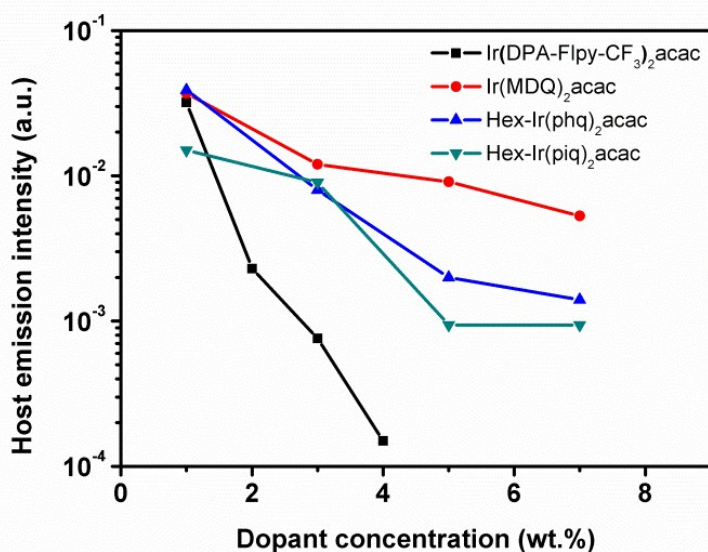


Figure S5. The derived exciplex emission intensity for red-PhOLEDs with different phosphor, i.e. Ir(DTA-Flpy-CF₃)₂acac, Ir(MDQ)₂acac, Hex-Ir(phq)₂acac and Hex-Ir(piq)₂acac, at different doping concentrations. (the host emission intensity is the exciplex EL intensity at 480nm for each normalized EL spectra shown in Figure 5 in main text and Figure S4 in the SI). Obviously, the host emission in the Ir(DTA-Flpy-CF₃)₂acac based red s-PhOLEDs is the lowest value at each doping concentration (2-7wt.%), indicating the most efficient energy transfer process from the exciplex host to this dopant.

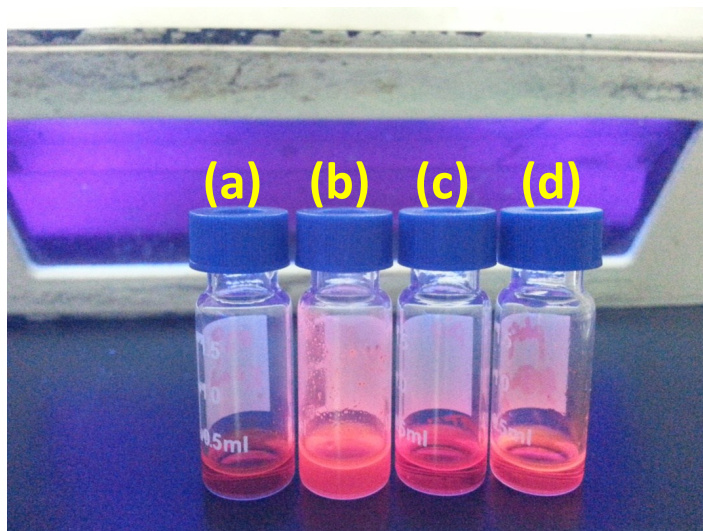


Figure S6. Under ultraviolet light radiation, the solution is as follows: (a) Ir(DPA-Flpy-CF₃)₂acac, (b) Ir(MDQ)₂acac, (c) Hex-Ir(piq)₂acac, (d) Hex-Ir(phq)₂acac (from left to right). The concentration of all the solution is 25 mg/mL in chlorobenzene. After adding the chlorobenzene, Ir(DPA-Flpy-CF₃)₂acac dissolved immediately, Hex-Ir(piq)₂acac, Hex-Ir(phq)₂acac dissolved for seconds, and Ir(MDQ)₂acac did not dissolve completely. The result indicates that the solubility of Ir(DPA-Flpy-CF₃)₂acac is best.

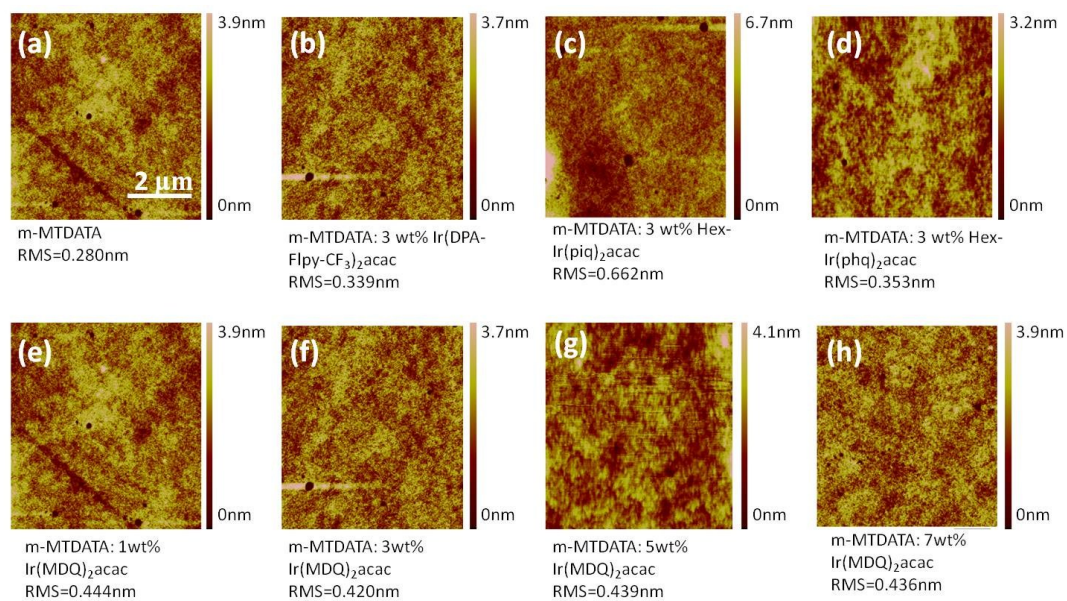


Figure S7. AFM topography images of pure m-MTDTA film and m-MTDTA doped films with different phosphors.

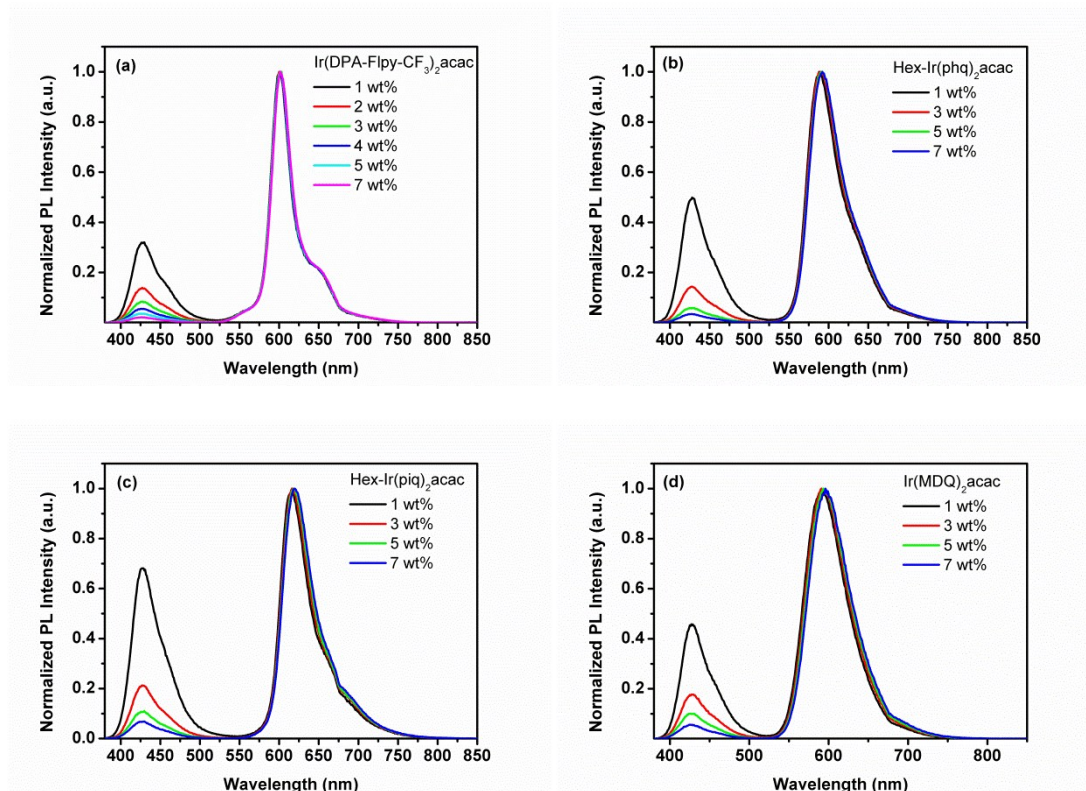


Figure S8. The PL spectra of m-MTDATA: emitters (a) Ir(DPA-Flpy-CF₃)₂acac (b)Hex-Ir(phq)₂acac, (c)Hex-Ir(piq)₂acac and (d)Ir(MDQ)₂acac films with different doping concentrations .All these films were excited at 344nm. As the doping concentration increasing from 1 wt% to 7 wt.%, the host emission is gradually lowered due to the enhanced host to guest energy transfer. Notice that the PL spectra of Hex-Ir(phq)₂acac, Hex-Ir(piq)₂acac and Ir(MDQ)₂acac had a slightly red shift with increasing the doping concentraion, indicating that aggregation process becomes more and more serious for these films.

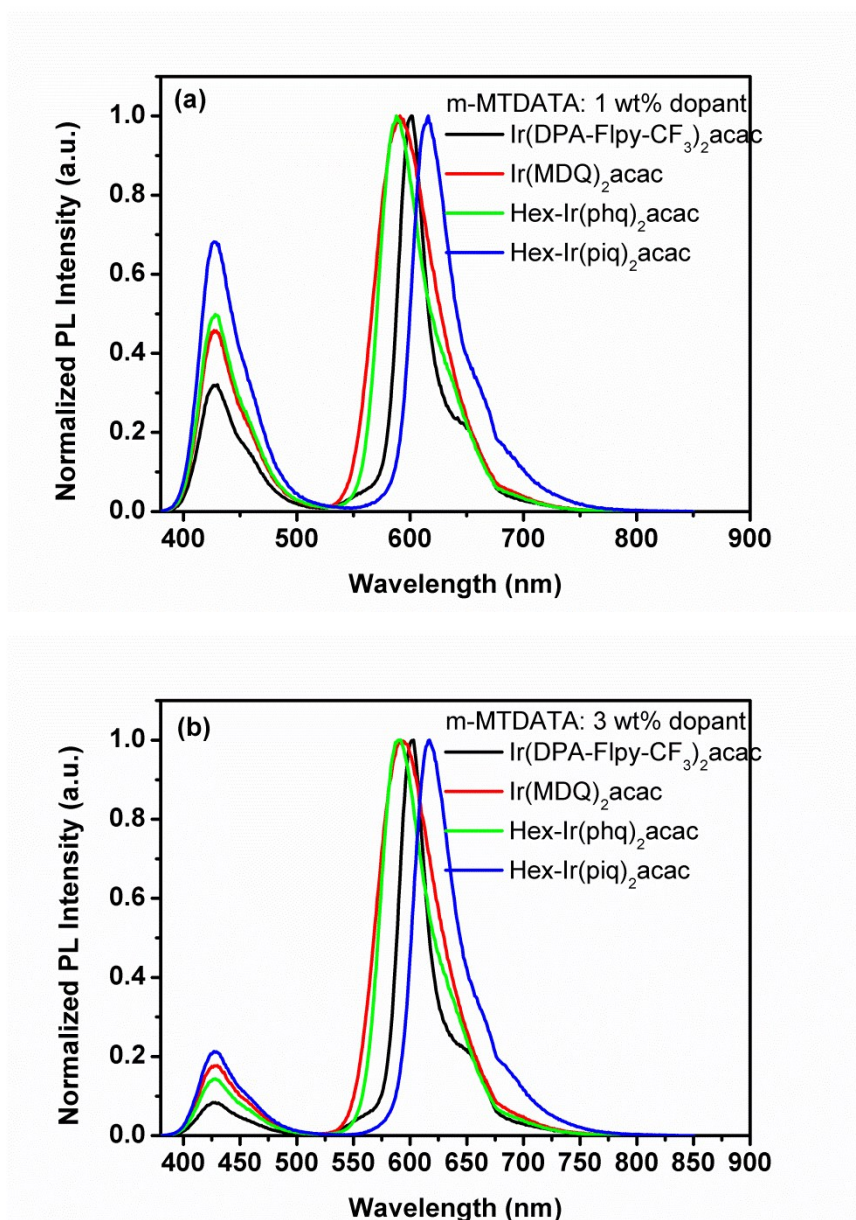


Figure S9. The PL spectra of m-MTDATA: emitters (Ir(DPA-FIpy-CF₃)₂acac Hex-Ir(phq)₂acac, Hex-Ir(piq)₂acac and Ir(MDQ)₂acac) films with different doping concentrations (a) 1 wt% (b) 3 wt%. All these films were excited at 344nm. At the same doping ratios, the host intensity of m-MTDATA: Ir(DPA-FIpy-CF₃)₂acac films is the lowest, indicating that energy transfer from host to this dopant is most efficient.

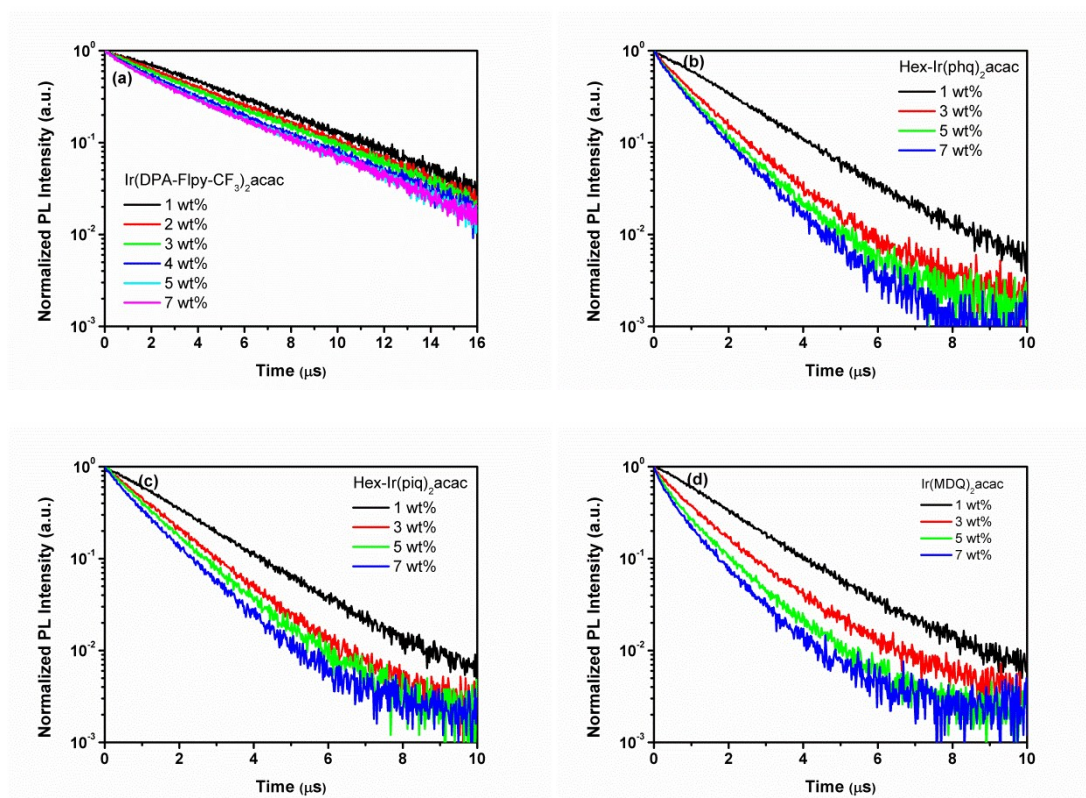


Figure S10. The transient phosphorescence decay spectra of m-MTDATA: dopants films with different ratios. All these films were excited at 375nm. Notice that as the doping concentration increasing from 1 wt% to 7 wt.%, the exciton lifetimes for Hex-Ir(phq)₂acac, Hex-Ir(piq)₂acac and Ir(MDQ)₂acac doped films were distinctly decreased, indicating that aggregation induced exciton quenching process is more serious for these samples as well as the corresponding devices.

Table S1 the lifetime of m-MTDATA: dopants films with different ratios.

m-MTDATA: dopant	Dopant ratio (wt.%)	A ₁	τ ₁ (μs)	A ₂	τ ₂ (μs)	τ _a (μs)
Ir(DPA-Flpy-CF ₃) ₂ acac	1		5.396			5.396
	2		4.459			4.459
	3	0.512	2.858	0.488	6.169	5.085
	4	0.258	1.440	0.742	4.515	4.208
	5	0.275	1.153	0.725	4.382	4.089
	7	0.268	1.073	0.732	4.254	3.985
Hex-Ir(phq) ₂ acac	1		1.875			1.875
	3	0.137	0.299	0.863	1.165	1.132
	5	0.252	0.321	0.748	1.082	1.013
	7	0.258	0.288	0.742	1.000	0.936
Hex-Ir(piq) ₂ acac	1		1.875			1.875
	3		1.305			1.305
	5	0.284	0.729	0.716	1.295	1.191
	7	0.226	0.417	0.774	1.135	1.065
Ir(MDQ) ₂ acac	1		1.750			1.750
	3	0.252	0.429	0.748	1.324	1.236
	5	0.399	0.338	0.601	1.147	1.015
	7	0.370	0.237	0.630	0.947	0.856

$$\tau_a = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

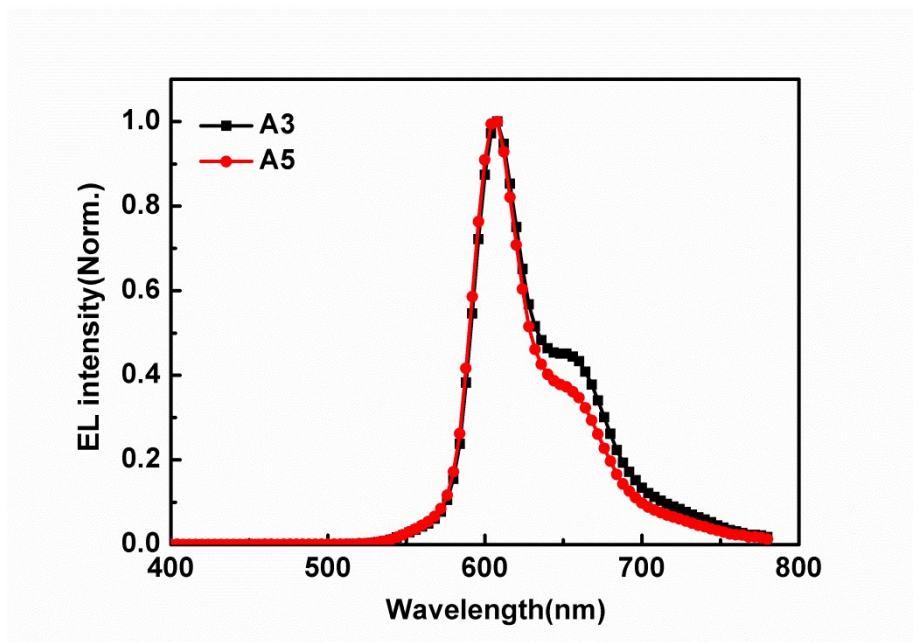


Figure S11. Electroluminescent spectra of the Ir(DPA-FIpy-CF₃)₂acac based red s-PhOLEDs using different ITO substrates with sheet resistance of 10 Ω/□ (A3) and 15 Ω/□ (A5), respectively.