

Supporting Information

Non-halogenated solvent-processed highly efficient green Ir(III) complexes with external quantum efficiency exceeding 23% for phosphorescent organic light-emitting diodes

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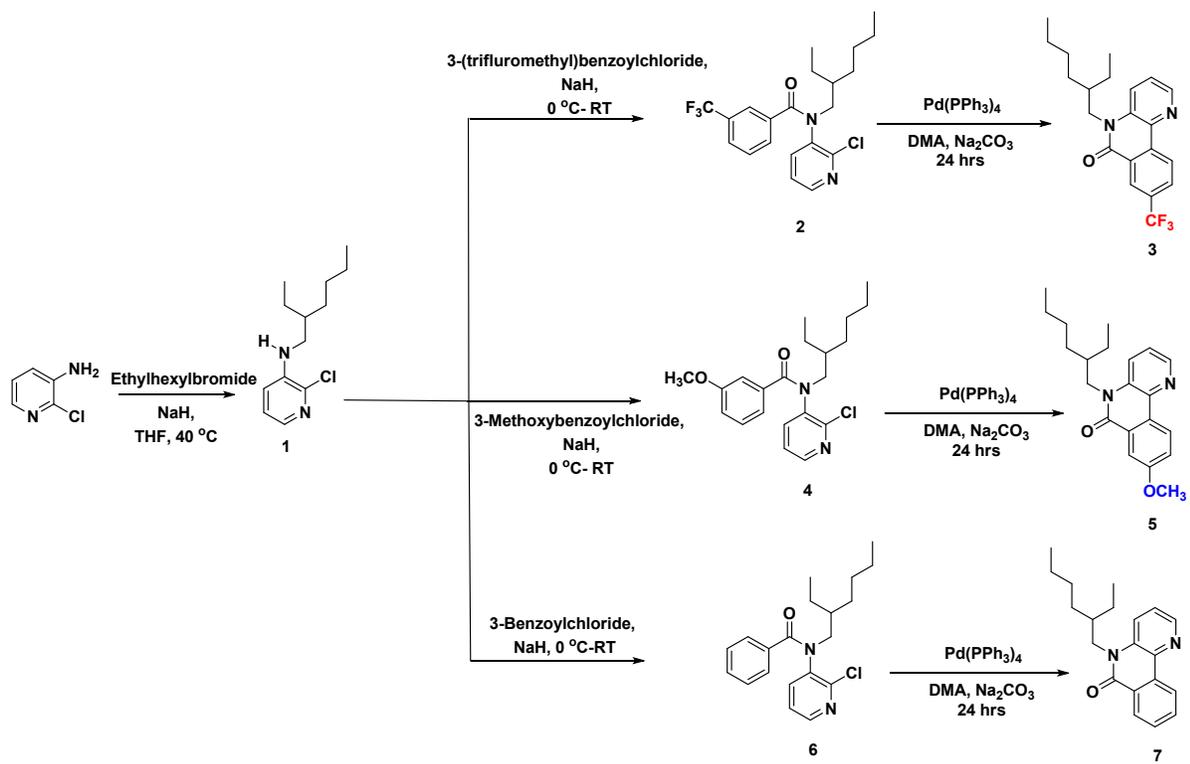
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General information

^1H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer in CDCl_3 using tetramethylsilane as an internal reference. The chemical shifts were reported in ppm relative to the singlet of DMSO-d_6 at 2.50 for the ^1H NMR. UV-visible and the emission spectra were recorded with a JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers at room temperature. Transient PL measurements were carried out using compact fluorescence lifetime spectrometer C11367 at room temperature. The absolute PLQYs of the doped films were measured using spectrofluorometer with an integrating sphere system (JASCO FP-8500) under an inert atmosphere. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e analyzer under N_2 atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Cyclic voltammetry (CV) studies were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 50 mV s^{-1} in anhydrous dichloromethane (CH_2Cl_2) solvent with 0.1 M TBAClO_4 as supporting electrolyte. A platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc^+).



Scheme S1. Synthetic routes of main ligands.

Synthetic procedures for main ligands

Synthesis of 2-chloro-N-(2-ethylhexyl)pyridin-3-amine (1). A solution of 3-amino-2-chloropyridine (10 g, 77.78 mmol) in anhydrous tetrahydrofuran (THF) (100 mL) was added to a suspension of sodium hydride (NaH) (3.1 g, 77.78 mmol, 60% dispersion in oil) and THF (50 mL) under N₂ atmosphere. The reaction mixture was stirred at room temperature (RT) for 3 h. Afterwards, 2-ethylhexyl bromide (11.66 mL, 77.78 mmol) was added and the reaction mixture was heated to 40 °C for 9 h. After cooling to RT, the solvent was removed and the crude material dissolved in DCM and filtered to remove any salt. The filtrate was purified by column chromatography on silica gel using ethyl acetate (EtOAc):n-hexane (10:90% v/v) as an eluent to afford compound **1** as a pale yellow liquid (8.5 g, yield: 85%). ¹H NMR (300 MHz, CDCl₃, δ): 7.64-7.63 (d, 1H), 7.06-7.02 (m, 1H), 6.84-6.81 (d, 1H), 4.33 (s, 1H), 3.01 (t, 2H), 1.57-1.55 (d, 1H), 1.41-1.28 (m, 8H), 0.87 (m, 6H).

Synthesis of N-(2-chloropyridin-3-yl)-N-(2-ethylhexyl)-3-(trifluoromethyl)benzamide (2). NaH (1.39 g, 58.14 mmol) was added to anhydrous THF (30 mL) and the mixture was cooled to 0 °C under N₂ atmosphere. Compound **1** (5 g, 29.07 mmol) was added to the reaction mixture and stirred for 1 h. After that, 3-(trifluoromethyl)benzoyl chloride (9.09 g, 43.61 mmol) was added and stirred for 8 h at RT. After completion of the reaction, the reaction mixture was quenched by the addition of ice cold water (50 mL). Finally, the organic layer was extracted with DCM, washed with brine solution and dried over anhydrous Na₂SO₄. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:n-hexane (10:90% v/v) as an eluent to afford **2** as a colorless liquid (3.5 g, yield: 70%). ¹H NMR (300 MHz, CDCl₃, δ): 8.25 (s, 1H), 7.45-7.56 (d, 4H), 7.32 (d, 1H), 7.18 (s, 1H), 7.18 (s, 1H), 4.15 (s, 1H), 3.25-3.23 (t, 1H), 1.32-1.22 (d, 8H), 0.98 (s, 6H).

Synthesis of 5-(2-ethylhexyl)-8-(trifluoromethyl)benzo[c][1,5]naphthyridin-6(5H)-one (3). The mixture of compound **2** (4 g, 10.62 mmol), Pd(PPh₃)₄ (0.6 g, 0.53 mmol), Na₂CO₃ (3.18 g, 53.10 mmol), and of 2-(dimethylamino)ethyl methacrylate (DMA) (30 mL) was stirred at 150 °C for 24 h. Then the reaction mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with DCM (100 mL) and the organic phase was dried over anhydrous Na₂SO₄. The solvent was evaporated off, and the solid residue was purified by column

chromatography on silica gel using EtOAc:n-hexane (10:90% v/v) as an eluent to afford **3** as a colorless liquid (3 g, yield: 75%). ¹H NMR (300 MHz, CDCl₃, δ): 8.99-8.96 (d, 1H), 8.79 (s, 1H), 8.61 (s, 1H), 8.03-8.01 (d, 1H), 7.73-7.70 (d, 1H), 7.51 (s, 1H), 4.38-4.27 (d, 2H), 1.90 (s, 1H), 1.40-1.29 (m, 8H), 0.94-0.87 (m, 6H).

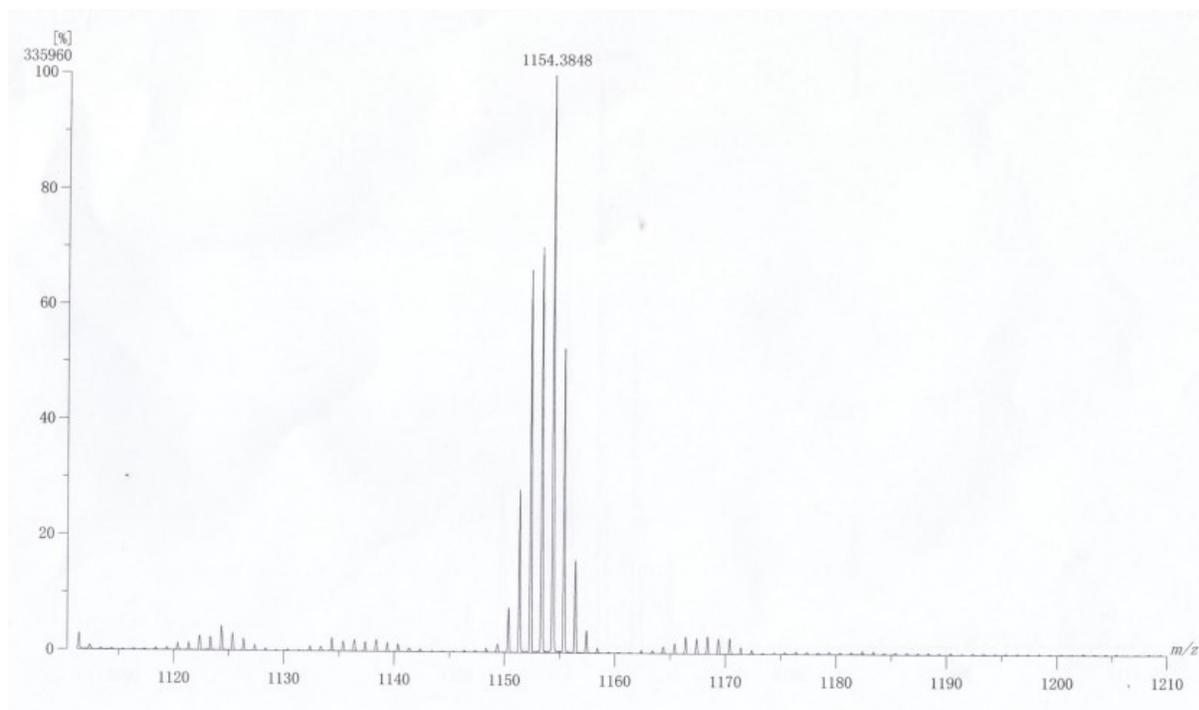
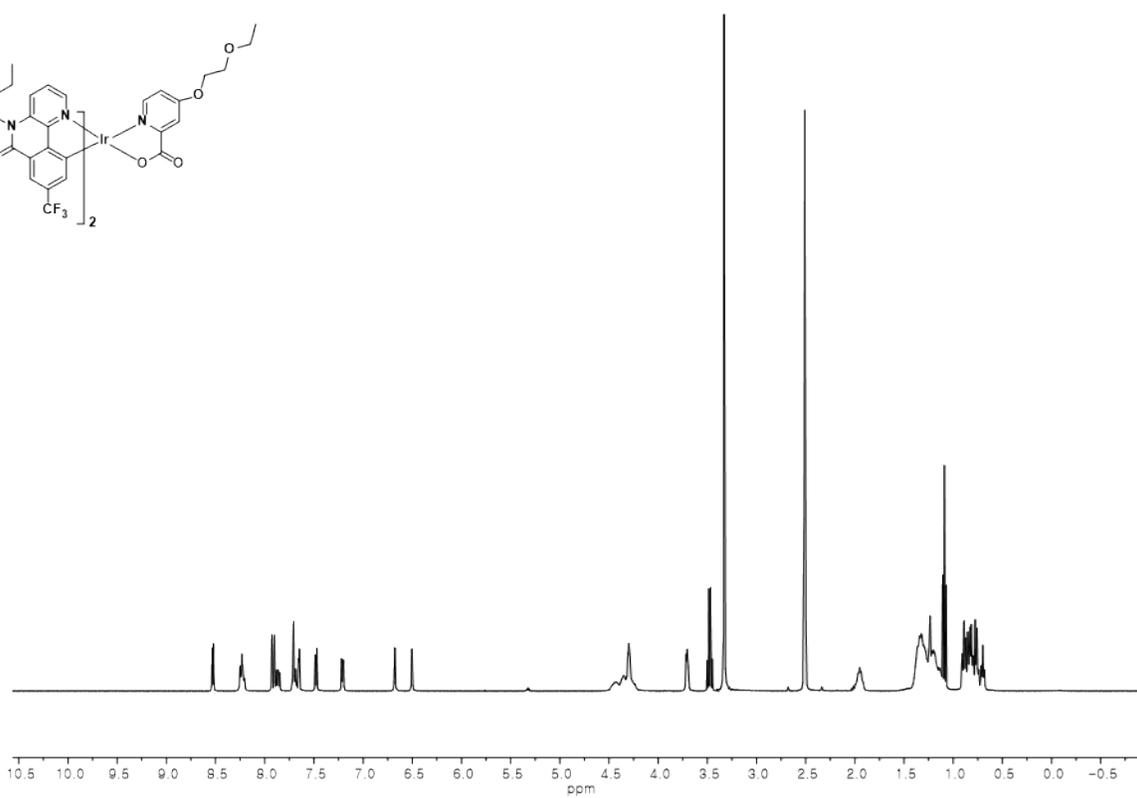
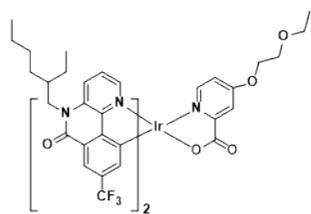
Synthesis of N-(2-chloropyridine-3-yl)-N-(2-ethylhexyl)-3-methoxybenzamide (4). NaH (1.66 g, 41.50 mmol) was added to anhydrous THF (30 mL) and the mixture was cooled to 0 °C under N₂ atmosphere. Compound (**1**) (5 g, 20.75 mmol) was added to the reaction mixture and stirred for 1 h. After that, 3-methoxybenzoyl chloride (4.25 mL, 31.15mmol) was added and stirred for 8 h at RT. After completion of the reaction, the reaction mixture was slowly quenched by the addition of ice cold water (50 mL). Finally, the organic layer was extracted with DCM, washed with brine solution and dried over anhydrous Na₂SO₄. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:n-hexane (10:90% v/v) as an eluent to afford **4** as a colorless liquid (3 g, yield: 63%). ¹H NMR (300 MHz, CDCl₃, δ): 8.24 (s, 1H), 7.71-7.37 (d, 2H), 7.13-7.05 (d, 2H), 6.85-6.77 (d, 2H), 4.32 (s, 1H), 3.69 (s, 3H), 3.43-3.34 (t, 1H), 1.46-1.25 (m, 8H), 0.89-0.82 (m, 6H).

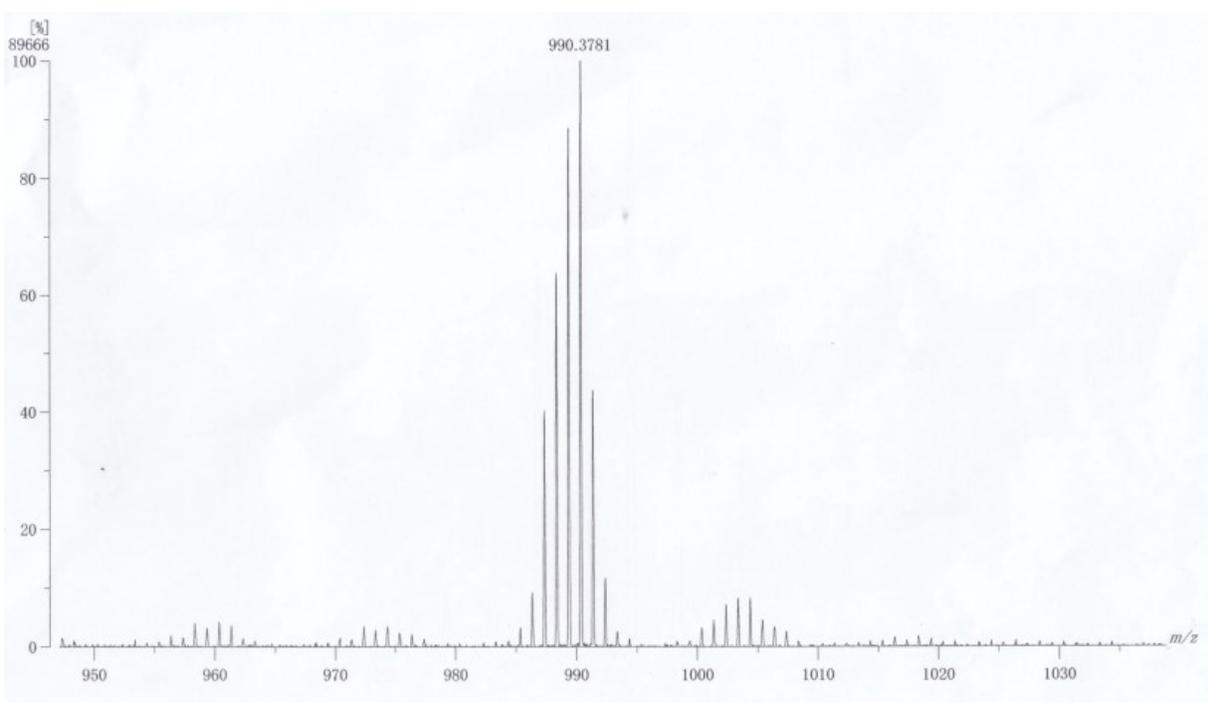
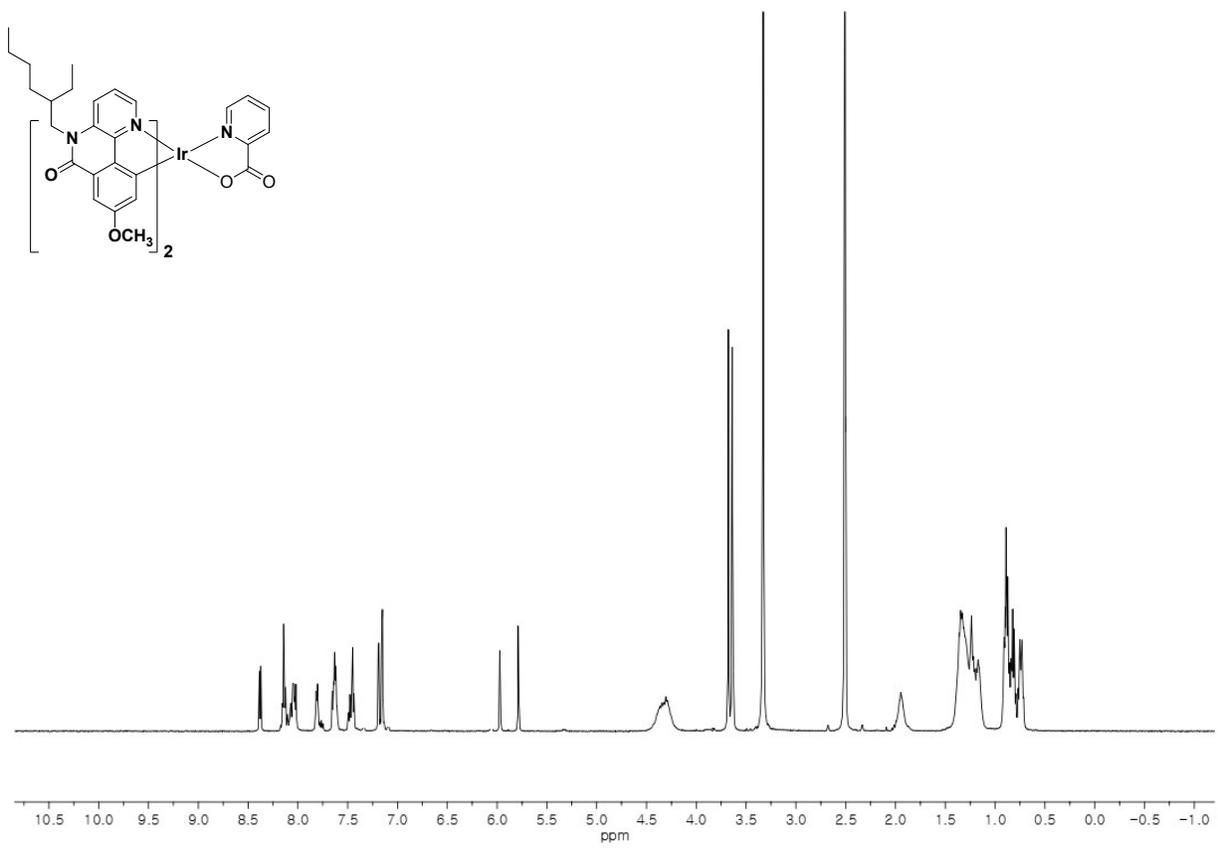
Synthesis of 5-(2-ethylhexyl)-8-methoxybenzo[c][1,5]naphthyridin-6(5H)-one (5). The mixture of compound (**4**) (1.25 g, 3.34 mmol), Pd(PPh₃)₄ (0.19 g, 0.16 mmol), Na₂CO₃ (1.76 g, 16.70 mmol), and of DMA (30 mL) was stirred at 150 °C for 24 h. Then the reaction mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with DCM (100 mL) and the organic phase was dried over anhydrous Na₂SO₄. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:n-hexane (10:90% v/v) as an eluent to afford **5** as a colorless liquid (0.7 g, yield: 56%). ¹H NMR (300 MHz, DMSO-d₆, δ): 8.70 (s, 1H), 8.53 (s, 1H), 7.91 (s, 1H), 7.76 (s, 1H), 7.54 (s, 2H), 4.34-4.28 (d, 2H), 3.92 (s, 3H), 1.87 (s, 1H), 1.30-1.19 (m, 8H), 0.84-0.82 (m, 6H).

Synthesis of N-(2-chloropyridin-3-yl)-N-(2-ethylhexyl)benzamide (6). NaH (1.66 g, 41.50 mmol) was added to anhydrous THF (30 mL) and the mixture was cooled to 0 °C under N₂ atmosphere. Compound (**1**) (5 g, 20.75 mmol) was added to the reaction mixture and stirred for 1 h. After that, 3-benzoyl chloride (4.25 mL, 31.15mmol) was added and stirred for 8 h at RT. After

completion of the reaction, the reaction mixture was quenched by the addition of water (50 mL). Finally, the organic layer was extracted with DCM, washed with brine solution and dried over anhydrous Na_2SO_4 . The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:n-hexane (20:80% v/v) as an eluent to afford **6** as a white solid (3.6 g, yield: 72%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.24 (s, 1H), 7.71-7.37 (d, 2H), 7.13-7.05 (d, 3H), 6.85-6.77 (d, 2H), 4.32 (s, 1H), 3.43-3.34 (t, 1H), 1.46-1.25 (m, 8H), 0.89-0.82 (m, 6H).

Synthesis of 5-(2-ethylhexyl)benzo[c][1,5]naphthyridin-6(5H)-one (7). The mixture of compound (**6**) (1.25 g, 3.34 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.19 g, 0.16 mmol), Na_2CO_3 (1.76 g, 16.70 mmol), and of DMA (30 mL) was stirred at 150 °C for 24 h. Then the reaction mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with DCM (100 mL) and the organic phase was dried over anhydrous Na_2SO_4 . The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc:n-hexane (10:90% v/v) as an eluent to afford **7** as a colorless liquid (0.8 g, yield: 70%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.88-8.85 (d, 1H), 8.57-8.49 (t, 2H), 7.85-7.80 (t, 1H), 7.68-7.66 (d, 2H), 7.46-7.42 (m, 1H), 4.37-4.28 (d, 2H), 1.19 (d, 1H), 1.40-1.27 (m, 8H), 0.95-0.86 (m, 6H).





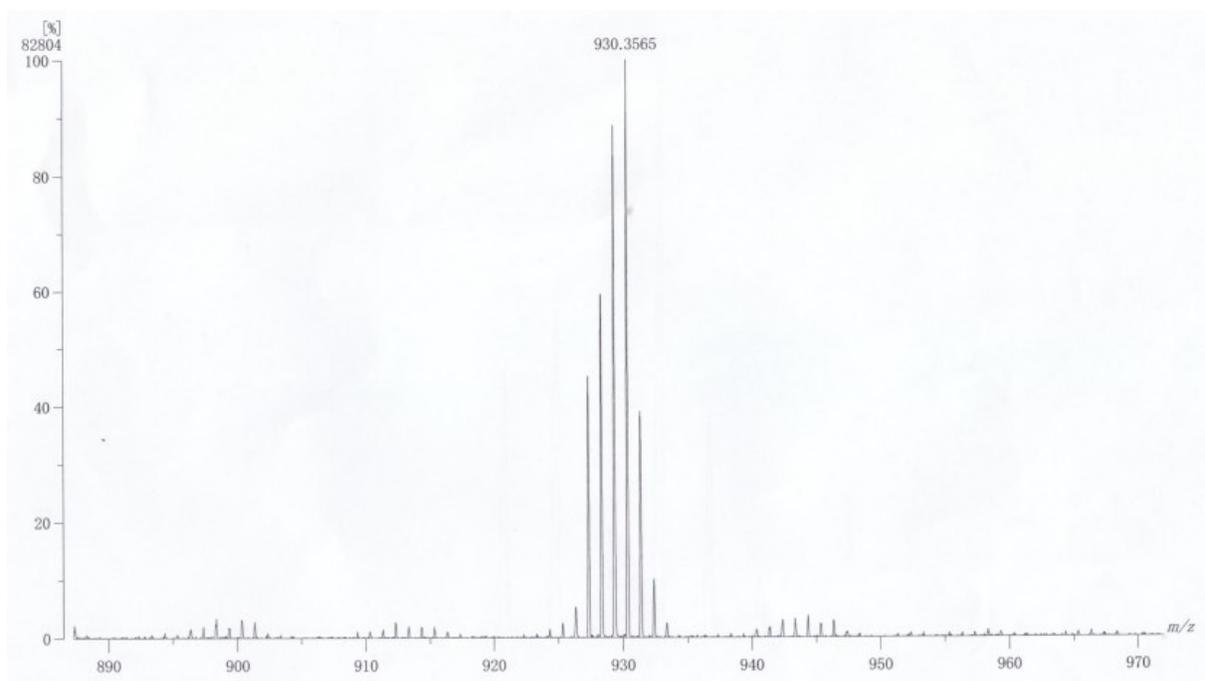
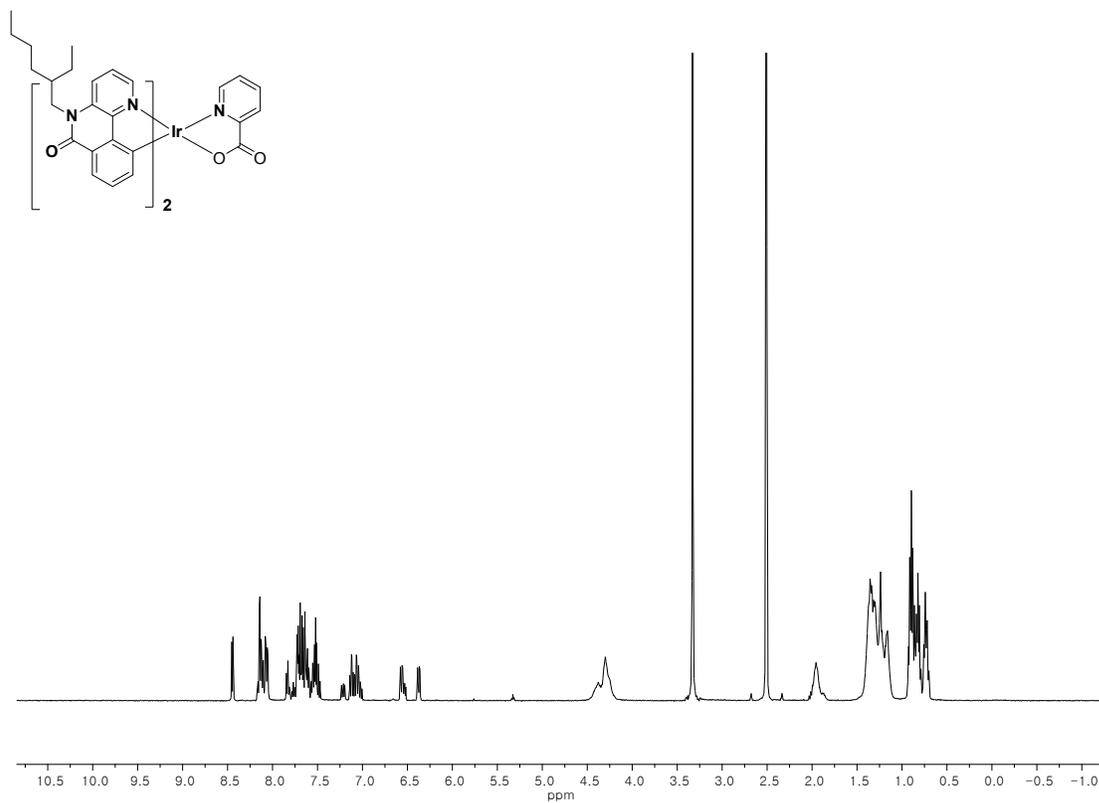


Fig. S1. ¹H NMR and mass spectra of Ir1, Ir2 and Ir3.

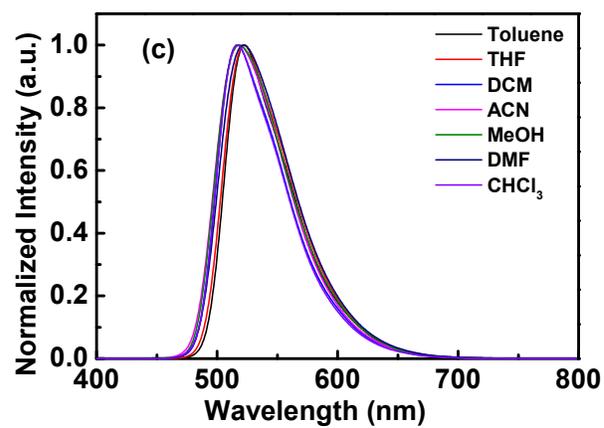
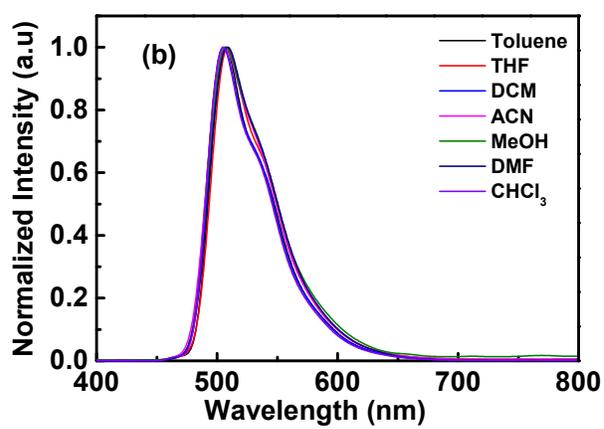
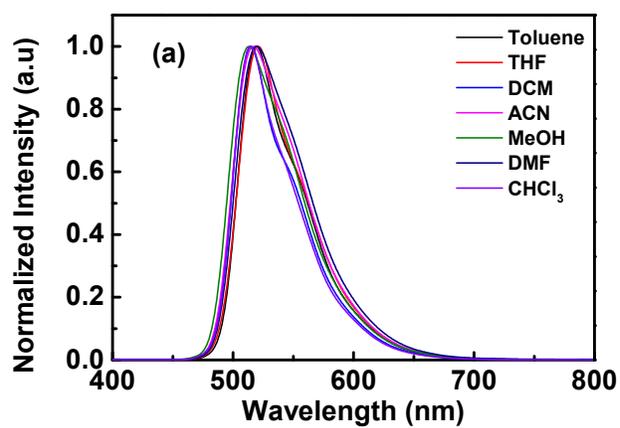


Fig. S2. PL spectra of Ir1 (a), Ir2 (b) and Ir3 (c) in different solvents.

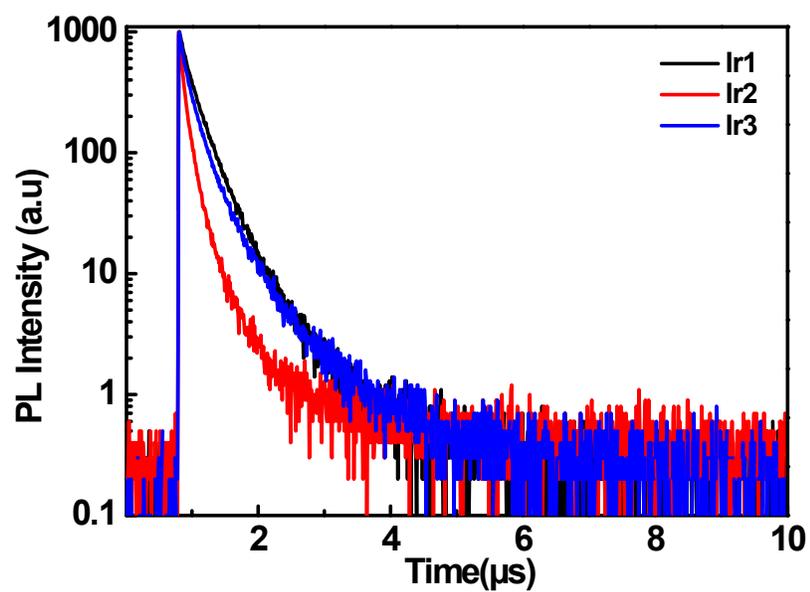


Fig. S3. PL decay curves for **Ir1**, **Ir2** and **Ir3** measured in CH₂Cl₂ solution.

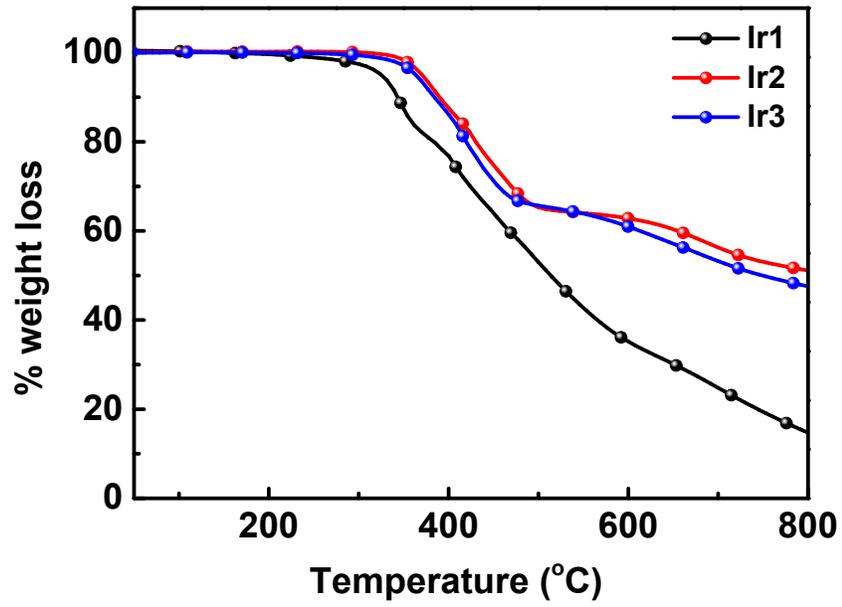


Fig. S4. TGA curve of Ir1, Ir2 and Ir3.

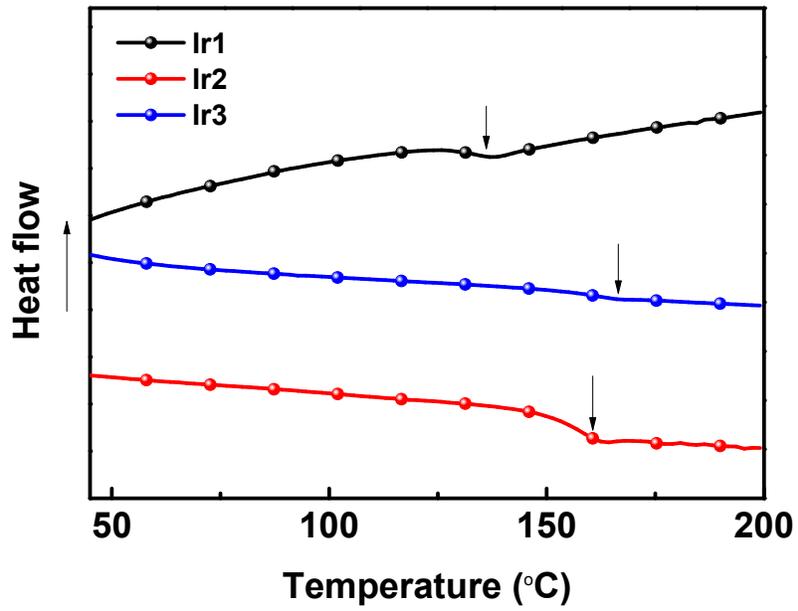


Fig. S5. DSC curve for Ir1, Ir2 and Ir3.

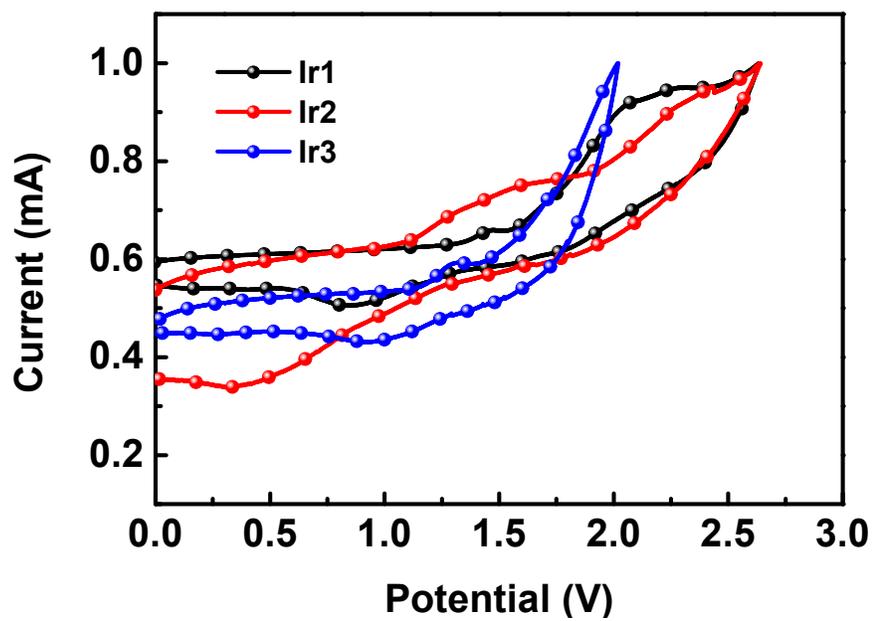


Fig. S6. CV of Ir1, Ir2 and Ir3.

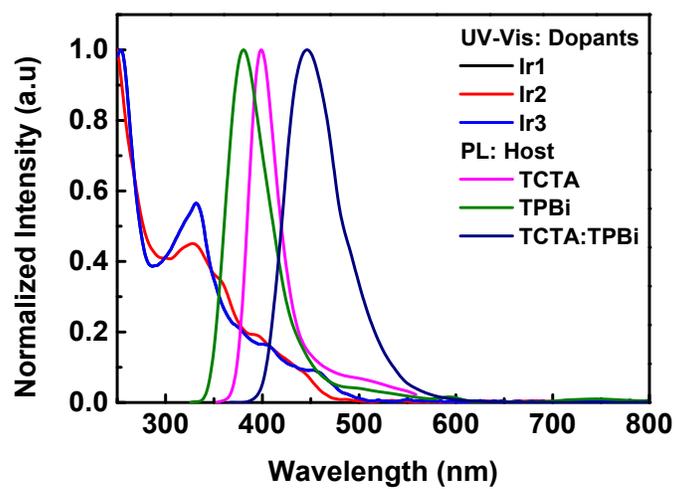


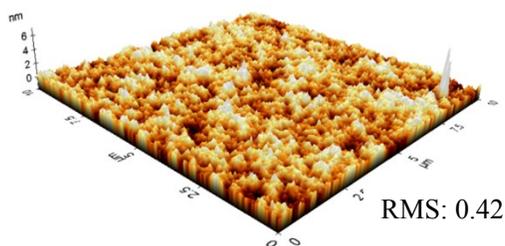
Fig. S7. The corresponding overlapping spectra between the PL and UV-Vis spectra of hosts and dopants in solid state.

Complexes

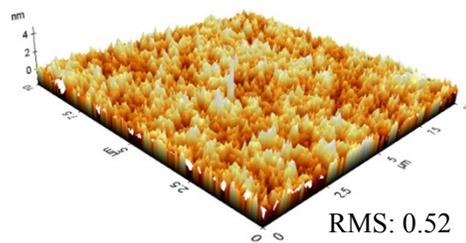
Chlorobenzene

Cyclohexanone

Ir1

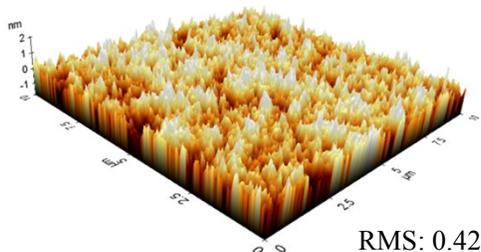


RMS: 0.42

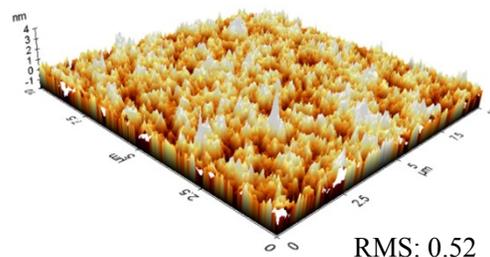


RMS: 0.52

Ir2

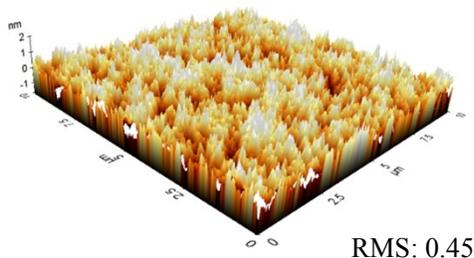


RMS: 0.42

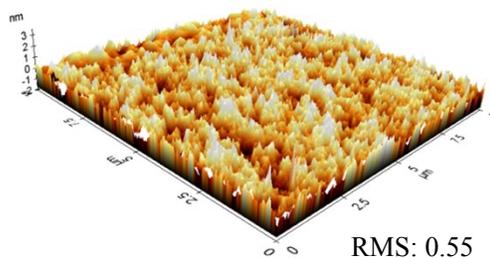


RMS: 0.52

Ir3



RMS: 0.45



RMS: 0.55

Fi

g. S8. Surface morphologies (3D images) studies with TCTA:TPBi:15% of dopants in chlorobenzene and cyclohexanone solvents processed films.

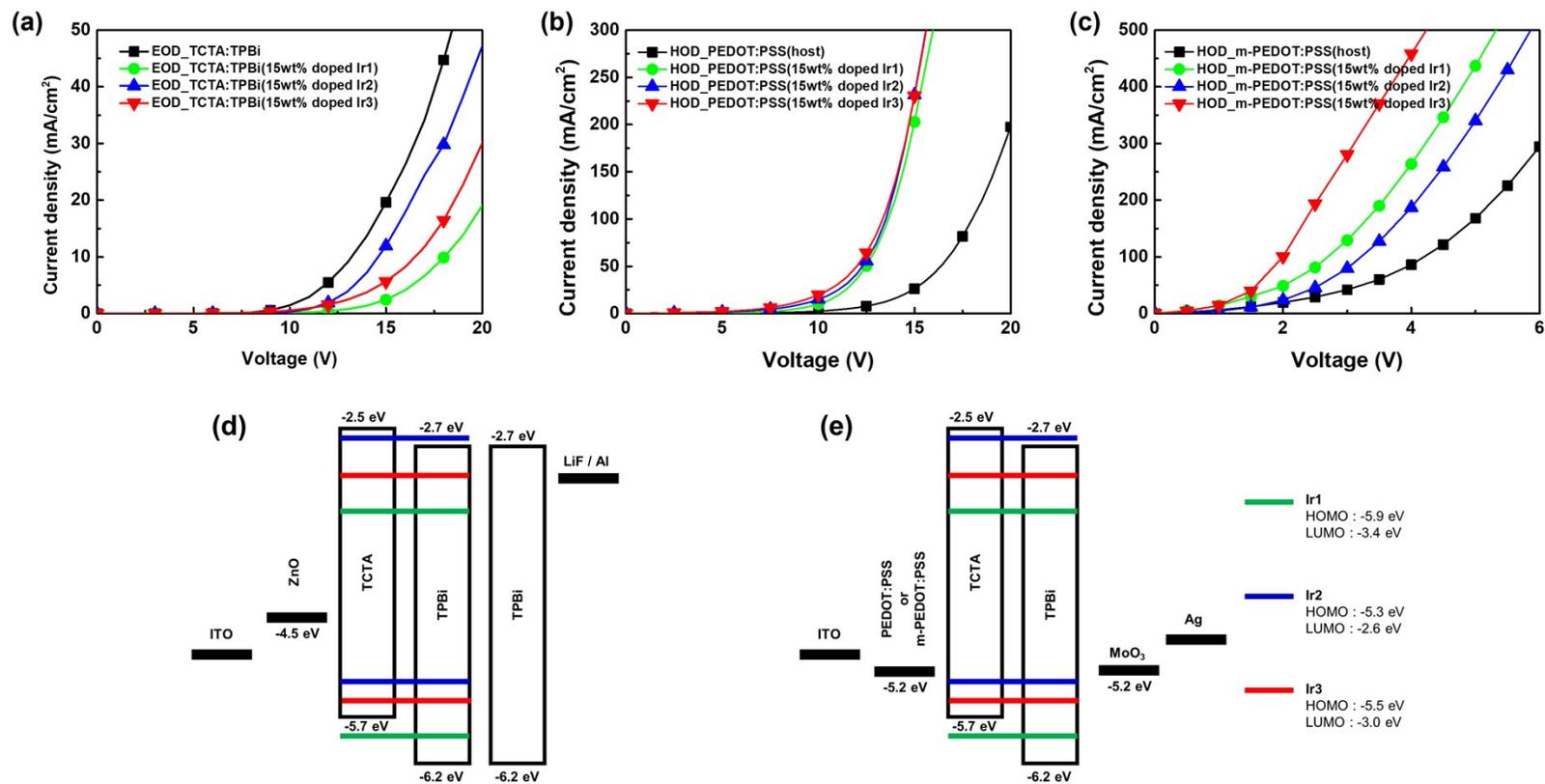


Fig. S9. a) J-V curves of EODs, b) J-V curves of HODs using commercial PEDOT:PSS, c) J-V curves of HODs using m-PEDOT:PSS, d) Energy levels diagram of EOD and, e) Energy levels diagram of HOD.

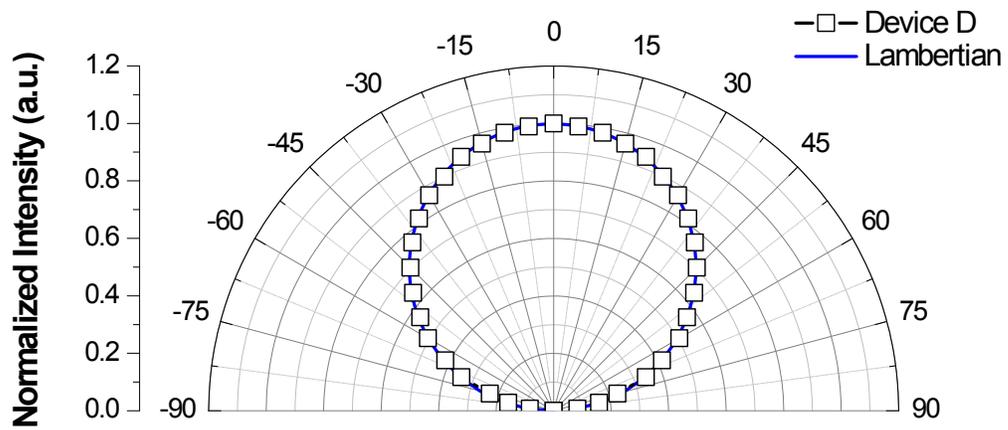


Fig. S10. Angle-dependent EL pattern of device

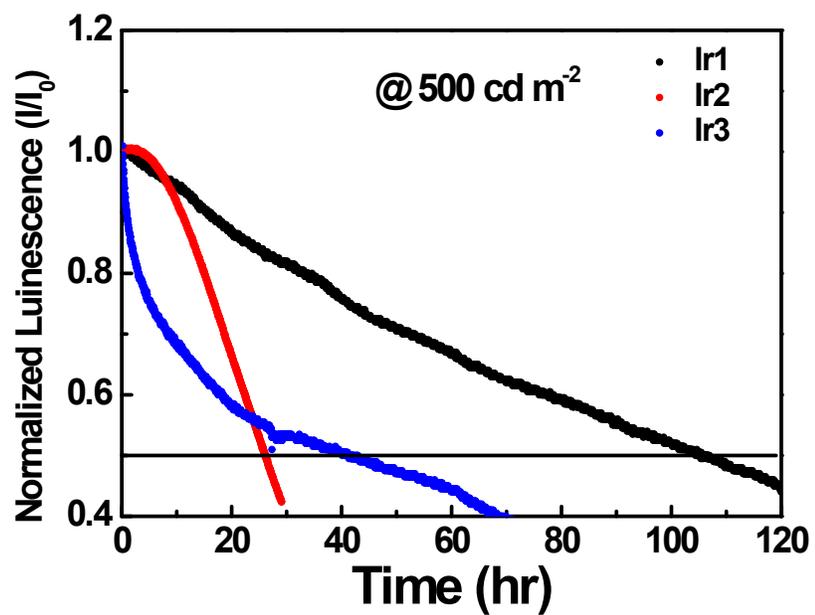


Fig. S11. Device lifetime for Ir1, Ir2 and Ir3 at initial luminescence 500 cd m^{-2} .

Table S1. Emission solvatochromism of **Ir1**, **Ir2** and **Ir3** in different solvents.

Solvents	Ir1	Ir2	Ir3
	λ_{max} Emission (nm)	λ_{max} Emission (nm)	λ_{max} Emission (nm)
Toluene	519	506	522
THF	521	509	523
Dichloromethane	515	504	517
Acetonitrile	517	506	518
Methanol	513	507	518
N,N- Dimethylformamide	520	508	522
Chloroform	514	505	516

Table S2. Sheet resistance and electrical conductivity of commercial PEDOT:PSS (A14083) and m-PEDOT:PSS.

Hole injection material	Sheet resistance (Ω/sq)	Thickness (nm)	Electrical conductivity (S/cm)
PEDOT:PSS(A14083)	35,150,000	40.4	0.007
m-PEDOT:PSS	201,828	39.8	1.245

Table S3. Literature summary of non-halogenated solvent-processed green PHOLEDs.

Dopant	EQE _{max} (%)	CE _{max} (cd/A)	Solvent for device fabrication	Reference
Ir1	23.60	85.22	Cyclohexanone	This work
Ir3	22.40	81.63	Cyclohexanone	This work
Ir(ppy) ₃	22	78	Tetrahydrofuran	1
Ir(mppy) ₃	15.5	54.0	Toluene	2
IrppyD	-	54	Toluene	3
IrG	13.75	49.50	Isopropanol	4
G2	21.2	68.4	Isobutanol	5
IrG1	10.8	38.43	n-butyl alcohol	6

References

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