

# Improved electroluminescence efficiency derived from functionalized decoration of 1,3,4-oxadiazole (OXD)-based Ir(III) complexes

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**Keywords:** Ir(III) complexes, Oxadiazole, Functionalized substituents, Electroluminescence

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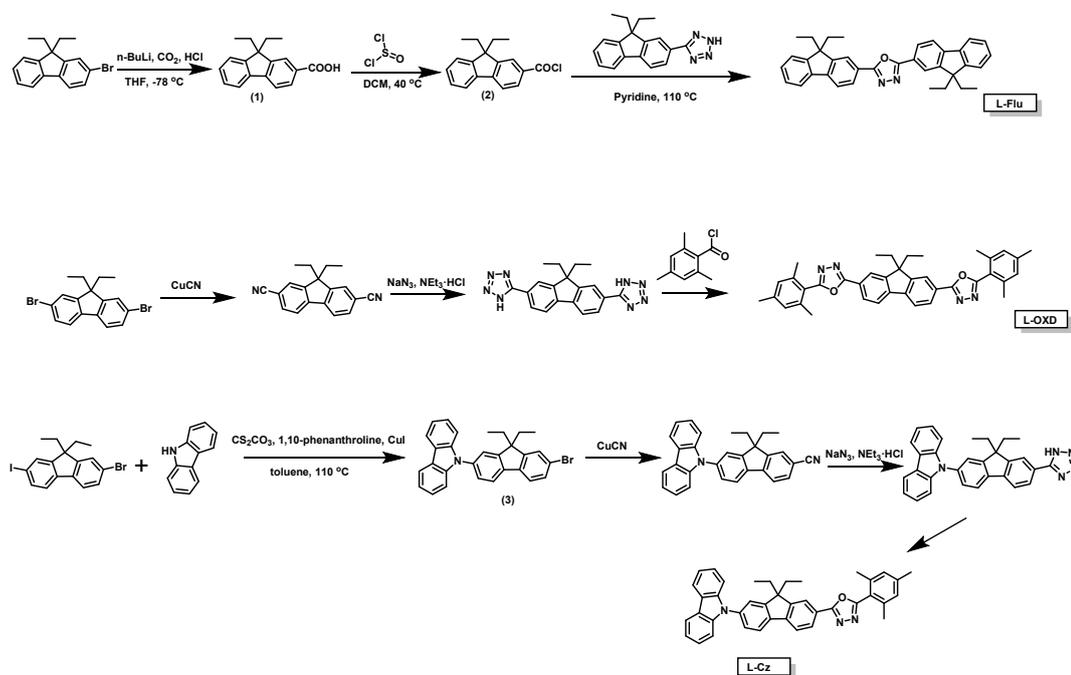
## 1. Materials and general methods

The chemical structures were fully characterized and confirmed via nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ :100 MHz). The matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS) measurements were carried out with a Shimadzu AXIMA-CFR mass spectrometer. UV-visible absorption spectra were recorded on a Shimadzu UV-3600. photoluminescence (PL) spectra were measured using a RF-5301PC spectrofluorophotometer. Electrochemical behavior was investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in a 0.1 M tetra-n-butylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in an ultra dry  $\text{CH}_2\text{Cl}_2$  at room temperature under nitrogen with a scanning rate of 100 mV/s. A platinum working electrode, a glassy carbon electrode, and an  $\text{Ag}/\text{AgNO}_3$  (0.1 M) reference electrode were used. The CV curves were calibrated using ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple (4.8 eV below the vacuum level) as the internal standard. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels could be calculated according to:  $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8)$  eV,  $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.8)$ , where  $E_{\text{ox}}$  and  $E_{\text{red}}$  is the onset oxidation and reduction potentials, respectively. Excited-state lifetime studies were measured on an Edinburgh LFS-920 spectrometer. The absolute quantum yield of the complex was performed through an absolute method by employing an integrating sphere.

Fabrication of doped thin film: The complexes (6% wt%) were doped into tris(4-carbazoyl-9-yl phenyl)amine (TCTA) and 2,6-bis[3-(9H-carbazol-9-yl)phenyl]pyridine (2,6-Dczppy). The sample films were fabricated by spin coating mixed chlorobenzene solution to quartz inside the glovebox.

Fabrication of OLEDs. The device structure used was indium tin oxide (ITO)/poly (3,4-ethylenedioxythiophene) doped poly (styrene sulfonic acid) (PEDOT:PSS) (40 nm)/TCTA:26-Dczppy (3:7): Ir(III) complex (45 nm)/Tmppyb (50 nm)/LiF (0.8 nm)/Al (100 nm). The patterned ITO glass substrate was ultrasonically

cleaned and dried in an oven at 120 °C for more than 1 h firstly. Then ultraviolet (UV) ozone treatment was performed for 8~10 min, and the thin hole injection layer of PEDOT: PSS was cast onto the transparent conductive ITO. After baking in an oven, the emitting layer (EML) of TCTA:2,6-Dczppy (3:7): 6% Ir(III) complex was coated on top of the PEDOT:PSS layer. TCTA:2,6-Dczppy was dissolved in chlorobenzene with the concentration of 12 mg/mL and 6 mg/mL complexes doped in it with the final doping concentration of 6%. Finally the layers of Tmpypb and LiF/Al were deposited on top of the EML by thermal evaporation under  $2\sim3\times 10^{-4}$  Pa. All the samples were measured directly in ambient atmosphere without encapsulation. The size of fabricated devices was 12 mm<sup>2</sup>.



**Scheme S1** Synthetic procedure and chemical structures of the materials.

**9,9-diethyl-9H-fluorene-2-carboxylic acid (1).** Under nitrogen atmosphere, a portion of 2-bromo-9,9-diethyl-9H-fluorene (5 g, 16.6 mmol) was put in a pre-dried 250 mL three-necked bottle, and freshly steamed THF was added as solvent. The reaction system was cooled down to -78 °C in dry ice acetone bath and stirred for half an hour. 2.5 M butyl lithium (9.96 mL, 24.9 mmol) was added to the system slowly by a 20 mL syringe, and stirred for 2 h at -78 °C. Excess dry CO<sub>2</sub> was bubbled and white solid

precipitated out. The reaction was stirred at low temperature for 2 h and then rose to room temperature. After the reaction mixture kept overnight, the THF was removed and deionized water was added to solve the lithium salt. Dilute hydrochloric acid was added to adjust the pH of the system to acidity. The precipitated white solid obtained by filtered operation was compound 1, which was used directly for next step without any purification. Yield: 70%.

**9,9-diethyl-9H-fluorene-2-carbonyl chloride (2).** A portion of compound 1 (3.09 g, 11.62 mmol) was put in pre-dried 250 mL three-necked bottle, and freshly steamed DCM was added as solvent. Thionyl chloride (2.76 g, 23.24 mmol) was added slowly, and the reaction was heated at 40 °C for 1 h. The solvent was evaporated from the crude product to obtain compound 2, which was used directly for next step without any purification.

**2,5-bis(9,9-diethyl-9H-fluorene-2-yl)-1,3,4-oxadiazole (L-Flu).** A mixture of compound 2 (3.31 g, 11.62 mmol) and 5-(9,9-diethyl-9H-fluorene-2-yl)-2H-tetrazole (3.38 g, 11.62 mmol) was heated at 110 °C in pyridine. After the reaction mixture were stirred for 24 h, the compound was extracted with dichloromethane and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated from the crude product, which was purified by column chromatography to get the target product F-Flu. Yield: 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 7.7 Hz, 4H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.81 (s, 2H), 7.41 (s, 6H), 2.16 (ddt, *J* = 20.4, 13.3, 6.8 Hz, 8H), 0.36 (t, *J* = 7.1 Hz, 12H). MS (MALDI-TOF, *m/z*) Calcd for C<sub>36</sub>H<sub>34</sub>N<sub>2</sub>O, 510.68; Found: 510.27.

**9,9-diethyl-9H-fluorene-2,7-dicarbonitrile (3).** Under nitrogen atmosphere, 2,7-dibromo-9,9-diethyl-9H-fluorene (5 g, 13.1 mmol) and CuCN (3.5 g, 39.3 mmol) were put in a pre-dried 250 mL three-necked bottle, and extra dry DMF was added as solvent. After the reaction mixture were stirred for 24 h, the compound was extracted with dichloromethane and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated from the crude product, which was purified by column chromatography to get the target product (3). Yield: 80%.

**5,5'-(9,9-diethyl-9H-fluorene-2,7-diyl)bis(1H-tetrazole) (4).** Under nitrogen

atmosphere, compound (3) (3.5 g, 12.8 mmol),  $\text{NaN}_3$  (2.5 g, 38.4 mmol) and  $\text{NEt}_3 \cdot \text{HCl}$  (5.3 g, 38.4 mmol) were put in a pre-dried 100 mL three-necked bottle, and extra dry DMF was added as solvent. After the reaction mixture were stirred for 24 h, the compound was extracted with dichloromethane and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated from the crude product, which was purified by column chromatography to get the target product (4). Yield: 65%.

**5,5'-(9,9-diethyl-9H-fluorene-2,7-diyl)bis(2-mesityl-1,3,4-oxadiazole) (L-OXD).**

The synthesized steps of L-OXD referred to the previous reference<sup>[1]</sup> and that of L-Flu. Yield: 72%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 0.9$  Hz, 2H), 8.11 (dd,  $J = 8.0, 1.5$  Hz, 2H), 7.91 (d,  $J = 8.0$  Hz, 2H), 7.02 (s, 4H), 2.41 (s, 12H), 2.29 (s, 6H), 2.19 (q,  $J = 7.3$  Hz, 4H), 0.37 (t,  $J = 7.3$  Hz, 6H). MS (MALDI-TOF,  $m/z$ ) Calcd for  $\text{C}_{39}\text{H}_{38}\text{N}_4\text{O}_2$ , 594.76; Found: 593.66.

**9-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)-9H-carbazole (5).** Under nitrogen atmosphere, a mixture of 2-bromo-9,9-diethyl-7-iodo-9H-fluorene (5 g, 11.7 mmol), 9H-carbazole (2.93 g, 17.55 mmol), cesium carbonate (5.72 g, 17.55 mmol), 1,10-phenanthroline (0.23 g, 1.17 mmol) and cuprous iodide (0.22 g, 1.17 mmol) were heated at 110 °C in toluene. After the reaction mixture were stirred for 24 h, the compound was extracted with dichloromethane and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated from the crude product, which was purified by column chromatography to get the target product. Yield: 85%.

**7-(9H-carbazol-9-yl)-9,9-diethyl-9H-fluorene-2-carbonitrile (6).** Under nitrogen atmosphere, compound (5) (2 g, 4.3 mmol) and  $\text{CuCN}$  (1.1 g, 12.9 mmol) were put in a pre-dried 100 mL three-necked bottle, and extra dry DMF was added as solvent. After the reaction mixture were stirred for 24 h, the compound was extracted with dichloromethane and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated from the crude product, which was purified by column chromatography to get the target product (6). Yield: 70%

**9-(9,9-diethyl-7-(1H-tetrazol-5-yl)-9H-fluoren-2-yl)-9H-carbazole (7).** Under nitrogen atmosphere, compound (6) (1.2 g, 2.9 mmol),  $\text{NaN}_3$  (0.56 g, 8.7 mmol) and

NEt<sub>3</sub>·HCl (1.2 g, 8.7 mmol) were put in a pre-dried 100 mL three-necked bottle, and extra dry DMF was added as solvent. After the reaction mixture were stirred for 24 h, the compound was extracted with dichloromethane and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated from the crude product, which was purified by column chromatography to get the target product (7). Yield: 55%.

**2-(7-(9H-carbazol-9-yl)-9,9-diethyl-9H-fluoren-2-yl)-5-mesityl-1,3,4-oxadiazole (L-Cz).** The synthesized steps of L-Cz referred to the previous reference<sup>[1]</sup> and that of L-Flu. Yield: 65% <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 – 8.09 (m, 4H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.51 – 7.40 (m, 4H), 7.40 – 7.29 (m, 2H), 7.03 (s, 2H), 2.38 (d, *J* = 2.9 Hz, 8H), 2.30 (s, 1H), 2.24 – 2.01 (m, 4H), 0.48 (t, *J* = 7.3 Hz, 6H). MS (MALDI-TOF, *m/z*) Calcd for C<sub>40</sub>H<sub>35</sub>N<sub>3</sub>O, 573.74; Found: 573.54.

## 2. MALDI-TOF and NMR spectra

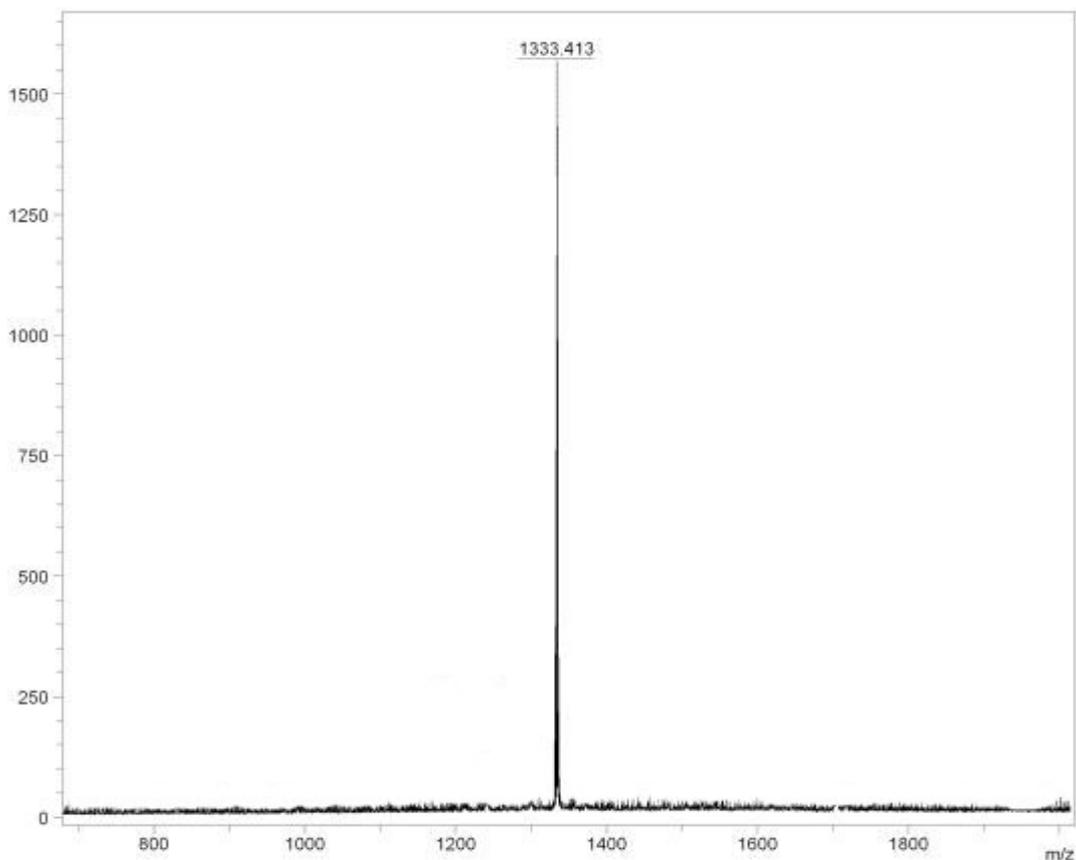


Figure S1. MALDI-TOF MS of Ir-Flu.

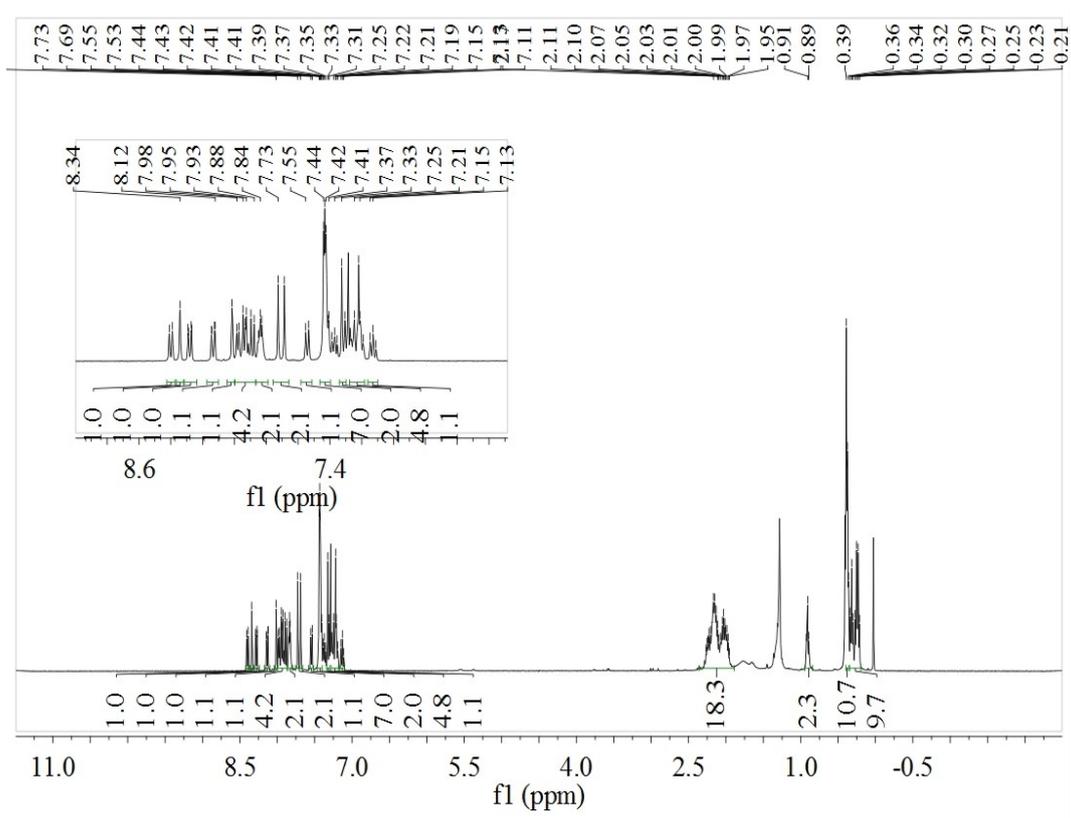


Figure S2.  $^1\text{H}$  NMR spectrum of Ir-Flu.

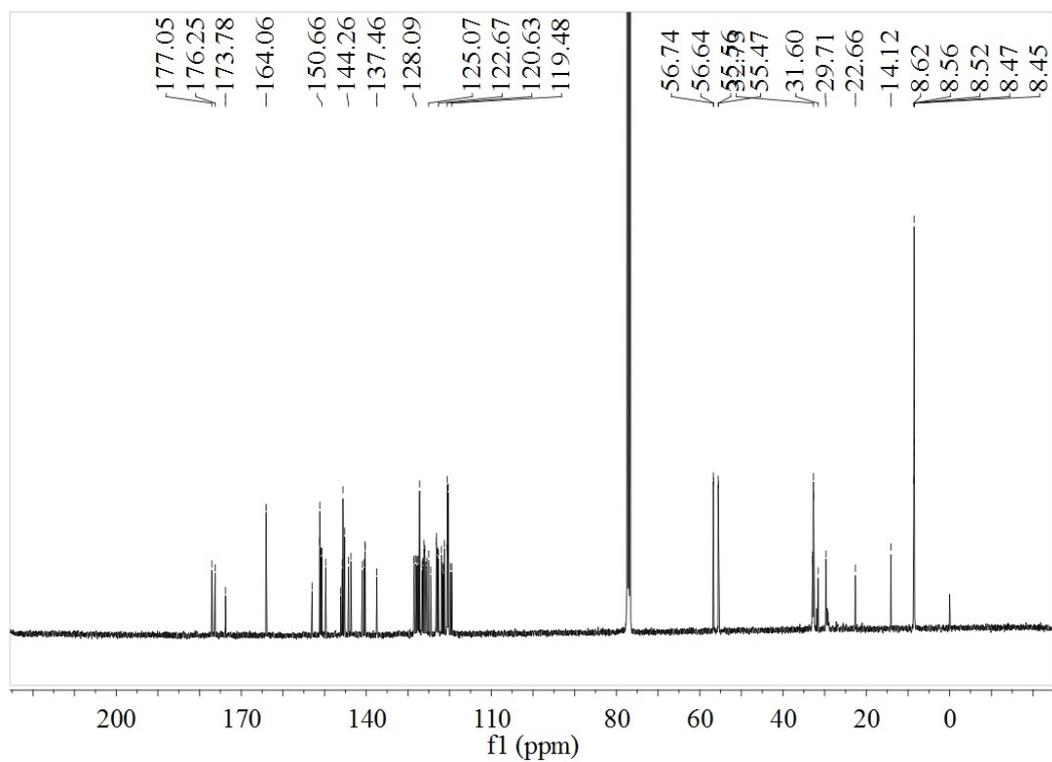
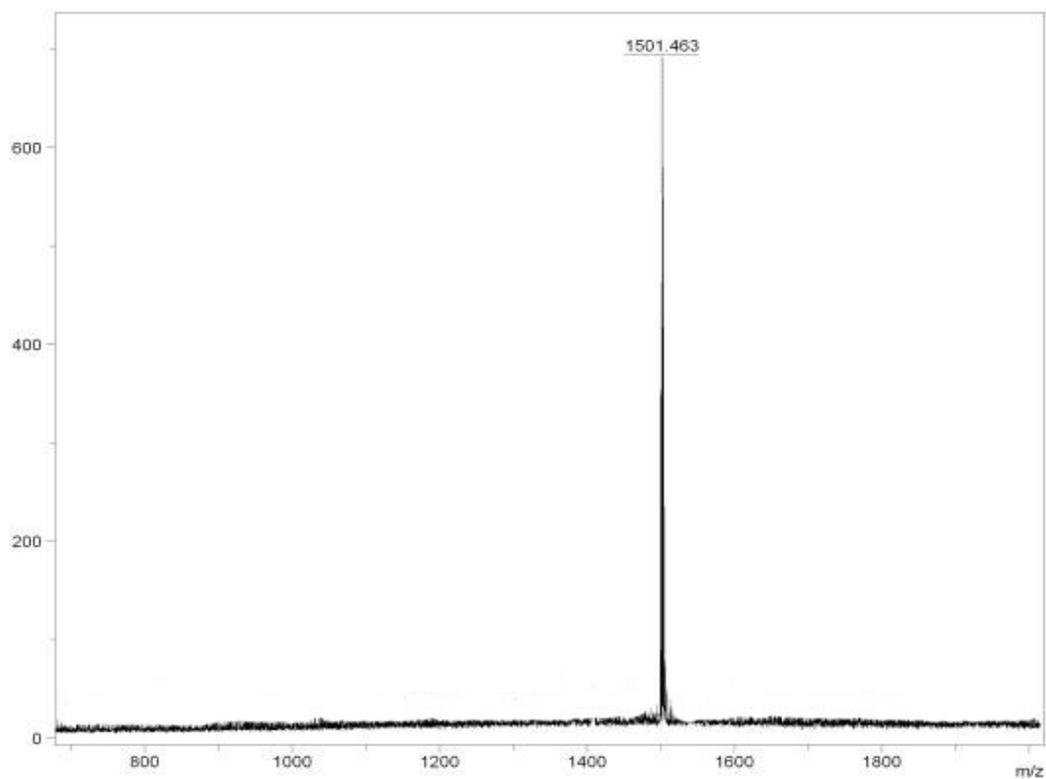
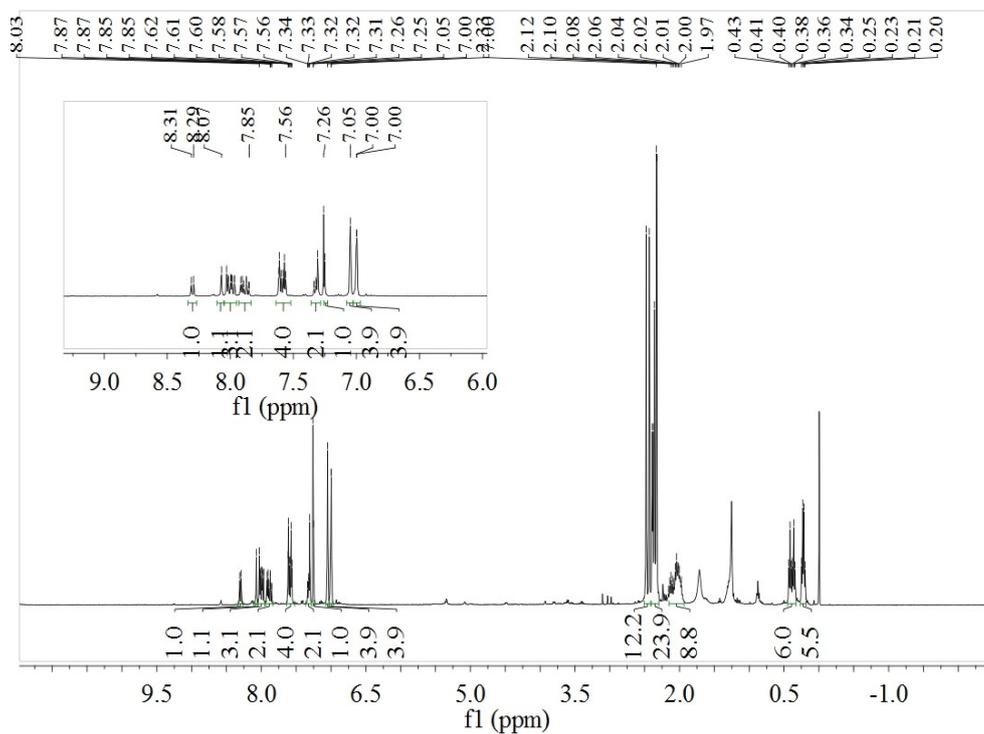


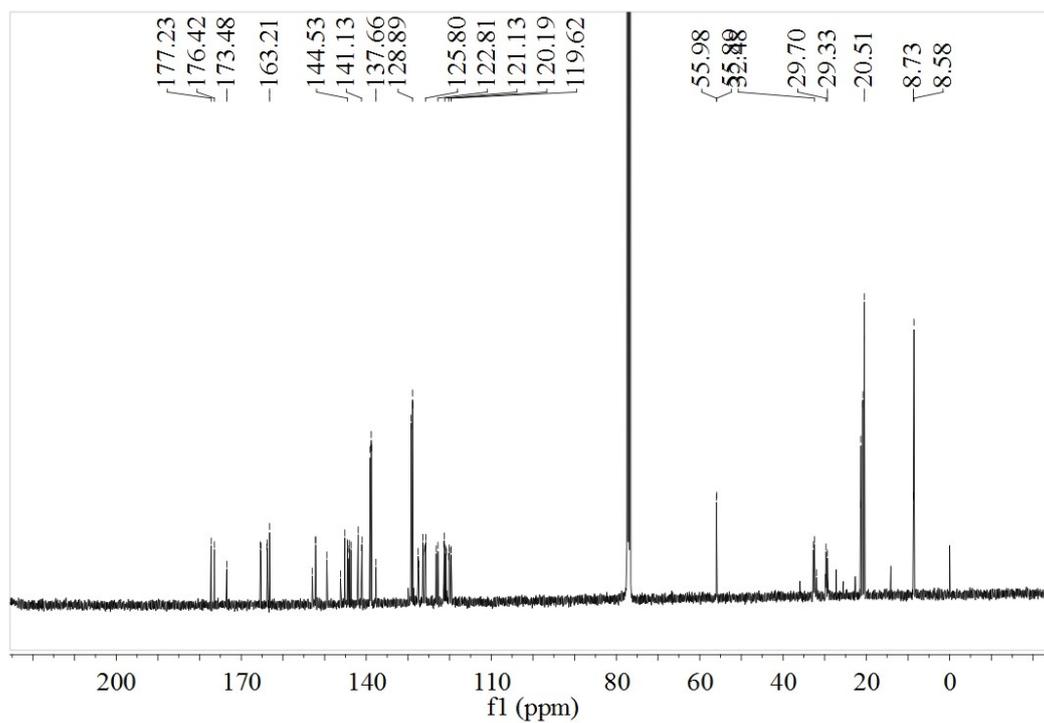
Figure S3.  $^{13}\text{C}$  NMR spectrum of Ir-Flu.



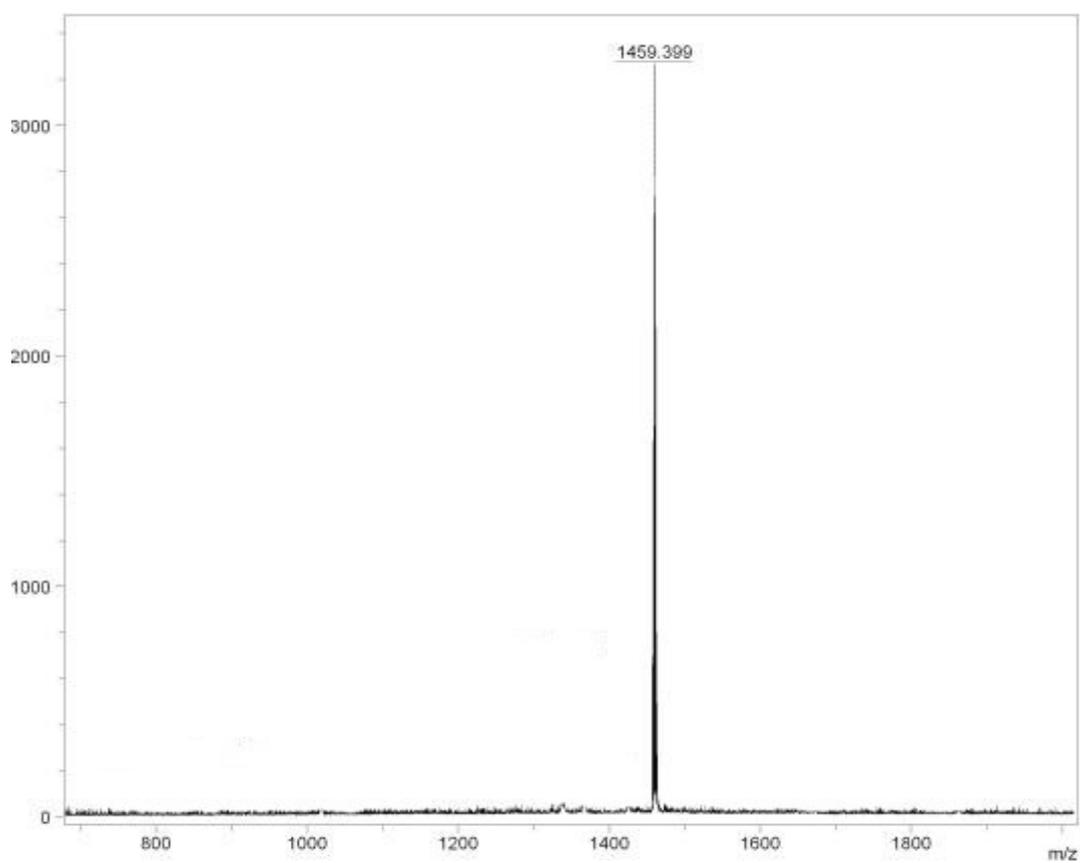
**Figure S4.** MALDI-TOF MS of Ir-OXD.



**Figure S5.** <sup>1</sup>H NMR spectrum of Ir-OXD.



**Figure S6.**  $^{13}\text{C}$  NMR spectrum of Ir-OXD.



**Figure S7.** MALDI-TOF MS of Ir-Cz.

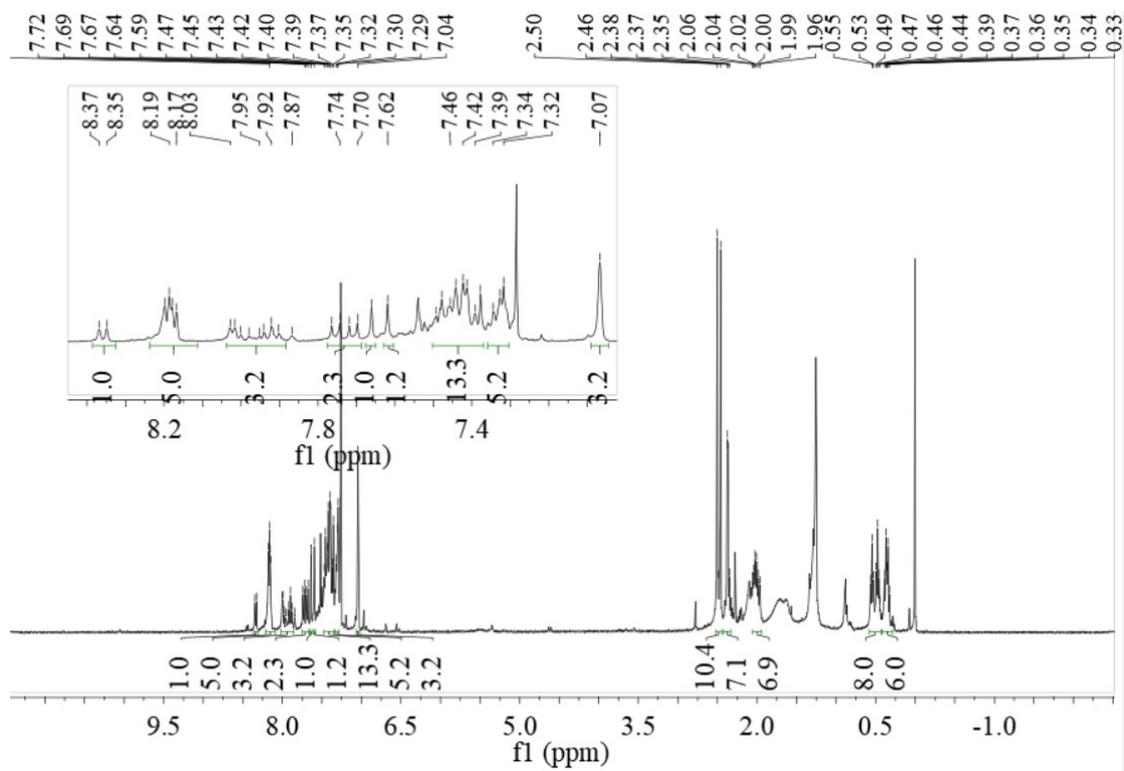


Figure S8.  $^1\text{H}$  NMR spectrum of Ir-Cz.

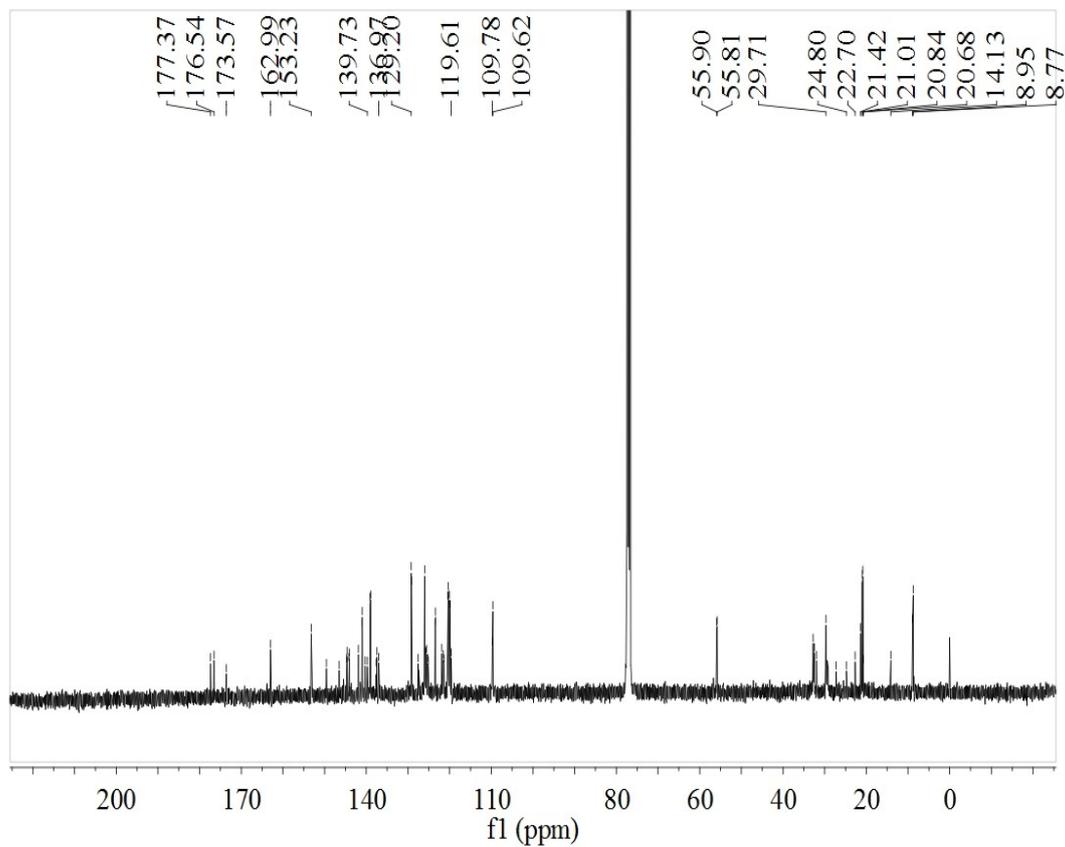
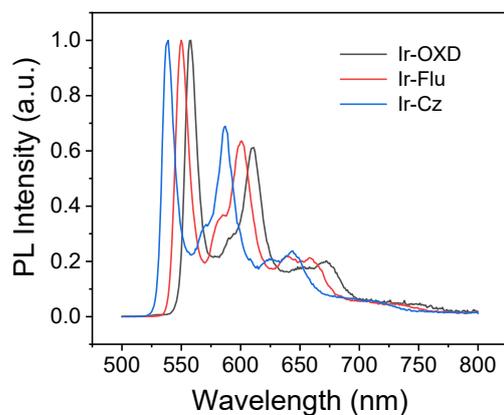
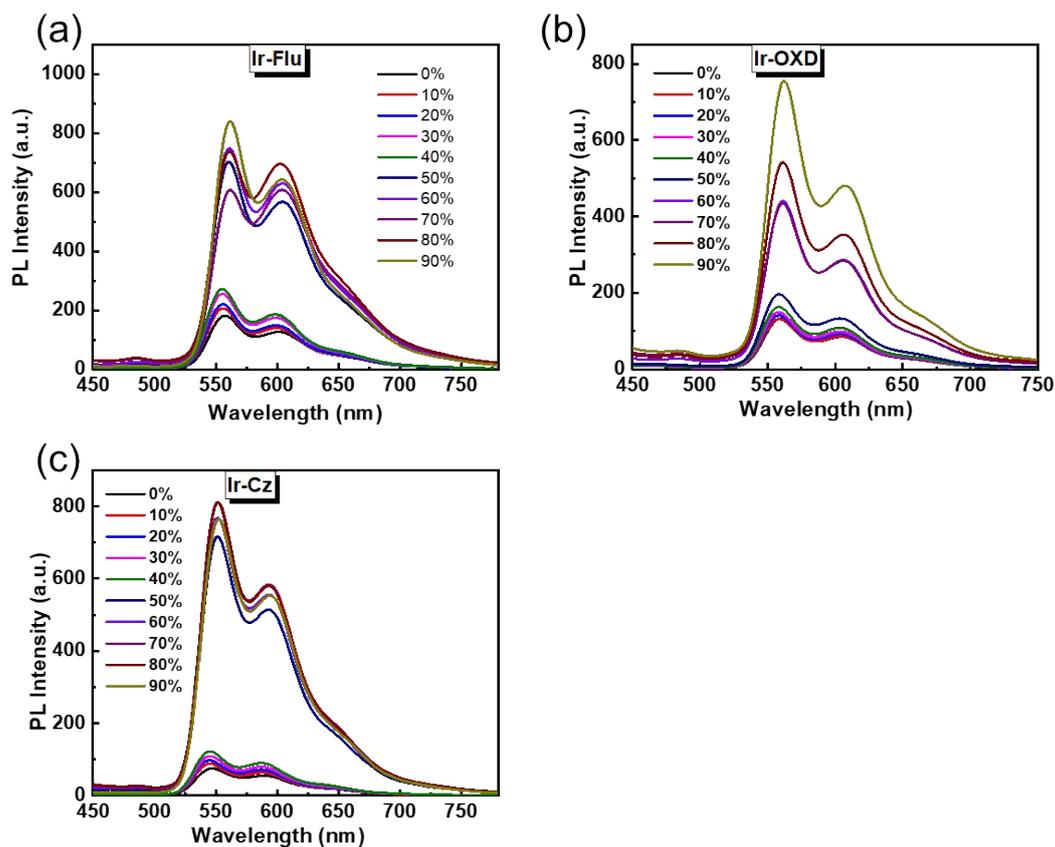


Figure S9.  $^{13}\text{C}$  NMR spectrum of Ir-Cz.

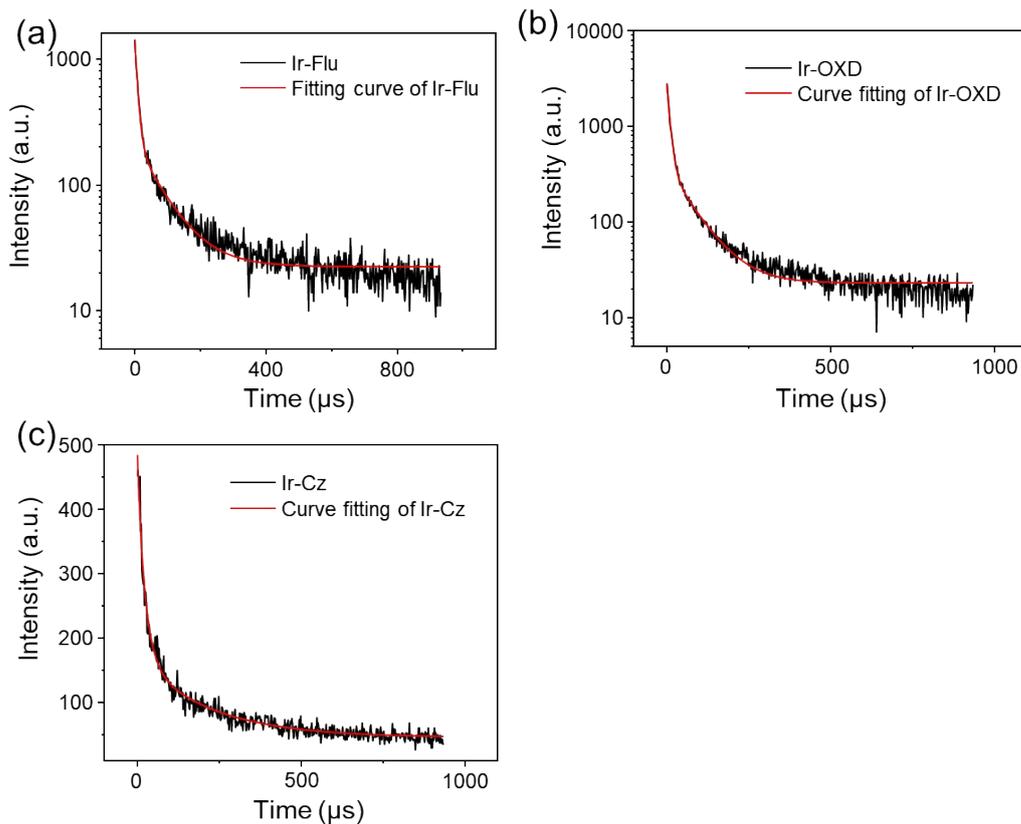
### 3. Photophysical properties



**Figure S10** Phosphorescence spectra of **Ir-Flu**, **Ir-OXD** and **Ir-Cz** ( $10^{-5}$  M) at 77 K in 2-Me THF ( $\lambda_{\text{exc}} = 420$  nm).



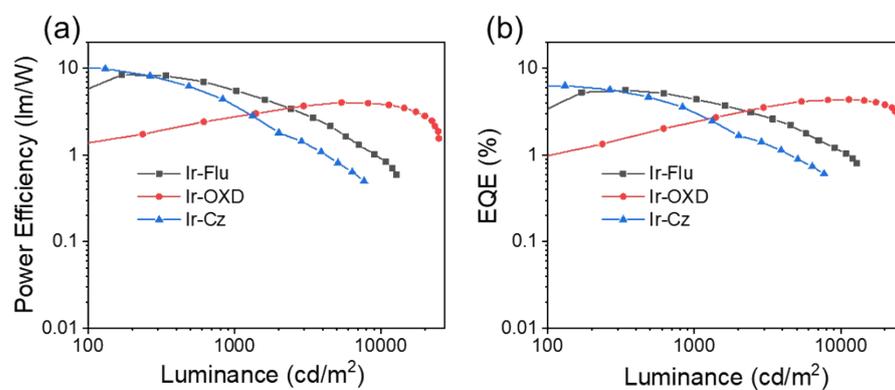
**Figure S11** Emission spectra of **Ir-Flu**, **Ir-OXD** and **Ir-Cz** ( $10^{-5}$  M) in acetone-water mixtures with different water fractions (0-90%) at room temperature ( $\lambda_{\text{exc}} = 420$  nm).



**Figure S12** Lifetime decay curves of complexes in doped thin film. ( $\lambda_{\text{ex}} = 420 \text{ nm}$ ).

**Table S1** Photophysical properties of complexes in doped thin film.

Name	Ir-Flu	Ir-OXD	Ir-Cz
$\Phi_{\text{PL}}$	0.46	0.41	0.42
$\tau$ ( $\mu\text{s}$ )	52	45	173



**Figure S13** (a) *PE-L* covers. (b) *EQE-L* covers.

[1] Liu J-W, Zhou H-C, Wang Z-K, Tang X, Wu H-Y, Wang S, et al. Distinct Ir (III) complexes containing unsymmetric ligands with fluorene-oxadiazole groups and their performance of organic light-emitting diodes. *Dyes Pigm* 2022; 202: 110252.