

The third strategy: modulating emission colors of organic light-emitting diodes with UV light during the device fabrication process

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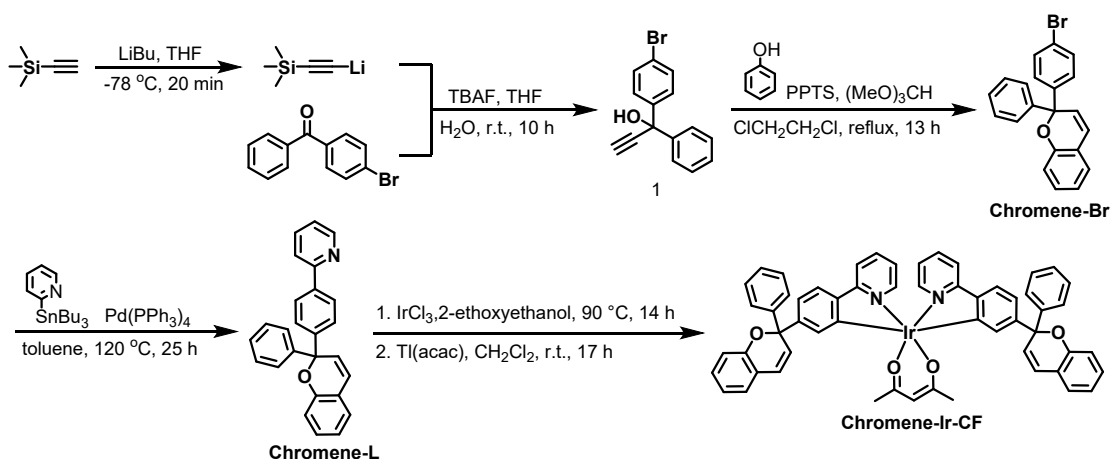
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General information:

All commercially available starting reagents were used without further purification. All reactions were carried out under nitrogen atmosphere and monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum plates. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer in CDCl_3 and chemical shifts are reported in ppm scale and were referenced internally to the residual solvent resonance. UV-Vis spectra were measured on a Shimadzu UV-2250 spectrophotometer. The photoluminescent properties and the phosphorescent lifetimes of the complexes were obtained using an Edinburgh Instruments (FLS920). The UV light was generated with a 3 W 365 nm handheld UV lamp. The phosphorescence quantum yields were determined in CH_2Cl_2 solutions at room temperature relative to the *fac*-[Ir(ppy) $_3$] standard (PLQY = 0.97). The thermal gravimetric analysis (TGA) was investigated with a NETZSCH STA 409C instrument under N_2 . Cyclic voltammetry curve was tested on the CHI660E Instrument in the acetonitrile solution with *n*-Bu $_4$ NPF $_6$ (0.1 M) as the supporting electrolyte, and ferrocene/ferrocenium (Fc/Fc $^+$) couple was used as the reference. Energy levels of HOMO (E_{HOMO}) was determined from the peak of oxidation potentials (E_{pa}) according to $E_{\text{HOMO}} = -(E_{\text{pa}} + 4.8)$ eV and energy levels of LUMO (E_{LUMO}) was determined from E_{HOMO} and optical band gap (E_{gap}) according to $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$ eV. Mass spectra (MS) were recorded with a micrOTOF-Q II mass spectroscopy.

Synthesis of materials:



Scheme S1. Synthesis of **Chromene-Ir-CF**.

Compound 1 A solution of trimethyl silyl acetylene (5.3 g, 54.0 mmol) in dry THF (30 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ under the nitrogen atmosphere, followed by the addition of *n*-BuLi (19.8 mL, 49.5 mmol). The mixture was stirred for 20 min at $-78\text{ }^{\circ}\text{C}$ and then 4-bromobenzophenone (11.75 g, 45.0 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h before a solution of tetrabutyl ammonium fluoride (TBAF) (11.76 g, 45.0 mmol) in water (50 mL) was added. After stirring at room temperature for 10 h, the mixture was extracted with CH_2Cl_2 several times. The organic layers were combined, dried over anhydrous MgSO_4 and concentrated. The residual was purified on a silica column using a mixture of petroleum ether and dichloromethane (v/v, 2:1) as eluent to give compound **1** as a white solid (11.9 g, 92.5% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.58$ (d, $J = 7.6$ Hz, 2H), 7.49–7.44 (m, 4H), 7.37–7.27 (m, 3H), 2.90 (s, 1H), 2.82 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 143.88, 143.47, 131.37, 128.43, 128.12, 127.75, 125.85, 121.96, 85.75, 75.91, 73.86$.

Chromene-Br Under a nitrogen atmosphere, a solution of **1** (1.5 g, 5.2 mmol), phenol (0.53 g, 5.6 mmol), trimethyl orthoformate (1.2 g, 11.3 mmol) and pyridinium

p-toluenesulfonate (PPTS) (65 mg, 0.26 mmol) in ClCH₂CH₂Cl (15 mL) was heated to reflux for 13 h. After cooling to room temperature, the solvent was removed under vacuum. The residual was purified on a silica column using a mixture of petroleum ether and dichloromethane (v/v, 15:1) as eluent to give compound **2** as a white solid (0.70 g, 55.1% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.46–7.41 (m, 4H), 7.36–7.29 (m, 4H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 9.6 Hz, 1H), 6.11 (d, *J* = 9.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 152.21, 144.39, 143.93, 131.21, 129.67, 128.82, 128.21, 127.66, 126.86, 126.63, 123.76, 121.65, 121.39, 120.97, 116.48, 82.10.

Ligand Chromene-L A mixture of **Chromene-Br** (0.65 g, 1.8 mmol), 2-(tributylstannyl)pyridine (1.0 g, 2.7 mmol), Pd(PPh₃)₄ (0.10 g, 0.08 mmol) and toluene (30 mL) was heated to 120 °C under a nitrogen atmosphere for 25 h with good stirring. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residual was purified on a silica column using a mixture of petroleum ether and diethyl ether (v/v, 5:1) as eluent to give ligand **Chromene-L** as a white solid (0.35 g, 53.8% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.67 (d, *J* = 4.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.75–7.68 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.22 (t, *J* = 6.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.20 (d, *J* = 9.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 157.04, 152.43, 149.66, 145.52, 144.77, 138.56, 136.70, 129.56,

128.66, 128.15, 127.56, 127.43, 127.03, 126.69, 126.57, 123.56, 122.11, 121.25, 121.11, 120.54, 116.53, 82.42.

Complex Chromene-Ir-CF The ligand **Chromene-L** (0.33 g, 0.91 mmol) and $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (0.13 g, 0.41 mmol) were dispersed in a mixture of 2-ethoxyethanol/water (v/v, 3:1) (20 mL). The reaction solution was heated to 90 °C under a nitrogen atmosphere for 14 h with good stirring. After cooling to room temperature, water (20 mL) was added to precipitate the μ -chloride-bridged Ir(III) dimer. The dimer was collected by centrifugation and dried in a vacuum oven. Then the dimer was dissolved in CH_2Cl_2 (25 mL) and stirred with thallium(I) acetylacetonate (0.11 g, 0.36 mmol) under nitrogen at room temperature for 17 h. Concentration and subsequent preparative silica gel TLC purification using a mixture of petroleum ether and diethyl ether (v/v, 4:1) as eluent gave **Chromene-Ir-CF** as a yellow powder (65 mg, 15.5 % yield). ^1H NMR (400 MHz, CDCl_3): 8.33 (d, $J = 24.0$ Hz, 2H), 7.68–7.59 (m, 4H), 7.37–7.33 (m, 3H), 7.11–6.95 (m, 14H), 6.69–6.74 (m, 6H), 6.57 (t, $J = 7.2$ Hz, 1H), 6.42–6.35 (m, 2H), 6.06 (d, $J = 12.0$ Hz, 1H), 5.94–5.91 (m, 2H), 5.82 (t, $J = 8.0$ Hz, 1H), 5.20 (t, $J = 8.0$ Hz, 1H), 1.77 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 184.50, 184.49, 168.03, 152.65, 152.48, 148.11, 148.06, 144.69, 144.17, 143.81, 143.70, 136.54, 131.11, 129.25, 129.19, 129.15, 129.09, 128.85, 127.68, 127.07, 127.03, 126.88, 126.30, 123.51, 122.48, 122.44, 122.14, 121.19, 121.11, 121.04, 120.87, 120.70, 120.63, 119.51, 118.33, 116.24, 100.39, 82.62, 28.72, 28.65.$

Computational details:

Geometrical optimizations were conducted using the popular B3LYP functional

theory. The basis set used for C, H, N, and O atoms was 6-311G(d, p) while effective core potentials with a LanL2DZ basis set were employed for metal atoms. The energies of the excited states of the complexes were computed by time-dependent (TD) DFT (TD-DFT) based on all the ground-state geometries. All calculations were carried out by using the Gaussian 16 program.

OLED fabrication and measurements:

The pre-cleaned ITO glass substrates were treated with ozone for 20 min. Then, the PEDOT:PSS was deposited on the surface of ITO glass by spin-coating method to form a 30 nm-thick hole-injection layer and cured at 120 °C for 30 min in the air. The chlorobenzene solutions of **Chromene-Ir-CF** and CBP were irradiated with 365 nm UV light for different durations, and then were spin-coated on the surface of PEDOT:PSS to obtain the emitting layers. Then the uncompleted devices were dried in air at 110 °C for 20 min and transferred into the deposition system to form layers of TPBI (40 nm), Cs₂CO₃ (2 nm) and Al cathode (100 nm) at a base pressure less than 10⁻⁶ Torr. The EL spectra and CIE coordinates were measured with a PR650 spectra colorimeter. The *L-V-J* curves of the devices were recorded by a Keithley 2400 sourcemeter and the luminance was measured using a PR650 spectra colorimeter. All the experiments and measurements were carried out under ambient conditions.

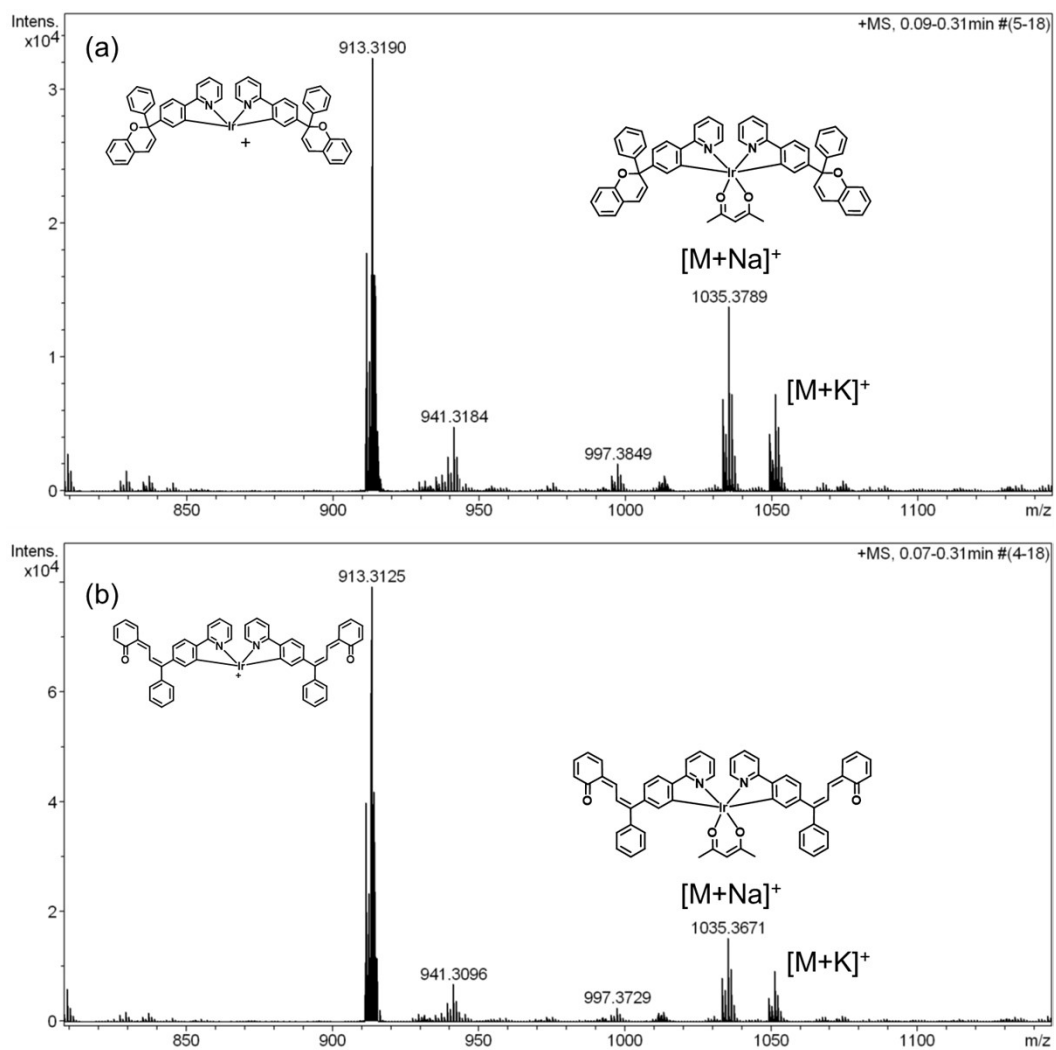


Fig. S1 The MS spectra of **Chromene-Ir-CF** (a) before and (b) after UV irradiation.

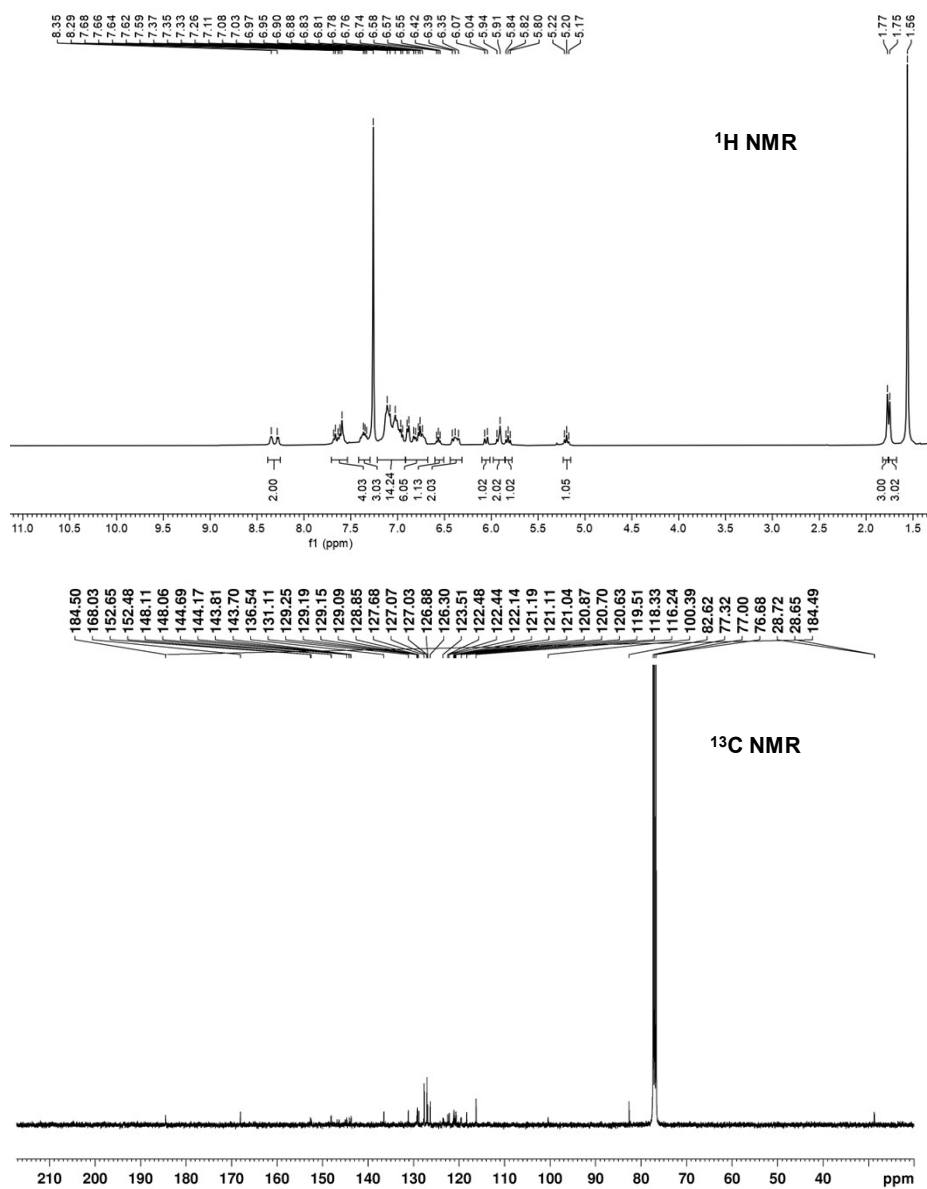


Fig. S2 The ¹H- and ¹³C-NMR spectra of Chromene-Ir-CF.

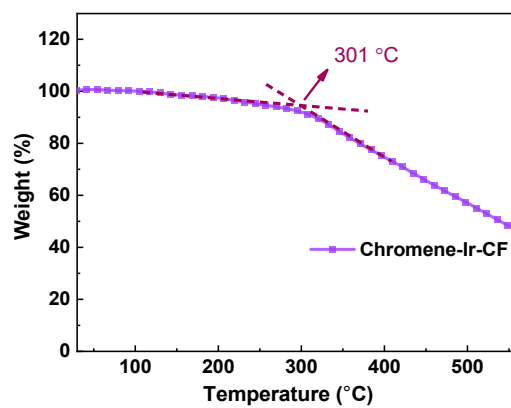


Fig. S3 The TGA curve of Chromene-Ir-CF at N₂ atmosphere.

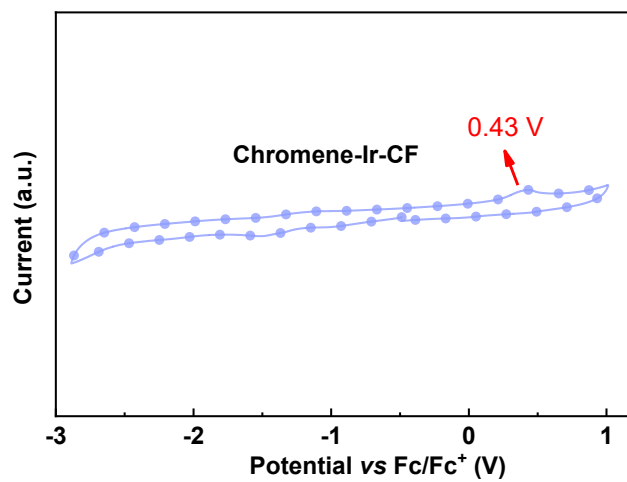


Fig. S4 The CV curve of **Chromene-Ir-CF** in acetonitrile solution.

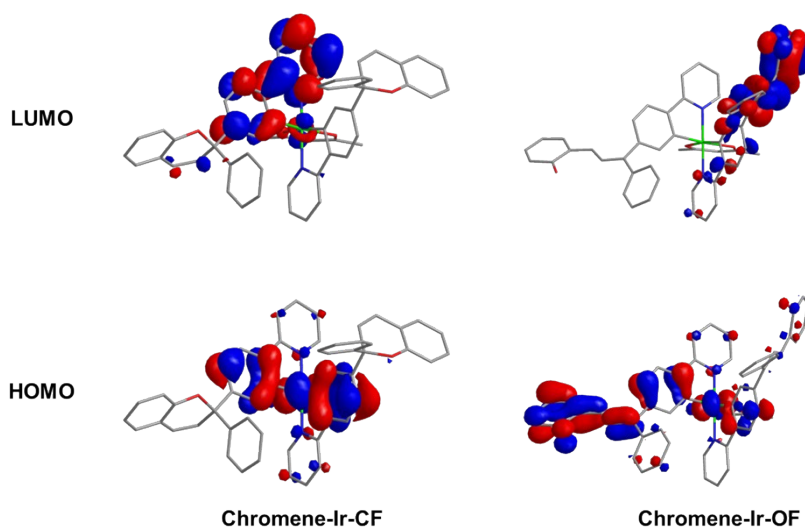


Fig. S5 The distribution pattern of HOMO and LUMO for Ir(III) complexes.

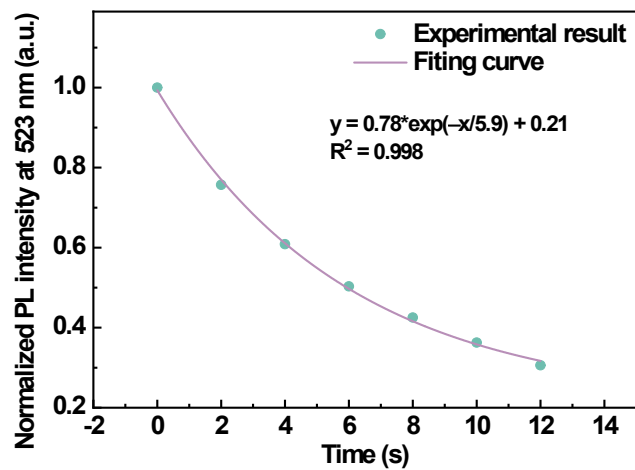


Fig. S6 The PL intensity at 523 nm with different UV irradiation time and corresponding fitting

result.

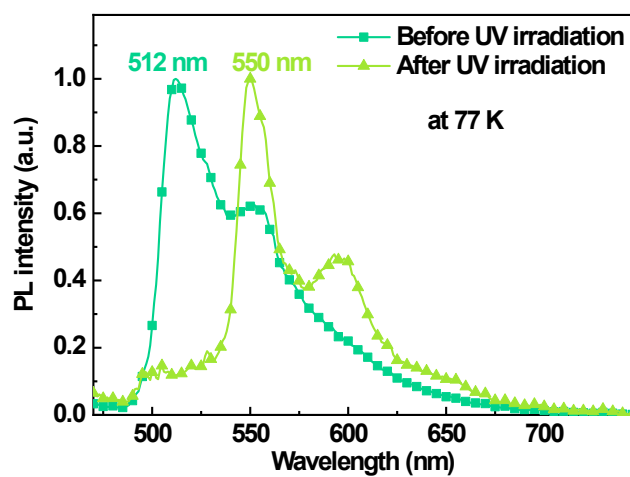


Fig. S7 PL spectra of Chromene-Ir-CF in CH_2Cl_2 before and after UV irradiation at 77 K.

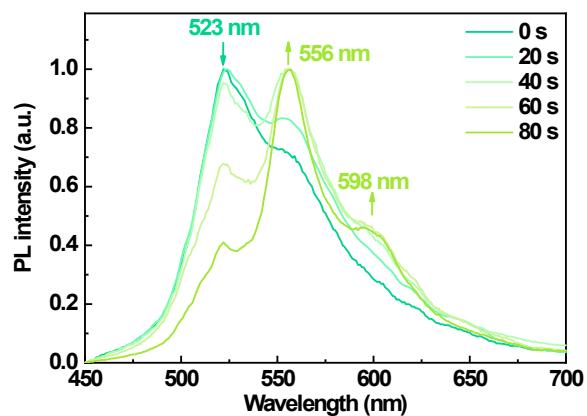


Fig. S8 PL spectra of doped films prepared from the mixture solutions of Chromene-Ir-CF and CBP with different UV exposure time.

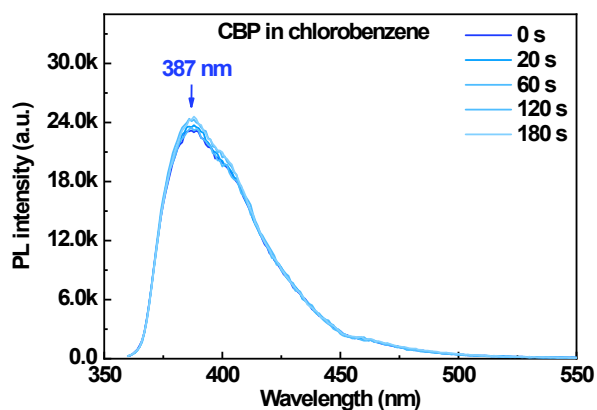


Fig. S9 PL spectra of CBP solution irradiated with 365 nm UV light for different time.

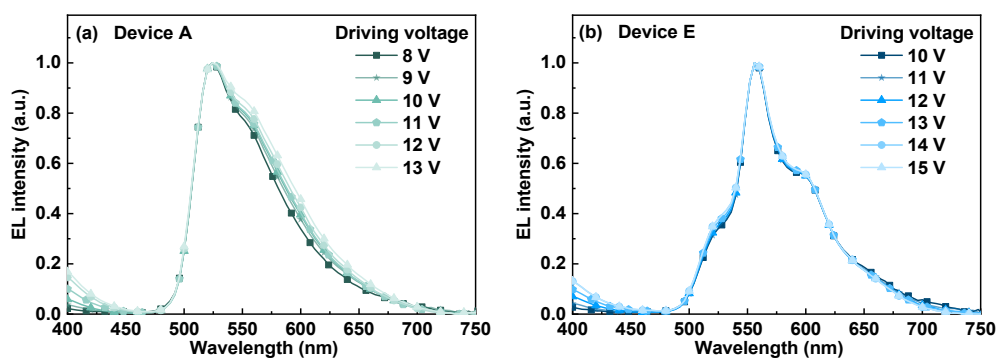


Fig. S10 EL spectra of device A and E at different driving voltages.