Pyrene-Based Non-Doped Blue Hot-Exciton OLEDs with Hybrid Local and Charge-Transfer States: Achieving High efficiency and Low Efficiency Roll-Off

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3. Experimental section

3.1. Synthesis of 1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (BpinCyBpin)

1,6-dibromopyrene (15.00 g, 41.66 mmol), Bis(pinacolato)diboron (31.74 g, 124.98 mmol), potassium acetate (20.44 g, 208.31 mmol), 1,4-dioxane (300 mL), [1,1'-bis(diphenylphosphino)ferrocene] palladium dichloride (914.52 mg, 1.25 mmol) were added to a 500 mL round-bottom flask, and the reaction was heated to 90 °C for 36 hours under nitrogen protection. After the reaction, it was cooled to room temperature, ethyl acetate and saturated brine were added to extract three times, anhydrous magnesium sulfate dried the organic phase, the organic solvent was removed by rotary evaporator, and purified by column chromatography, and the eluent was dichloromethane and petroleum ether in a ratio of 1:2. 17.3 g of white solid was obtained, and the yield was 91.4%.^{1}H NMR (400 MHz, Chloroform-d) δ 9.14 (d, *J* =

9.2 Hz, 2H), 8.56 (s, 2H), 8.20 (s, 2H), 8.16 (s, 1H), 8.14 (s, 1H), 1.50 (s, 24H).

3.2. Synthesis of 4,4,5,5-tetramethyl-2-(6-(4-(phenylsulfonyl)phenyl)pyren-1-yl)-1,3,2-dioxaborolane(BpinCyDPS)

1-bromo-4-(phenylsulfonyl) benzene (5.00 g, 16.83 mmol), compound BpinCyBpin (11.46 g, 25.24 mmol), potassium carbonate (11.63 g, 84.13 mmol), toluene (100 mL), methanol (50 mL), deionized water (50 mL), Tetrakis(triphenylphosphine)palladium (972.18 mg, 841.28 μmol), The reaction was heated to 90 °C for 18 hours under nitrogen protection. After the reaction, it was cooled to room temperature, saturated salt water and methylene chloride were added to extract three times, the organic phase was dried with anhydrous magnesium sulfate, the organic solvent was removed by rotary evaporator, and purified by column chromatography, the eluent was dichloromethane and petroleum ether in a ratio of 3:1. 5.1g of white solid was obtained, with a yield of 55.4%.^{1}H NMR (500 MHz, Chloroform-d) δ(ppm) 9.12 (d, *J* = 9.2 Hz, 1H), 8.56 (d, *J* = 7.7 Hz, 1H), 8.24 (s, 1H), 8.17 – 8.00 (m, 8H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.59 (s, 3H), 1.50 (s, 12H).

3.3. Synthesis of 9-(3-(5-(4-(phenylsulfonyl)phenyl)pyren-1-yl)phenyl)-9H-carbazole(*m*CPS)

9-(3-bromophenyl)carbazole (1.00g, 3.10mmol), DPSCyBpin (2.03g, 3.72mmol), potassium carbonate (2.14g, 15.52mmol), toluene (20mL), methanol (10mL), deionized water (10mL), tetras(triphenylphosphine) palladium (107.59mg, 93.11μmol), nitrogen were added to a 100mL round-bottom flask. After the reaction, it was cooled to room temperature, saturated salt water and methylene chloride were added to extract three times, the organic phase was dried with anhydrous magnesium sulfate, the organic solvent was removed by rotary evaporator, and purified by column chromatography, the eluent was dichloromethane and petroleum ether in a ratio of 1:1, and 1.8 g of light yellow solid was obtained, with a yield of 88.7%.^{1}H NMR (500 MHz, Chloroform-d) δ(ppm) 8.34 (d, *J* = 9.2 Hz, 1H), 8.22 (d, *J* = 15.5 Hz, 2H), 8.19 -8.13 (m, 4H), 8.09 (s, 4H), 8.06 (s, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.86 (s, 1H), 7.83 -7.71 (m, 5H), 7.62 (dd,

J = 17.1, 7.6 Hz, 5H), 7.45 (s, 2H), 7.31 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ(ppm): 146.32, 142.77, 141.49, 140.61, 140.21, 137.72, 136.82, 135.42, 133.12, 131.28, 130.81, 130.34, 129.70, 129.38, 129.22, 128.73, 128.53, 128.44, 127.93, 127.75, 127.64, 127.58, 127.34, 125.84, 125.67, 125.30, 124.90, 124.85, 124.80, 124.56, 124.44, 123.30, 120.20, 119.89, 109.62. MALDI-TOF MS (mass m/z): [M+]. calcd for C46H29NO2S, 659.80; found, 660.1562 [M+].

3.4. Synthesis of 9-(4-(5-(4-(phenylsulfonyl)phenyl)pyren-1-yl)phenyl)-9H-carbazole (*p*CPS)

9-(4-bromophenyl)carbazole (1.00g, 3.10 mmol), DPSCyBpin (2.03 g, 3.72 mmol), potassium carbonate (2.14 g, 15.52 mmol), toluene (20 mL), methanol (10 mL), deionized water (10 mL), tetras(triphenylphosphine) palladium (107.59 mg, 93.11 μmol), nitrogen protection were added to a 100mL round-bottom flask and heated to 90 °C for 18 hours. After the reaction, it was cooled to room temperature, saturated salt water and dichloromethane were added to extract three times, the organic phase was dried with anhydrous magnesium sulfate, the organic solvent was removed by rotary evaporator, and the eluent was purified by column chromatography in the ratio of dichloromethane and petroleum ether in a ratio of 1:1, and 1.8 g of light yellow solid was obtained, with a yield of 86.5%.^{1}H NMR (500 MHz, Chloroform-d) δ(ppm) 8.37 (d, *J* = 9.2 Hz, 1H), 8.31 – 8.07 (m, 12H), 7.94 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 4H), 7.62 (t, *J* = 8.0 Hz, 5H), 7.50 (s, 2H), 7.35 (t, *J* = 7.4 Hz, 2H). 13C NMR (126 MHz, Chloroform-d) δ(ppm) 141.25, 133.72, 132.41, 131.88, 129.81, 128.58, 128.43, 128.24, 128.19, 128.07, 127.95, 127.32, 126.43, 126.08, 125.52, 125.43, 125.00, 123.92, 120.80, 120.50, 110.29, 77.16. MALDI-TOF MS (mass m/z): [M+]. calcd for C46H29NO2S, 659.80; found, 660.1674 [M+].

3.5. The derivation process of the RISC rates

The fluorescence quantum yield (Φ_{PLQY}) of the neat films for *m*CPS and *p*CPS were measured to be 88% and 81%, respectively. And the corresponding prompt fluorescence quantum yield (Φ_{PF}) and delayed fluorescence quantum yield (Φ_{DF}) in the

neat films were calculated using the following equation.

$$\Phi_{PF} = \Phi_{PLQY} \cdot \frac{A_1\tau_{PF}}{A_1\tau_{PF} + A_2\tau_{DF}}$$

$$\Phi_{DF} = \Phi_{PLQY} \cdot \frac{A_2\tau_{DF}}{A_1\tau_{PF} + A_2\tau_{DF}}$$

where the prompt fluorescence lifetime (τ_{PF}) and delayed fluorescence lifetime (τ_{DF}) in neat films were obtained from transient PL decay measurement. Both *m*CPS and *p*CPS exhibit biexponential decay kinetics, with decay lifetimes of 3.02 ns and 13.74 ns for *m*CPS, and 2.50 ns and 11.31 ns for *p*CPS (Table S1). A1 and A2 are the pre-exponential amplitudes corresponding to τ_{PF} and τ_{DF}, respectively, with values of 5.63 and 0.74 for *m*CPS, and 6.39 and 0.62 for *p*CPS. Accordingly, the Φ_{PF} and Φ_{DF} were calculated to be 55.06% and 32.94% for *m*CPS, and 56.30% and 24.70% for *p*CPS.

According to the following equation:

$$\Phi_{PF} = \frac{K_R}{K_R + K_{NR} + K_{ISC}}$$

where K_R, K_{NR}, and K_{ISC} represent radiative transition rate, non-radiative transition rate, and intersystem crossing rate, respectively.

Accordingly, K_{ISC} can be derived as:

$$K_{ISC} = \frac{K_R}{\Phi_{PF}} - K_R - K_{NR}$$

The radiative and non-radiative transition rates were calculated using the following equations:

$$K_R = \frac{\Phi_{PF}}{\tau_{PF}}$$

$$K_{NR} = \frac{\Phi_{PLQY}}{K_R} - K_R$$

The obtained values of K_R and K_{NR} are 1.823×10^8 s^{-1} and 2.49×10^7 s^{-1} for *m*CPS, and

2.252×10^8 s^{-1} and 5.28×10^7 s^{-1} for *p*CPS, respectively. Thus, the calculated value of K_{ISC} is 1.24×10^8 s^{-1} and 1.22×10^8 $s^{-1}$for *m*CPS and *p*CPS.

The reverse intersystem crossing rates (K_{RISC}) in neat films was determined using the following equation.

$$K_{RISC} = \frac{K_{PF}K_{DF}\Phi_{DF}}{K_{ISC}\Phi_{PF}}$$

where K_{PF} and K_{DF}represent the prompt fluorescence rate constant and delayed fluorescence rate constant, respectively. They were calculated by $K_{PF} = \frac{1}{\tau_{PF}}$, $K_{DF} = \frac{1}{\tau_{DF}}$.

Based on the above-calculated Φ_{PF}, Φ_{DF}, and K_{ISC}, the K_{RISC} was determined to be 1.16×10^8 s^{-1} and 1.27×10^8 s^{-1} for *m*CPS and *p*CPS, respectively.

3.6. Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and 500 MHz spectrometer in Germany, using deuterated chloroform as the solvent and tetramethylsilane as the internal standard. Mass spectrometry was performed via MALDI-TOF-MS using a MXIMA-CFR instrument. Differential Scanning Calorimetry (DSC) analysis was performed using a TA Instruments TRIOS DSC 2500 analyzer, with a nitrogen flow rate of 10°C/min and temperature scanning from 40°C to 400°C. Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TGA 2 instrument at a heating rate of 20°C/min, with the temperature ranging from 30°C to 800°C, under continuous nitrogen flow during the heating process. Cyclic voltammetry tests were conducted on a CHI630E electrochemical workstation using a three-electrode system. The working electrode was a glassy carbon electrode, the reference electrode was a saturated calomel electrode, and the counter electrode was a platinum wire. The electrolyte consisted of 0.1 M ammonium hexafluorophosphate in anhydrous acetonitrile. The measurements were performed under a nitrogen atmosphere at a scan rate of 50 mV s^{-1}. Low-temperature fluorescence spectroscopy was performed using a HORIBA FluoroMax spectrometer. The measurements were

conducted by placing the sample solution in a long quartz tube, with temperature controlled by immersing the tube in a Dewar flask filled with liquid nitrogen. The devices were fabricated using vacuum evaporation, with the evaporation equipment being the ZHDS-400 Organic Metal Thin Film Evaporation System from Beijing Top Scientific Instrument Co., Ltd. The substrate of the devices was indium tin oxide (ITO)-coated glass, with a thickness of 135 nm and a sheet resistance of 15 Ω. The ITO glass was ultrasonically cleaned multiple times with acetone, isopropanol, detergent, deionized water, and isopropanol, followed by drying. Before evaporation, the ITO substrate underwent 5 minutes of oxygen plasma treatment. During evaporation, the chamber pressure was maintained below 2×10^{-5} Pa. The deposition rate of organic materials was controlled at 1-2 Å/s, while the deposition rates of lithium fluoride (LiF) and aluminum (Al) were 0.1 Å/s and 4-5 Å/s, respectively. Film thickness and deposition rates were monitored using a quartz crystal microbalance from Inficon (USA). The current density–voltage–luminance (I–V–L) characteristics of the devices were measured using a system consisting of a Keithley 2400 source meter and a C200 color luminance meter, controlled by an SQC–310 monitor. Electroluminescence (EL) spectra were obtained using a PR745 spectroradiometer. The external quantum efficiency (EQE) was calculated based on the measured luminance, current density, and EL spectra, assuming Lambertian distribution for the device's light emission.

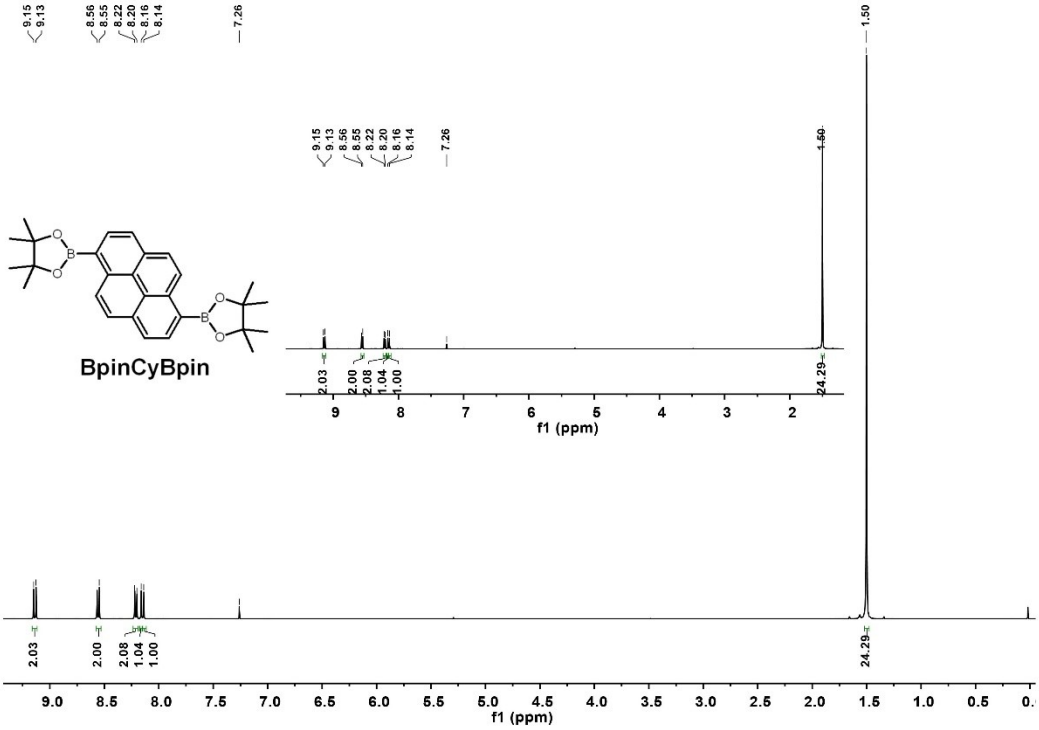

Figure S1 ^{1}H NMR Spectrum of BpinCyBpin in $CDCl_3$.

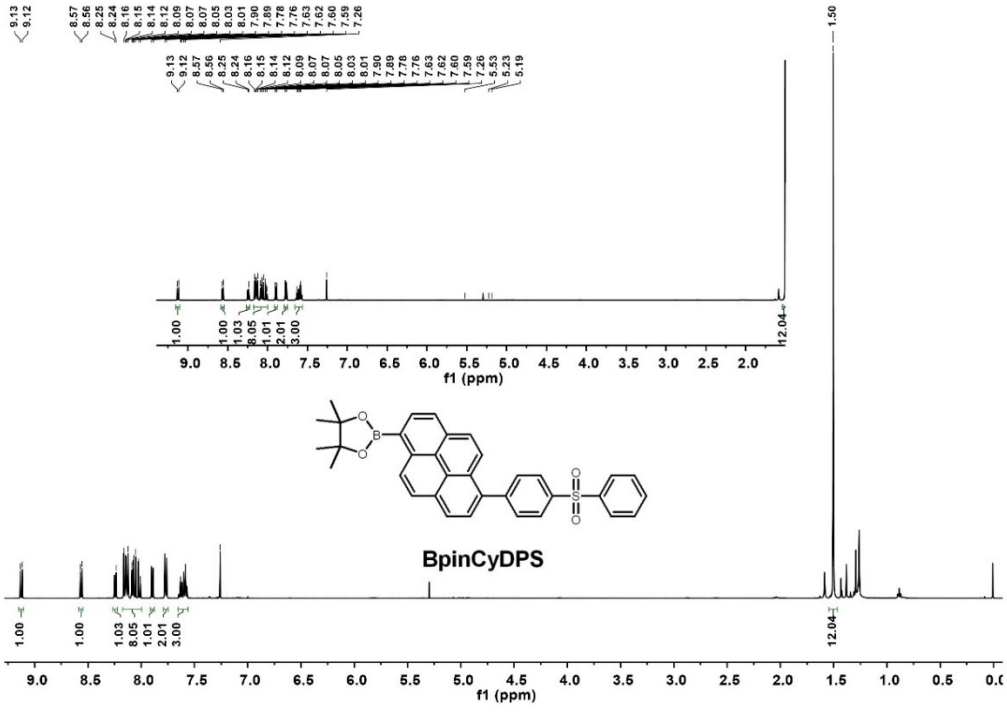

Figure S2 ^{1}H NMR Spectrum of BpinCyDPS in $CDCl_3$.

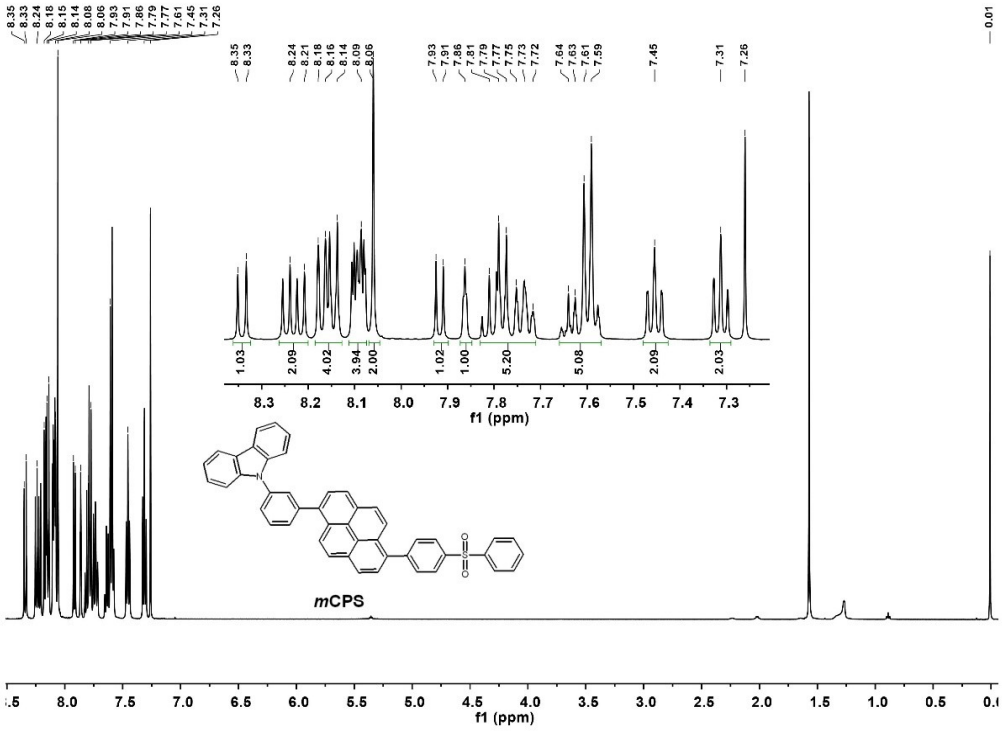

Figure S3 ^{1}H NMR Spectrum of *m*CPS in $CDCl_3$.

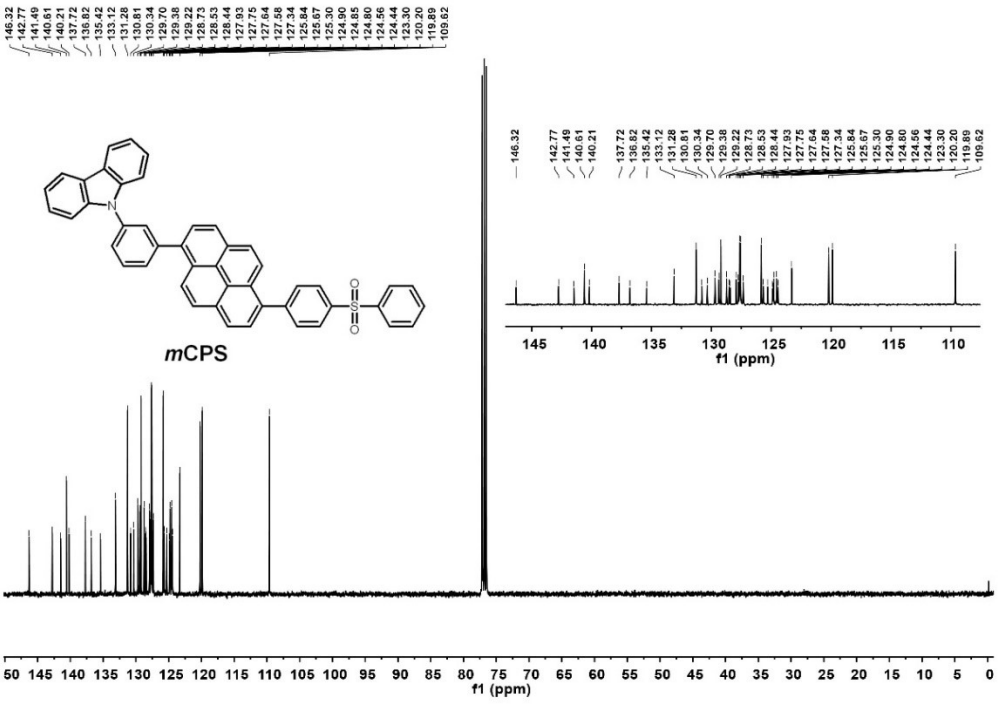

Figure S4 ^{13}C NMR Spectrum of *m*CPS in $CDCl_3$.

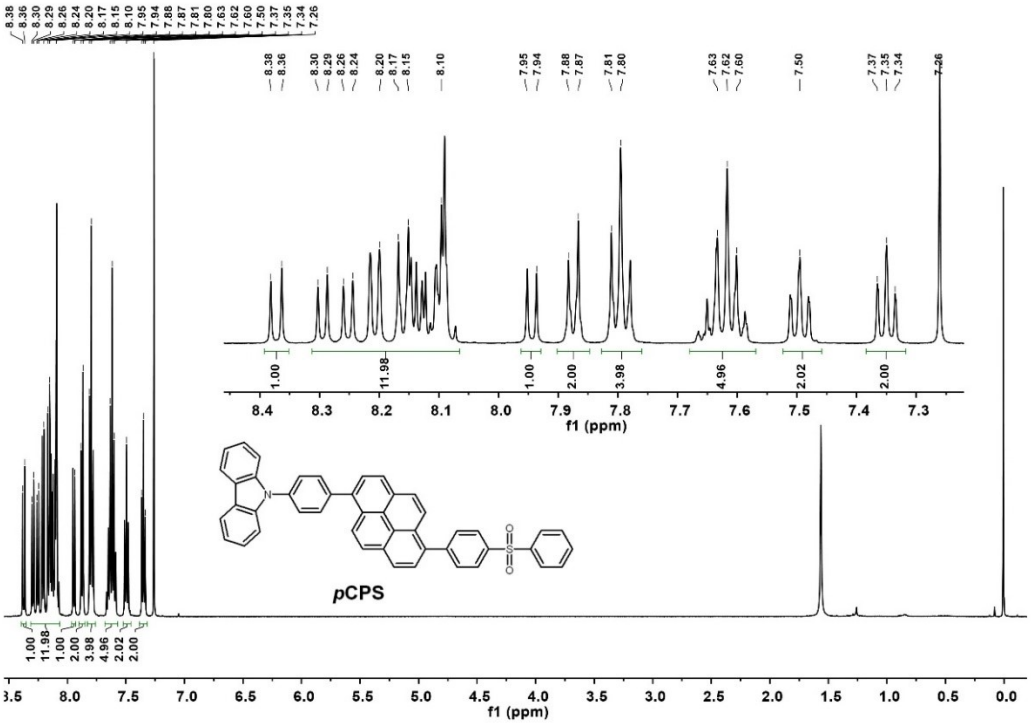

Figure S5 ^{1}H NMR Spectrum of *p*CPS in $CDCl_3$.

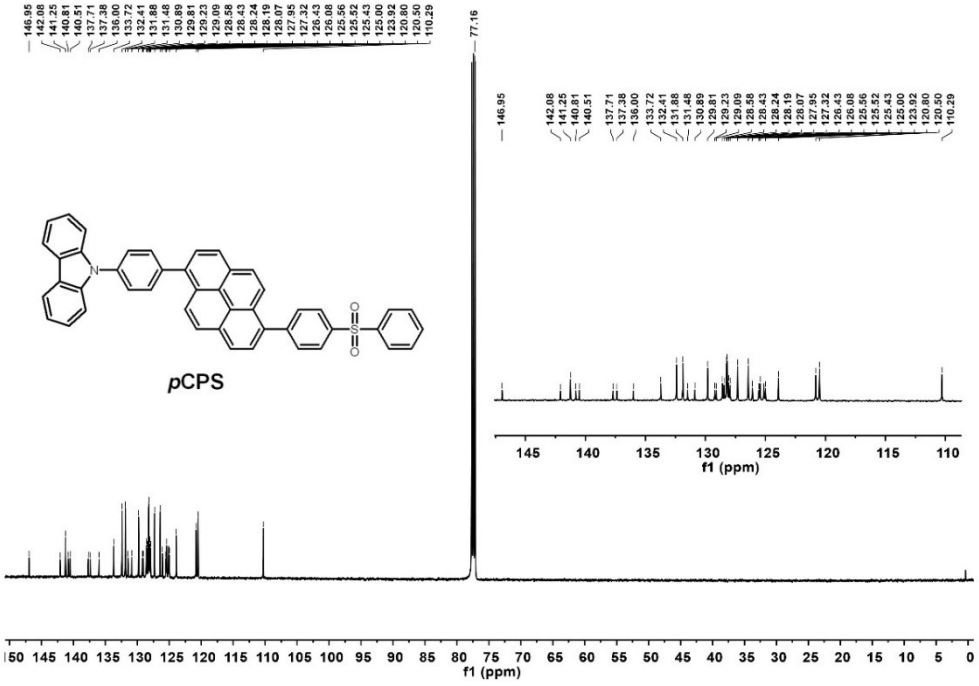

Figure S6 ^{13}C NMR Spectrum of *p*CPS in $CDCl_3$.

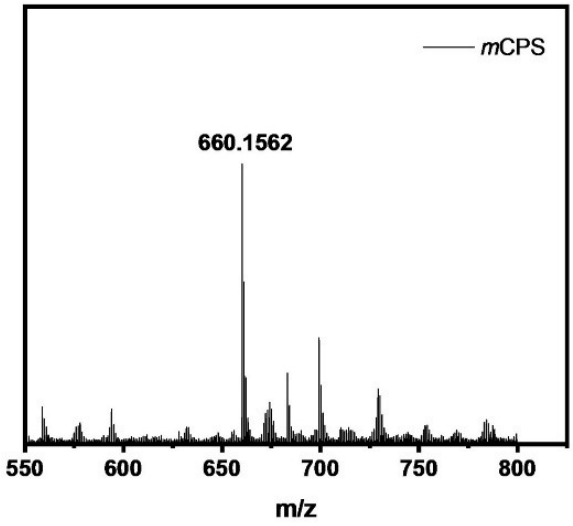

Figure S7 Mass Spectrum (M+H+) of *m*CPS.

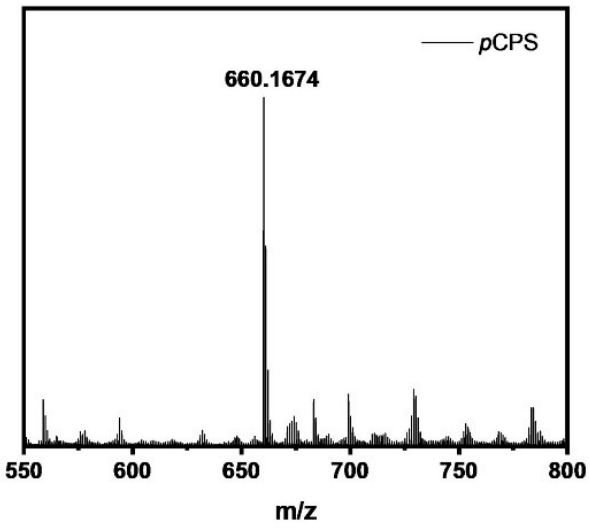

Figure S8 Mass Spectrum (M+H+) of *p*CPS.

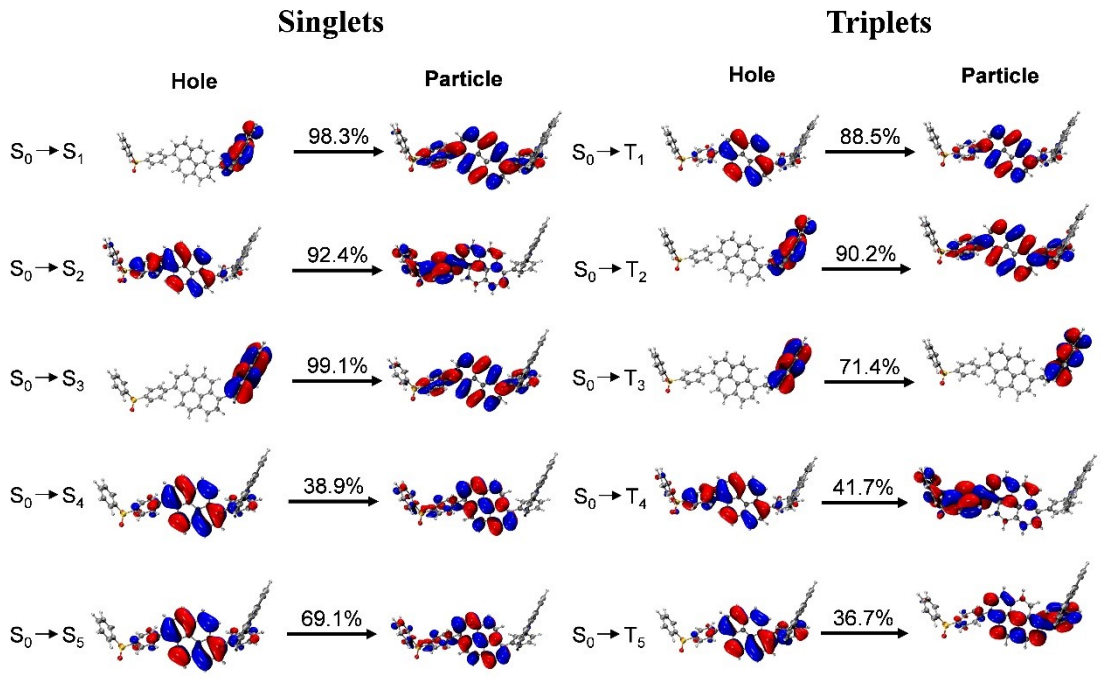

Figure S9 the NTOs for the first five excited states of *m*CPS.

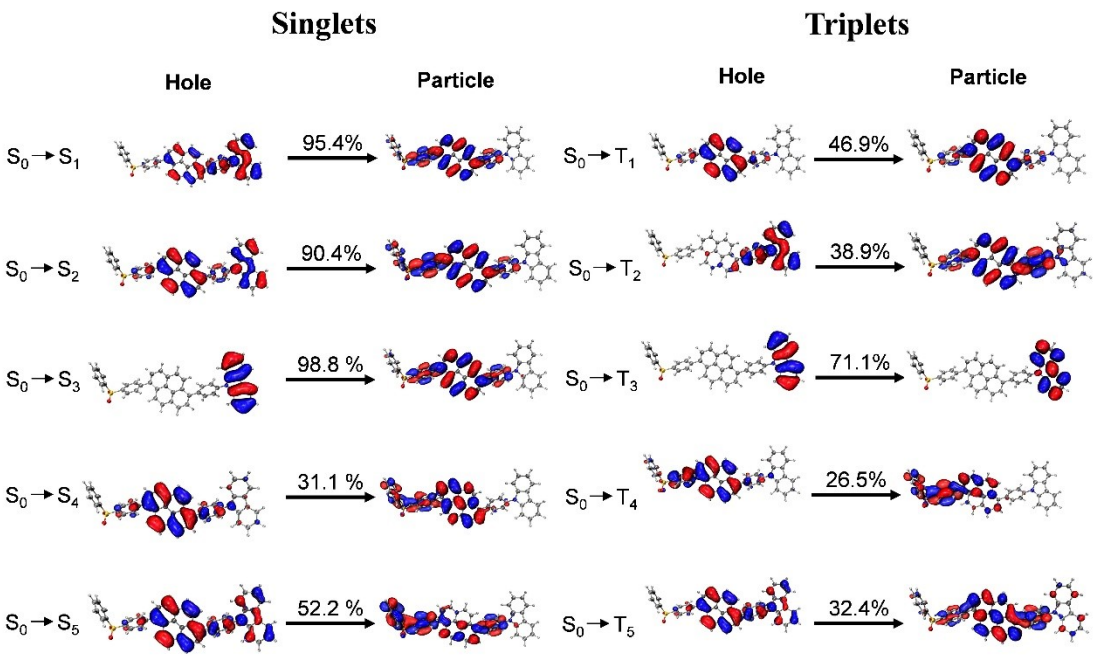

Figure S10 the NTOs for the first five excited states of *p*CPS.

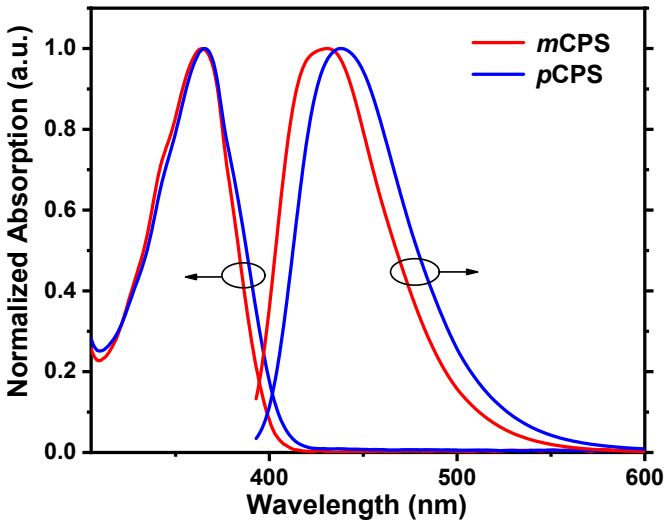

Figure S11 UV-vis absorption and PL spectra of *m*CPS and *p*CPS in toluene (10^{-5} M).

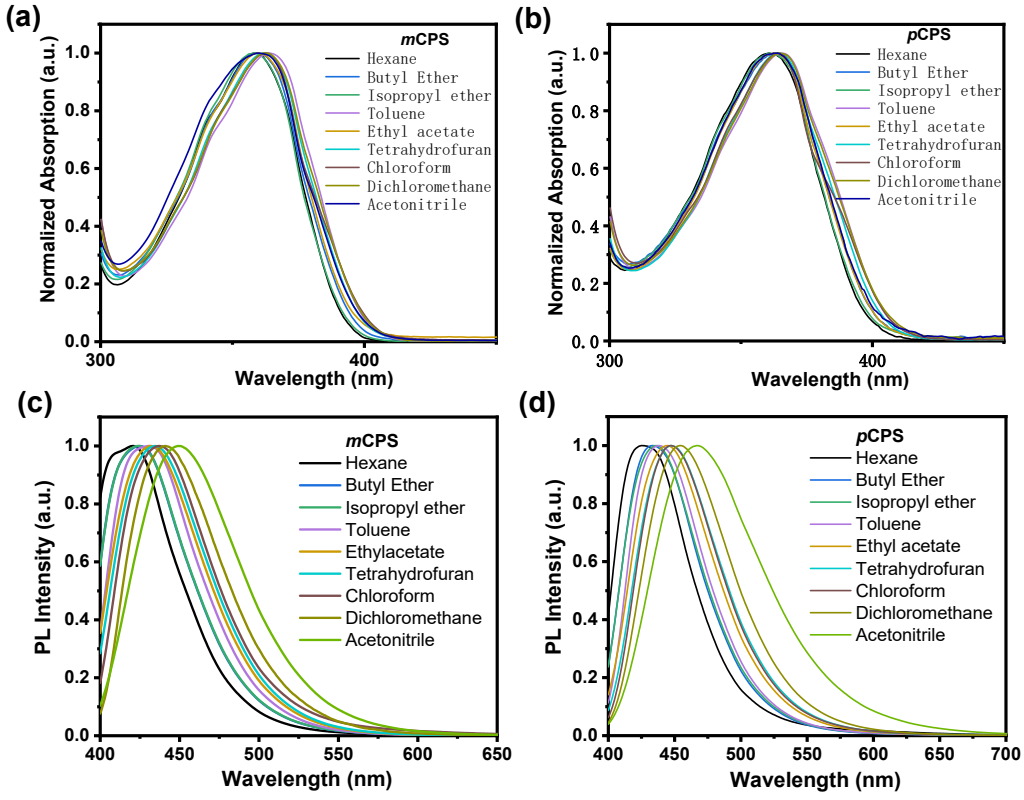

Figure S12 (a-b) UV-vis absorption and (c-d) PL spectra of *m*CPS and *p*CPS in various solvents (10^{-5} M).

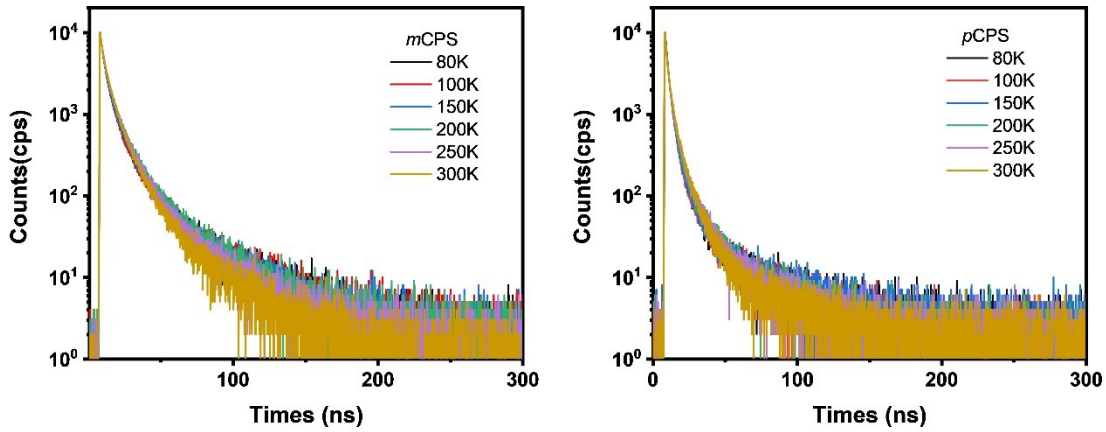

Figure S13 Transient PL decay curve of *m*CPS and *p*CPS in neat film at various temperature.

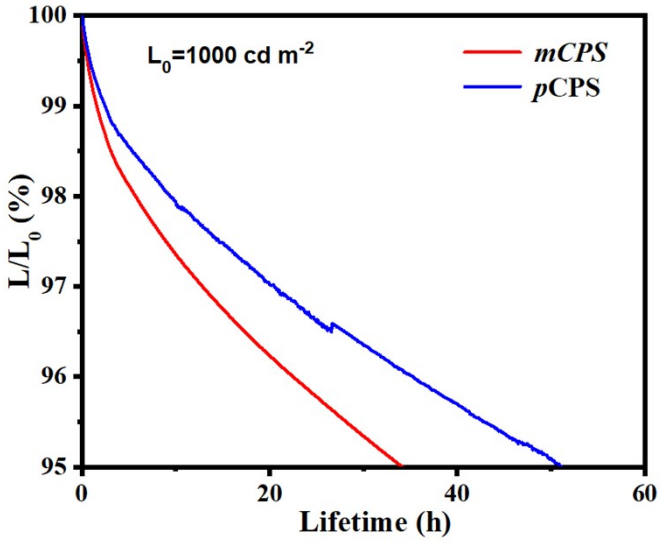

Figure S14 Relative luminescence vs time curve of all the devices.

Table S1 Neat film kinetic parameters of *m*CPS and *p*CPS.

Compound	τ_{PF} [a] [ns]	τ_{DF} [b] [ns]	Φ [c] [%]	Φ_{PF} [d] [%]	Φ_{DF} [e] [%]	K_R [f] [10^7 s^{-1}]	K_{NR} [g] [10^7 s^{-1}]	K_{ISC} [h] [10^8 s^{-1}]	K_{RISC} [i] [10^8 s^{-1}]
*m*CPS	3.02	13.74	88	55.06	32.94	18.23	2.49	1.24	1.16
*p*CPS	2.50	11.31	81	56.30	24.70	22.52	5.28	1.22	1.27

[a] prompt fluorescence lifetime in neat film.

[b] delayed fluorescence lifetime in neat film.

[c] fluorescent quantum yield in neat film.

[d] prompt fluorescent quantum yield in neat film.

[e] delayed fluorescent quantum yield in neat film.

[f] radiative transition rates in neat film.

[g] non-radiative transition rates in neat film.

[h] intersystem crossing rates in neat film.

[i] reverse intersystem crossing rates in neat films.

Table S2 Prompt and delayed fluorescence lifetime in neat film for *m*CPS and *p*CPS.

Compound	Temperature [K]	τ_{PF} [ns]	τ_{DF} [ns]
*m*CPS	80	4.48	25.05
	100	4.31	25.68
	150	4.51	24.90
	200	4.95	23.29
	250	4.84	20.87
	300	4.80	18.20
*p*CPS	80	2.47	18.17
	100	2.51	20.61
	150	2.46	17.25
	200	2.55	16.18
	250	2.58	13.47
	300	2.52	10.86