Supporting information

Hybrid Local and Charge Transfer Emitters Using Pyrene as π-Bridge Towards Negligible Efficiency Roll-Off Non-doped OLED

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General methods

Molecular Structure Characterization: ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in chloroform-*d* ($CDCl_3$) as the solvent on the Switzerland Bruker and tetramethylsilane (TMS, δ=0.00 ppm) as the internal standard. High-resolution electrospray molecular mass spectra was determined by Bruker Ultraflextreme MALDI-TOF mass spectrometer.

Single Crystal Testing and Analysis: Single crystals were obtained via a mixed solvent evaporation method. Single crystal data were collected using a Bruker D8 Venture X-ray single crystal diffraction system, employing a copper (CuKα, λ = 1.54184) source at a voltage of 50 kV and a current of 0.8 mA. The diffraction angle was set from 8° to 140°, and the temperature was maintained at 295 K. The single crystal structure was analyzed using Mercury software.

Theoretical Calculations: The ground state structures were optimized using density functional theory (DFT) with the B3LYP and the 6-31G(d) basis set. The excited states natures were calculated using time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) and DEF2VP levels. These calculations were performed using Gaussian09 software. The spin-orbit coupling (SOC) of the compound was calculated using ORCA software.

Thermal Stability Testing: Thermal stability was measured using a NETZSCH STA449 simultaneous thermal analyzer. The compound was heated from room temperature to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere to obtain the thermal weight loss curve (Thermal Gravimetry Analysis, TGA). The decomposition temperature (T_d) was determined at the temperature when the mass loss reached 5% of initial weight. Additionally, Differential scanning calorimetry (DSC) were carried out on NETZSCH DSC 200 PC instrument. The sample was heated from room temperature to 300 ℃ at a rate of 10 ℃/min, maintaining this temperature for 3 minutes, and then

rapidly cooling to room temperature. After, the sample was reheated to 300 °C at the same rate. The curve obtained during the second heating was the differential scanning calorimetry curve (DSC) to obtain the glass-transition temperature.

Electrochemical Characteristics Testing: The electrochemical properties were investigated using a CHI 660E electrochemical workstation to obtain the cyclic voltammograms. A three-electrode system consisting of a glassy carbon electrode (as the working electrode), a platinum wire electrode (as the auxiliary electrode), and a saturated calomel electrode (as the reference electrode) were employed. The electrolyte was a 0.1 mol/L tetrabutylammonium perchlorate solution in acetonitrile. Ferrocene/ferrocenium (Fc^+/Fc) was used as an internal standard. The compound was dissolved in dichloromethane at a concentration of 1×10^{-5} mol/L and mixed with the electrolyte for testing. Parameters such as the oxidation onset potential of the compound and the onset position of the absorption peak in dichloromethane solution were used to calculate the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

$$E_{HOMO} = -4.8 - (E_C^{\ OX} - E_{\mathrm{f}}^{\ OX})\mathrm{eV} \quad (1)$$

$$E_{LUMO} = E_{HOMO} + E_{\mathrm{g}} \quad (2)$$

$$E_{\mathrm{g}} = \frac{1240}{\lambda} \quad (3)$$

In the above formula, the onset oxidation potential of the materials is represented by E_c^{OX}, while the oxidation potential of ferrocene is denoted as E_f^{OX}. E_g corresponds to the energy gap, and λ represents the wavelength corresponding to onset position of the absorption peak .

Photophysical properties: The UV-visible (UV-Vis) absorption spectra, photoluminescence (PL) spectra, and transient photoluminescence spectra along with the photoluminescence quantum yield (PLQY) were characterized using a Hitachi U-3900 UV spectrophotometer, a Fluoromax-4700

fluorescence spectrometer, and an Edinburgh FLS 980 transient fluorescence spectrometer, respectively.

The S_1 energy level of **TPAPyCP/2mTPAPyCP** was determine from emission maximum peaks in 2-MeTHF solution at 77 K without any delayed. T_1 energy level was calculated using the phosphorescence spectra of PtOEP & **TPAPyCP/2mTPAPyCP**at 77 K in 2-MeTHF with 5 ms delayed, in which PtOEP was employed as sensitizer. The T_1 states of TPAPyCP/2mTPAPyCP were sensitized by phosphorescent dye PtOEP with a low E_{T1}(1.91 eV). There are new emission peaks at 716 (1.73 eV) and 704 nm (1.76 eV) in the delayed phosphorescent spectra (Figure 5) with 5 ms delayed, and were attibuted to the T_1 states of TPAPyCP/2mTPAPyCP .

Calculation of rate constants: The performance parameters of the materials were calculated using the following equations.

$$\Phi_{\mathrm{p}} = \Phi_{PL} \times R_p; \ \ \Phi_{\mathrm{d}} = \Phi_{PL} \times R_{\mathrm{d}} \qquad (4)$$

$$k_r = \Phi_{\mathrm{p}} / \tau_{\mathrm{p}}; \ \ k_{nr} = (1 - \Phi_{PL}) / \tau_{\mathrm{p}} \qquad (5)$$

$$\Phi_{PL} = k_r / (k_r + k_{IC}) \qquad (6)$$

$$\Phi_{\mathrm{p}} = k_r / (k_r + k_{IC} + k_{ISC}) \qquad (7)$$

$$k_{hRISC} = (k_{\mathrm{p}} \times k_{\mathrm{d}} \times \Phi_{\mathrm{d}}) / (k_{ISC} \times \Phi_{\mathrm{d}}) \qquad (8)$$

$$k_{\mathrm{p}} = 1/\tau_{\mathrm{p}}; \qquad k_{\mathrm{d}} = 1/\tau_{\mathrm{d}} \qquad (9)$$

Φ_{PL} denotes PLQY, while Φ_{p} and Φ_{d} represent the components of prompt and delayed fluorescence, respectively. R_{p} and R_{d} are the proportions of prompt and delayed fluorescence components; τ_{p} and τ_{d} are the lifetimes of prompt and delayed fluorescence. k_r and k_{nr} are the radiative and non-radiative transition rate constants, respectively. k_{IC} refers to the internal conversion rate constant, k_{ISC} is the intersystem crossing rate constant, and k_{hRISC} is the reverse intersystem crossing rate constant.

Solvatochromic Effects: The absorption and emission spectra of the materials were tested in solvents with varying polarities. The Stokes shift in different solvents was calculated, and the relationship between Stokes shift（$\nu_a - \nu_f$) and solvent polarity（Δf）was fitted. Additionally, the molecular excited-state dipole moment μ_e was calculated based on the Lippert-Mataga equation.

$$hc(\nu_a - \nu_f) = hc(\nu_a{}^0 - \nu_f{}^0) + \frac{2(\mu_e - \mu_g)^2}{\alpha_0{}^3} f(\varepsilon, n) \qquad (10)$$

The dielectric constant (ε), solvent refractive index (n), excited-state dipole moment (μ_e), and ground-state dipole moment (μ_g) are defined, while α_0 represents the Onsager radius. h and c denote Planck's constant and the speed of light in vacuum, respectively.

Preparation and Characterization of OLED Devices: Organic light-emitting diodes (OLEDs) with an area of 3×3 mm² were fabricated on indium tin oxide (ITO) glass substrates using a vacuum deposition method. Prior to fabrication, the ITO glass substrates were sequentially cleaned with deionized water, acetone, and isopropanol. After cleaning, the substrates were dried with nitrogen gas and placed in an oven at 120 °C for further drying. The organic layers were deposited at a rate of 0.1 nm/s within a high vacuum chamber under inert gas glovebox conditions, maintaining a pressure below 5.0×10^{-4} Pa. The thickness of the deposited films was monitored using a quartz crystal oscillator.

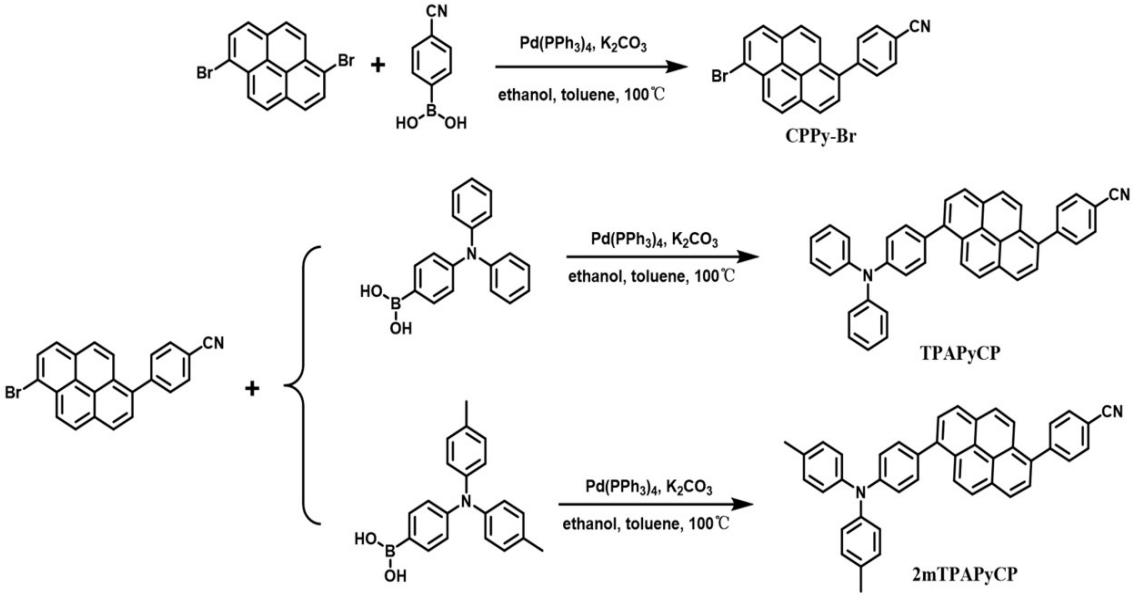
The electroluminescence spectra and CIE coordinates： These data were characterized using a PR-655 spectrophotometer. The current density-voltage-brightness (*J-V-L*) characteristics of the OLEDs were measured using a Keithley 2400 source meter integrated with a BM-70A light source, controlled by a computer. The external quantum efficiency EQE was calculated from the $J-V-L$ curves and spectral data. All devices were characterized at room temperature without packaging.

Exciton utilization efficiency (EUE) of OLED devices: *EUE* can be calculated using Equation :

$$EQE = \gamma \times \Phi_{PL} \times EUE \times \eta_{out} \quad (11)$$

where γ is the exciton recombination rate, which is taken as 100% in this study, Φ_{PL} refers to the absolute photoluminescence quantum yield of the emitting layer material, and η_{out} is the device's external coupling efficiency, assumed to be 20% in this work.

Experimental section



Scheme S1. Synthetic route of **TPAPyCP** and **2mTPAPyCP**

Synthesis of Intermediate CPPy-Br

1,6-Dibromopyrene (720.1 mg, 2 mmol), 4-cyanophenylboronic acid (264.6 mg, 1.8 mmol), and tetrakis(triphenylphosphine)palladium (200 mg, 0.17 mmol) were dissolved in a mixture of 10 mL (2 M) potassium carbonate solution, 20 mL toluene, and 20 mL ethanol. The reaction mixture was heated to reflux in the nitrogen atmosphere for 24 h. After cooling to room temperature, the crude product was extracted with dichloromethane (DCM) and water. The organic phase was collected and dried, then purified by column chromatography using petroleum ether (PE)/DCM (4:1, v/v) as the eluent. The product was recrystallized from DCM to yield a pale yellow solid powder (543 mg, 79% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.39 (d, *J* = 9.2 Hz, 1H), 8.17 (dd, *J* = 8.0, 5.2 Hz, 2H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.95 (d, *J* = 9.2 Hz, 1H), 7.94-7.86 (m, 2H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.81-

7.73 (m, 2H), 7.68-7.60 (m, 2H).

Synthesis of Target Molecule TPAPyCP

The intermediate CPPy-Br (382 mg, 1 mmol), 4-(diphenylamino)phenylboronic acid (260.2 mg, 0.9 mmol), and tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (100 mg, 0.09 mmol) were dissolved in a mixture of 10 mL (2 M) K_2CO_3 solution, 20 mL toluene, and 10 mL ethanol. The mixture was heated under reflux in a nitrogen atmosphere for 24 h. After cooling to room temperature, the crude product was extracted with DCM and water. The organic phase was collected and dried, then purified by column chromatography using PE/DCM (4:1, v/v) as the eluent. The final product was recrystallized from DCM to yield a yellow-green solid powder (399 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.35 (d, *J* = 9.2 Hz, 1H), 8.21 (dd, *J* = 7.9, 2.1 Hz, 2H), 8.11-7.97 (m, 4H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.79-7.70 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.38-7.29 (m, 4H), 7.25 (t, *J* = 8.7 Hz, 6H), 7.13-7.02 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 147.74, 147.27, 146.29, 138.21, 135.34, 134.77, 132.22, 131.40, 131.36, 131.24, 130.04, 129.41, 128.31, 128.10, 127.33, 127.21, 126.17, 125.03, 124.70, 124.51, 124.09, 123.23, 123.17, 119.00, 111.10. HRMS (FAB+, m/z): calcd for $C_{46}H_{36}N_2$, 546.217; found 546.235.

Synthesis of 2mTPAPyCP

The synthesis process for 2mTPAPyCP was similar with that of **TPAPyCP**. The final product was a yellow-green powder solid with a yield of 78%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.35 (d, *J* = 9.3 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 2H), 8.11-7.99 (m, 4H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.27-7.07 (m, 10H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 147.68, 146.32, 145.27, 138.40, 133.73, 132.88, 132.22, 131.36,

131.25, 130.03, 129.95, 128.68, 128.32, 128.12, 127.30, 127.12, 126.27, 125.20, 125.02, 124.99, 124.45, 124.01, 121.93, 119.01, 111.08, 20.89. HRMS (FAB+, m/z): Calcd for $C_{45}H_{30}N_2$, 574.240; found 574.239.

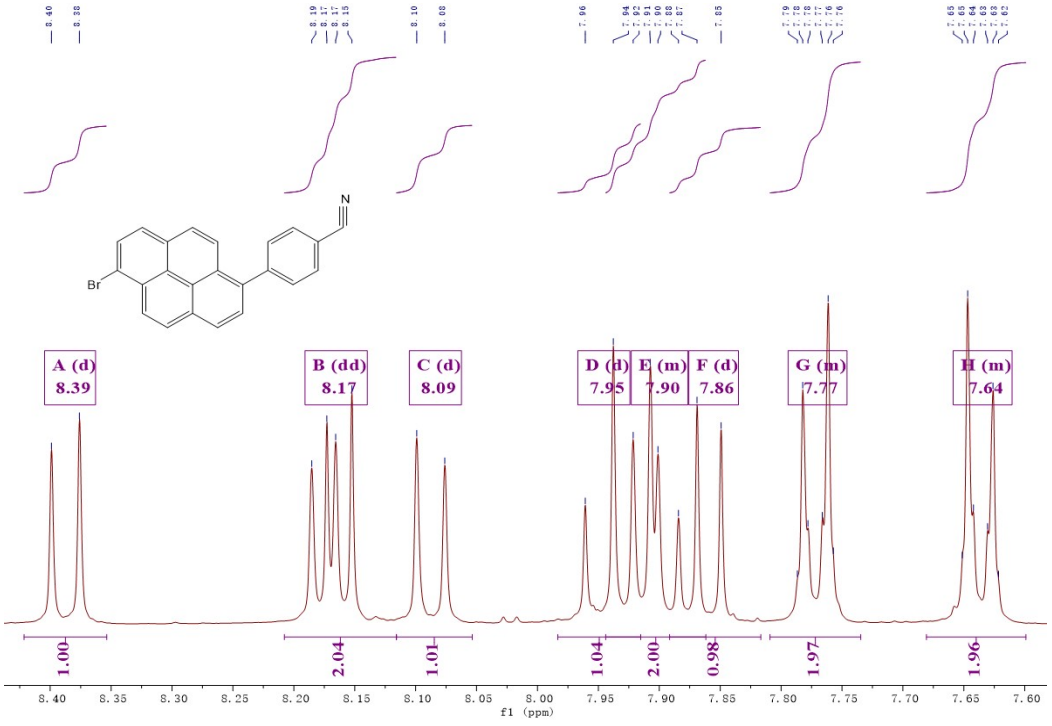


Figure S1 ^{1}H NMR spectra of CPPy-Br

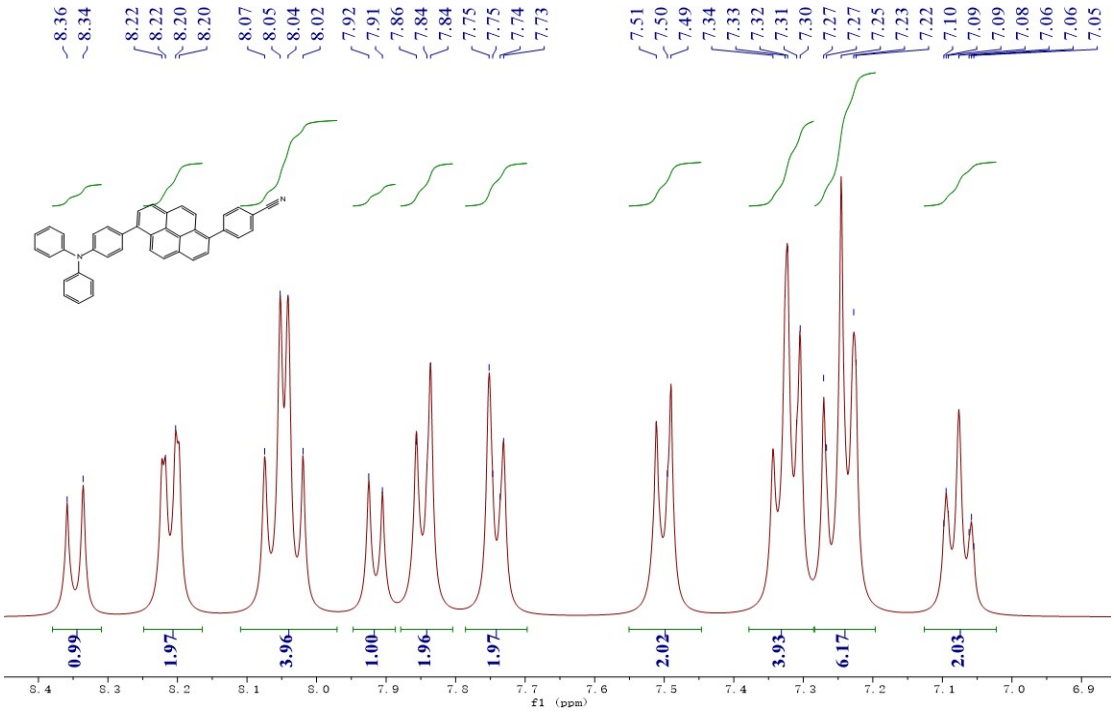


Figure S2 ^{1}H NMR spectra of **TPAPyCP**

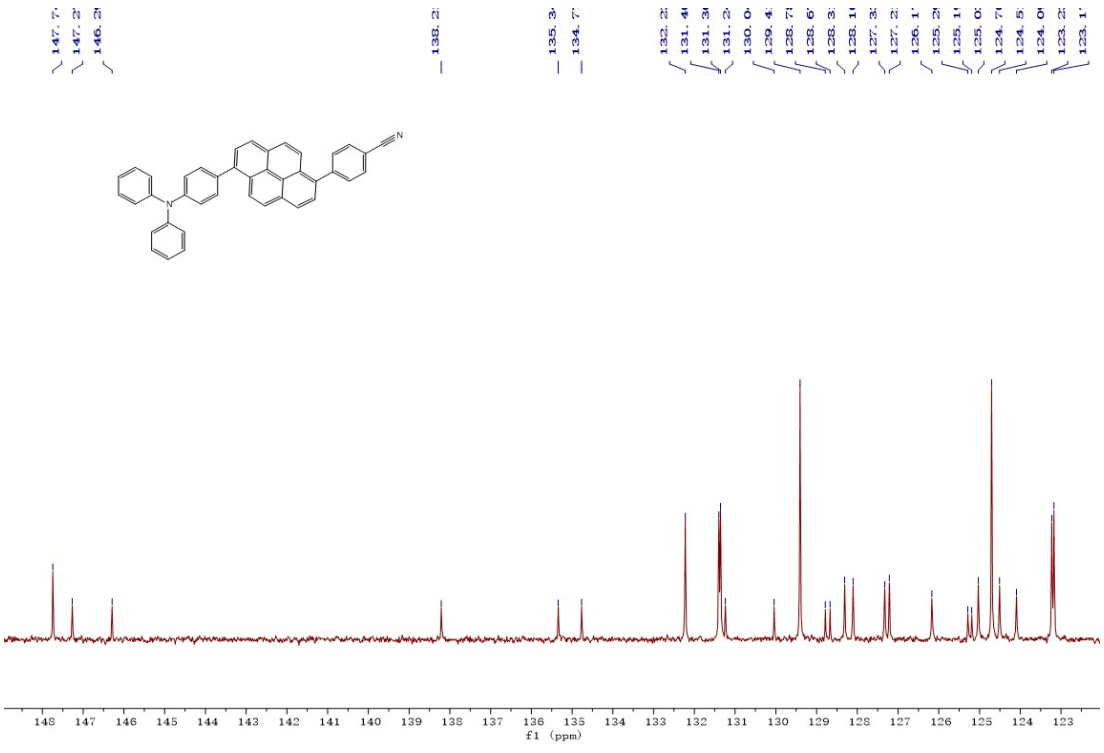


Figure S3 ^{13}C NMR spectra of **TPAPyCP**

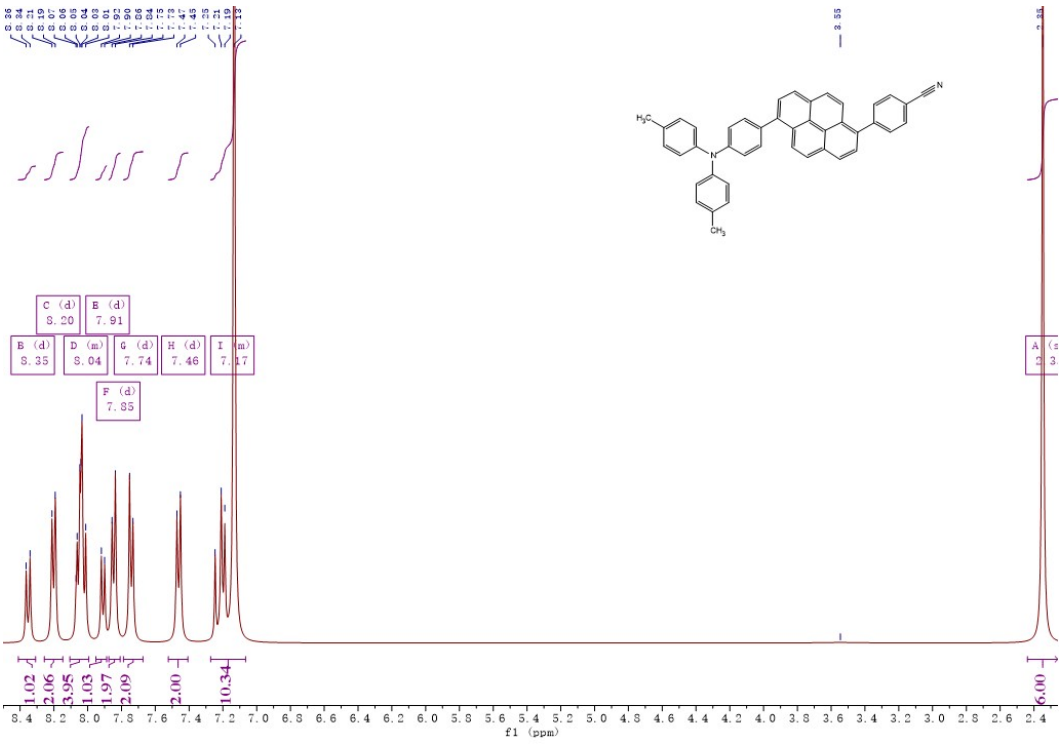


Figure S4 [1]H NMR spectra of **2mTPAPyCP**

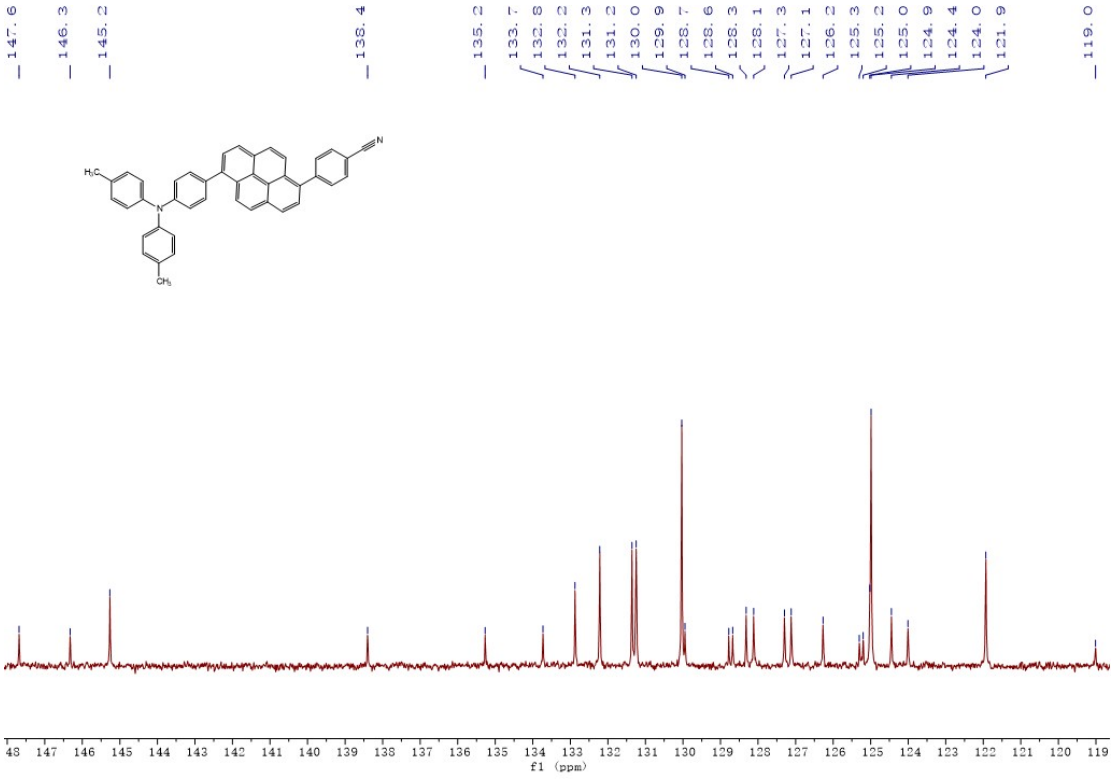


Figure S5 [1]C NMR spectra of **2mTPAPyCP**

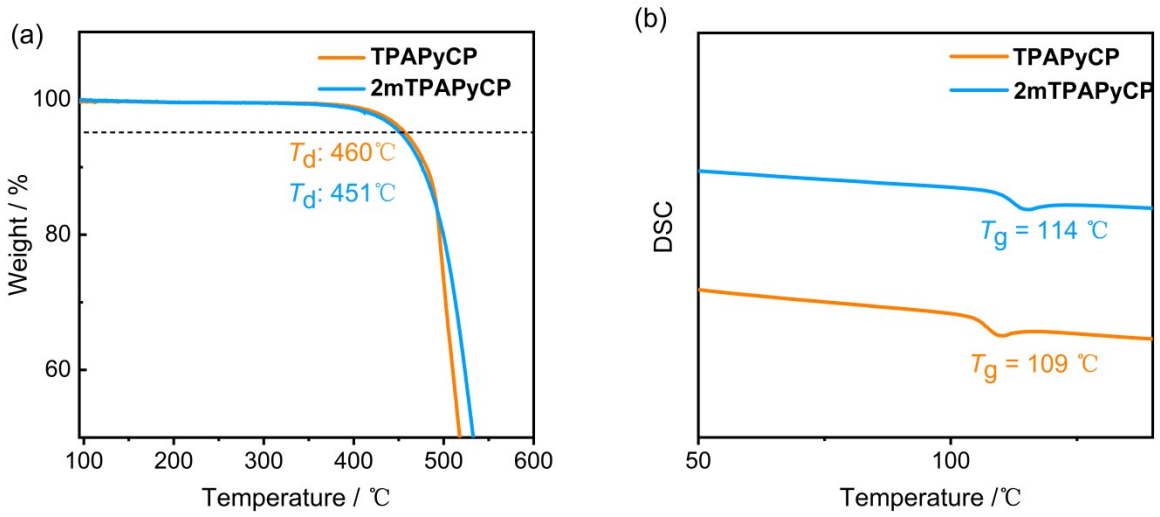


Figure S6 TGA and DSC curves of **TPAPyCP** (a) and **2mTPAPyCP** (b)

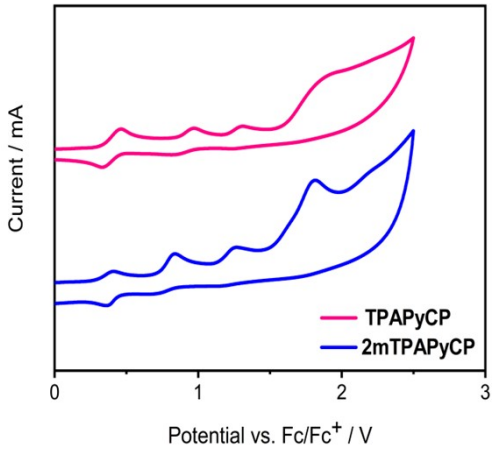


Figure S7 CV curves of **TPAPyCP** and **2mTPAPyCP**

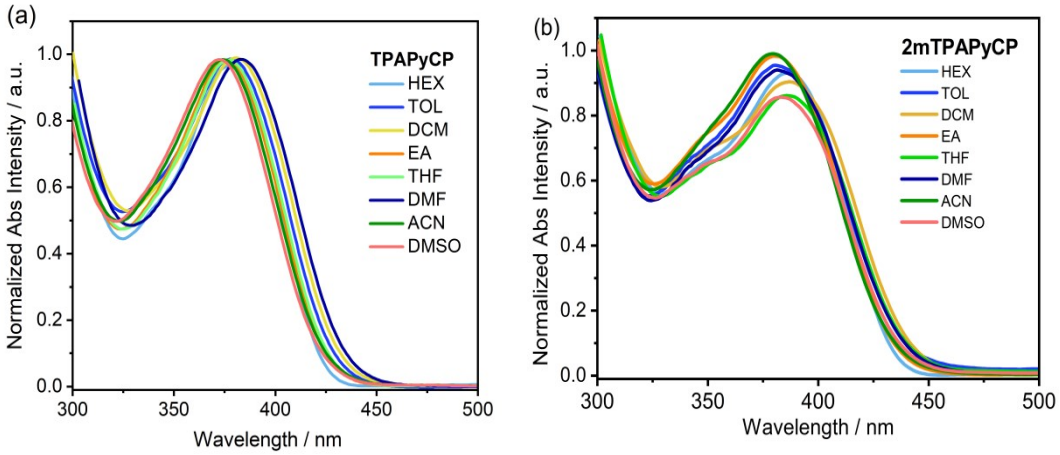


Figure S8 UV-Vis spectra of **TPAPyCP** (a) and **2mTPAPyCP** (b) in different solvents

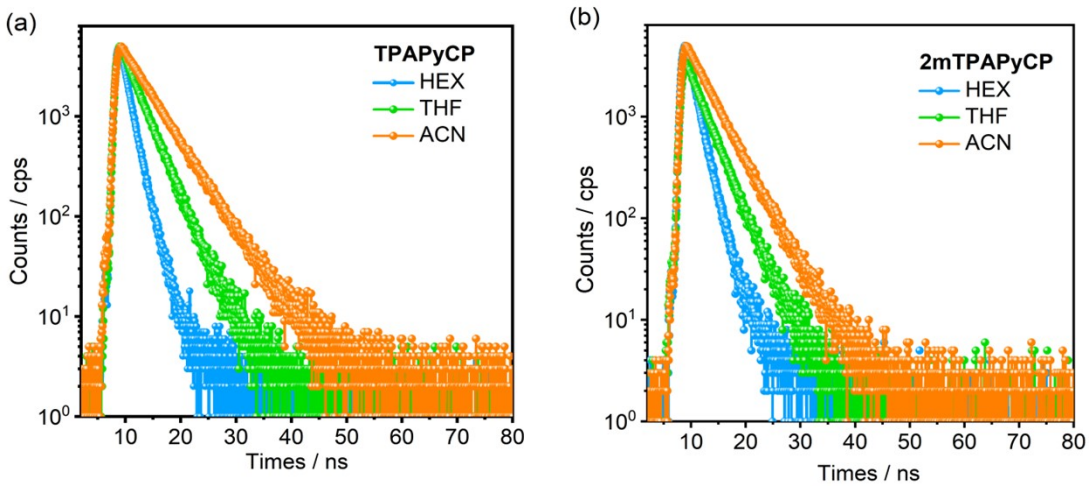


Figure S9 Transient decay curves of **TPAPyCP** (a) ; **2mTPAPyCP** (b) in n-hexane, tetrahydrofuran and acetonitrile

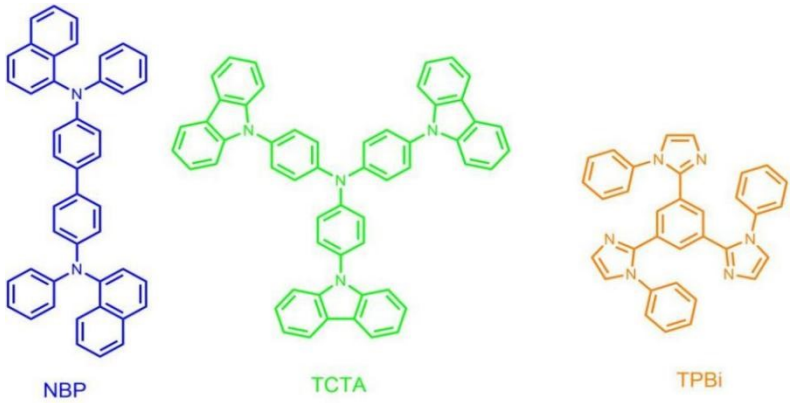


Figure S10 Molecular structures used in non-doped OLEDs

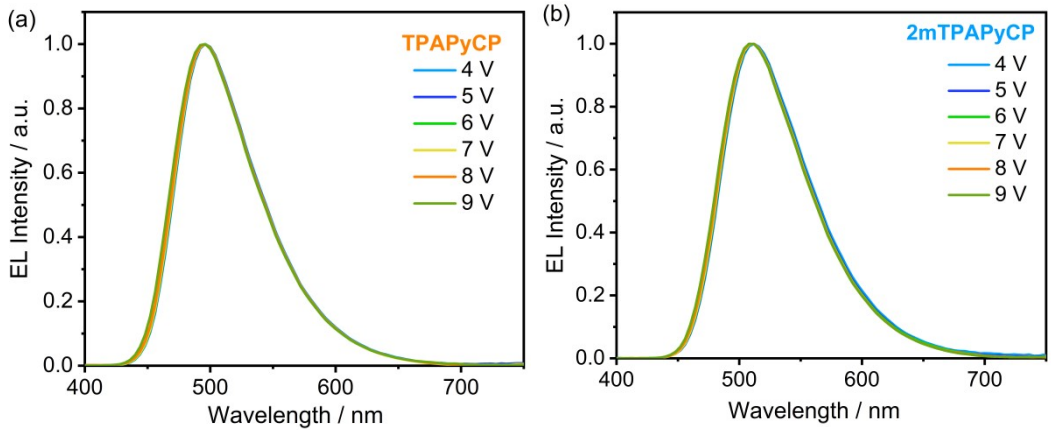


Figure S11 EL spectra at different voltages of **TPAPyCP** (a) and **2mTPAPyCP** (b) based-devices

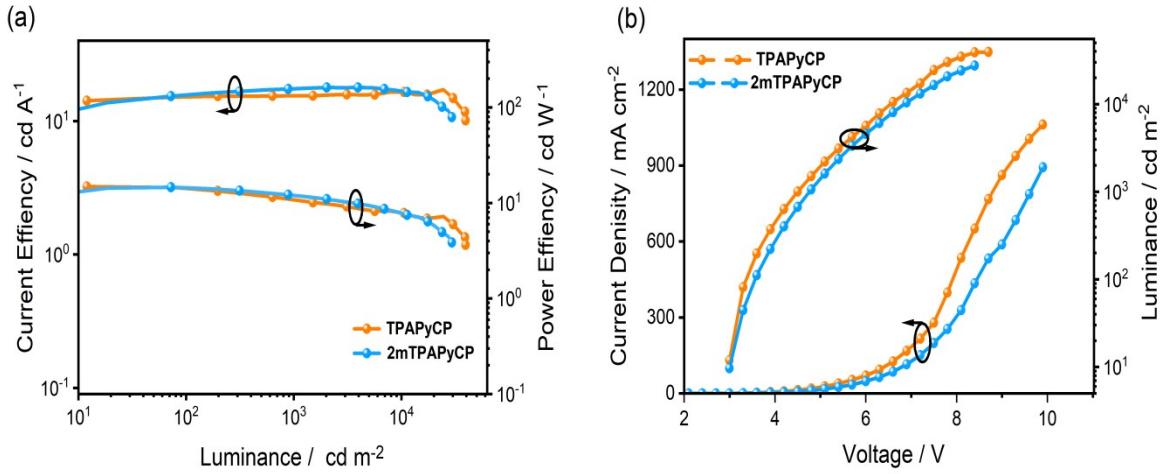


Figure S12 The CE-L-PE (a) and J-V-L (b) curves of non-doped devices based on **TPAPyCP** and **2mTPAPyCP**

Supporting Tables

Table S1.Single crystal structural parameters of **2mTPAPyCP**

Identification code	**2mTPAPyCP**
Empirical formula	$C_{43}H_{30}N_2$
Formula weight	574.69
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.6245(8)
b/Å	11.3457(11)
c/Å	18.9104(16)
α/°	98.867(7)
β/°	96.371(8)
γ/°	104.220(9)
Volume/Å^3	1547.7(3)
Z	2
ρ_{calc} g/cm^3	1.233
μ/mm^{-1}	0.071
F(000)	604.0
Crystal size /mm^3	0.12×0.11×0.02
Radiation	MoKα(λ=0.71073)
2Θ range for data collection/°	3.77 to 52.746
Index ranges	-9≤h≤9, -14≤k≤14, -23≤1≤23
Reflections collected	22644
Independent reflections	6231[R(int)=0.1021, Rsigma=0.1074]
Data/restraines/parameters Goodness-of-fit on F^2	6321/0/4091.002
Final R indexes [I>=2σ(I)]	R1=0.0693,wR2=0.1559
Final R indexes [all data]	R1=0.1451,wR2=0.1898
Largest diff.peak/hole/e Å^{-3}	0.23/-0.24

Table S2 Electrochemical and Photophysical Properties of **TPAPyCP** and **2mTPAPyCP**

Compound	λ_{abs} (nm)		λ_{pl} (nm)		PLQY[c]	k_r	k_{RISC}
	Solution[a]	Film[b]	Solution[a]	Film[b]	(%)	($\times 10^8 s^{-1}$)	($\times 10^8 s^{-1}$)
TPAPyCP	300, 377	300, 388	478	511	73.2	2.90	9.53
2mTPAPyCP	300, 385	300, 388	488	522	65.8	2.05	7.91

[a] 10^{-5} mol/L concentration solution at room temperature; [b] in neat film at room temperature; [c] absolute photoluminescence quantum yield in neat thin film at room temperature.