Supplementary Information

Blue fluorescent emitter based on HLCT and AIE: acidichromism behaviors and narrow-band emission in OLEDs application

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Contents

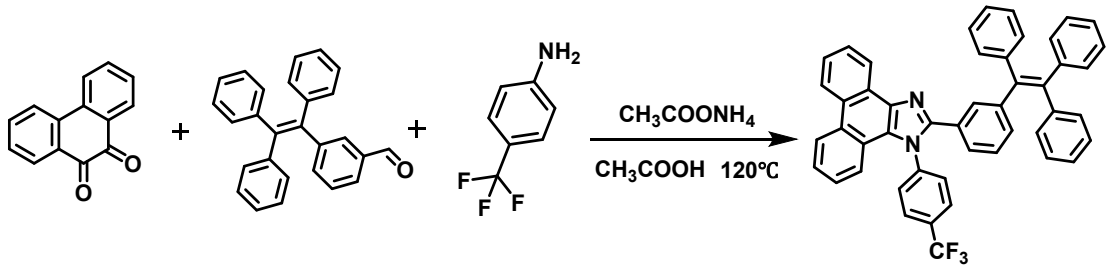
1. General information

All chemicals and solvents were procured from Aladdin Company and utilized without additional purification unless otherwise specified.

The ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AVANCE-600 MHz instrument, with tetramethylsilane (TMS) employed as the internal reference standard. HRMS was conducted using a Bruker maXis mass spectrometer. Powder X-ray diffraction (PXRD) patterns were measured with a Bruker D2 PHASER Gen2 diffractometer. Fourier transform-infrared (FT-IR) spectra was conducted using a Nicolet™ IS50 FTIR. The scanning range was from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}. Differential scanning calorimetry (DSC) measurements were acquired using a METTLER-TOLEDO DSC3+ instrument. The thermogravimetric analysis (TGA) measurements were measured with a METTLER-TOLEDO TGA/DSC1_* instrument. Cyclic voltammetry (CV) was performed using an AUTOLAB PGSTAT 302 N Electrochemical Analyzer, which employed a three-electrode configuration consisting of a glassy carbon electrode as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the pseudo-reference electrode. The measurements were conducted in dichloromethane containing tetrabutylammonium hexafluorophosphate (Bu4NPF6) at a concentration of 0.1 M. The theoretical calculations utilizing density functional theory (DFT) and time-dependent DFT (TD-DFT) were conducted using the Gaussian 09 software at the B3LYP/6-31G(d) level. All EL performance data were tested by Shaanxi Lighte Optoelectronics Material Co., Ltd. (LTOM)

2. Synthesis details

2.1 Synthesis route



CF_3-PPI-TPE

Scheme S1 Synthesis route of CF_3-PPI-TPE

2.2 Synthesis and characterization

The compounds of CF_3-PPI-TPE were obtained by Debus-Radziszewski reaction. The synthetic routes of these compounds were shown in **Scheme S1**.

Synthesis of 1-(4-(trifluoromethyl)phenyl)-2-(3-(1,2,2-triphenylvinyl)phenyl)-1H-phenanthro[9,10-d]imidazole (CF_3-PPI-TPE)

Phenanthrene-9,10-dione (0.57 g, 2.69 mmol), 4-(1,2,2-triphenylethenyl) benzalde hyde (1 g, 2.69 mmol) , 4-(trifluoromethyl) aniline (2.21 g,13.46 mmol, 1.7 ml) and CH_3COONH_4 (1 g, 13 mmol) were dissolved in 40 mL of CH_3COOH. Th e mixture was stirred and refluxed for 1 hour at 120 °C under nitrogen atmos phere. Upon completion of the reaction, the mixture was allowed to cool to ro om temperature. After the solvent was evaporated, the residue was purified by silica gel column chromatography employing an ethyl acetate/petroleum ether (EA/PE = 1/4, v/v) gradient as the eluent. The resulting crude product was pou red into a large amount of methanol solution and heated and stirred for 30 mi nutes. It was then filtered to obtain a light green powder (1.78 g, 92.46 % yie lds). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, J=8.0 Hz, 1H), 8.77 (d, J=8.4 H z, 1H), 8.70 (d, J=8.3 Hz, 1H), 7.83 (d, J=7.9 Hz, 2H), 7.74 (s, 1H), 7.66 (s, 1H), 7.57 (d, J=8.0 Hz, 2H), 7.53 (s, 1H), 7.30 (t, J=7.7 Hz, 1H), 7.22 (d, J=

8.0 Hz, 2H), 7.14 (s, 1H), 7.11 (t, J=5.6 Hz, 8H), 7.08 (d, J=7.4 Hz, 1H), 7.0 2-6.99 (m, 6H), 6.97 (d, J=7.8 Hz, 2H) (**Figure S1**). ^{13}C NMR (101 MHz, C DCl_3) δ 143.5, 143.2, 140.3, 131.5, 131.4, 131.4, 131.2, 128.7, 128.6, 128.3, 1 27.8, 127.6, 126.7, 126.2 (**Figure S2**). HR-MS (ESI, m/z): Found: $[M+H]^+$ 693.2 471, molecular formula $C_{48}H_{31}F_3N_2$ requires 692.7840. (**Figure S3**). Element analy sis for CHN, Found: C, 82.8, H, 4.3, N, 4.2%; molecular formula $C_{48}H_{31}F_3N_2$ requires C, 83.2, H, 4.5, N, 4.0% (**Figure S4**). FT-IR spectrum: 3050 cm^{-1} (Ar -H), 1613 cm^{-1} (-C=N), 1474 cm^{-1} (-C=C), 1322 cm^{-1} (-CN), 1131 cm^{-1} (-CF), 858, 756, 702 cm^{-1} (-Ar-CH) (**Fiqgure S5**).

3. HMRS and NMR

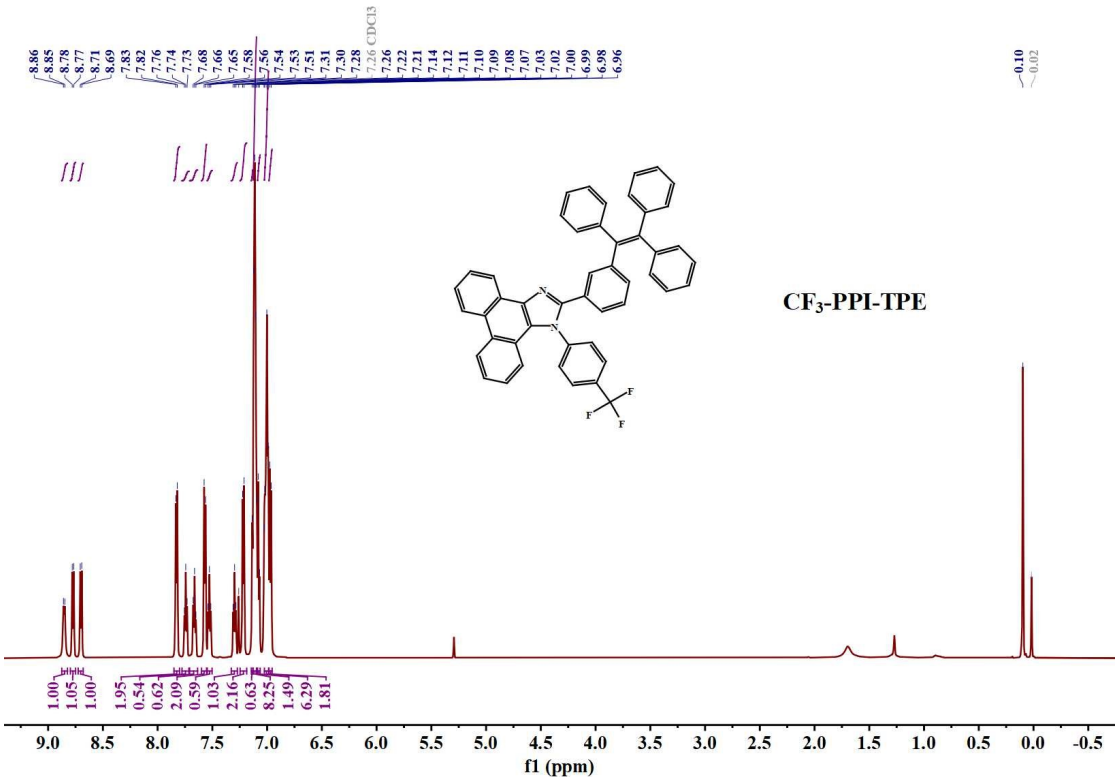


Figure S1. ^{1}H-NMR spectra of CF_3-PPI-TPE in $CDCl_3$

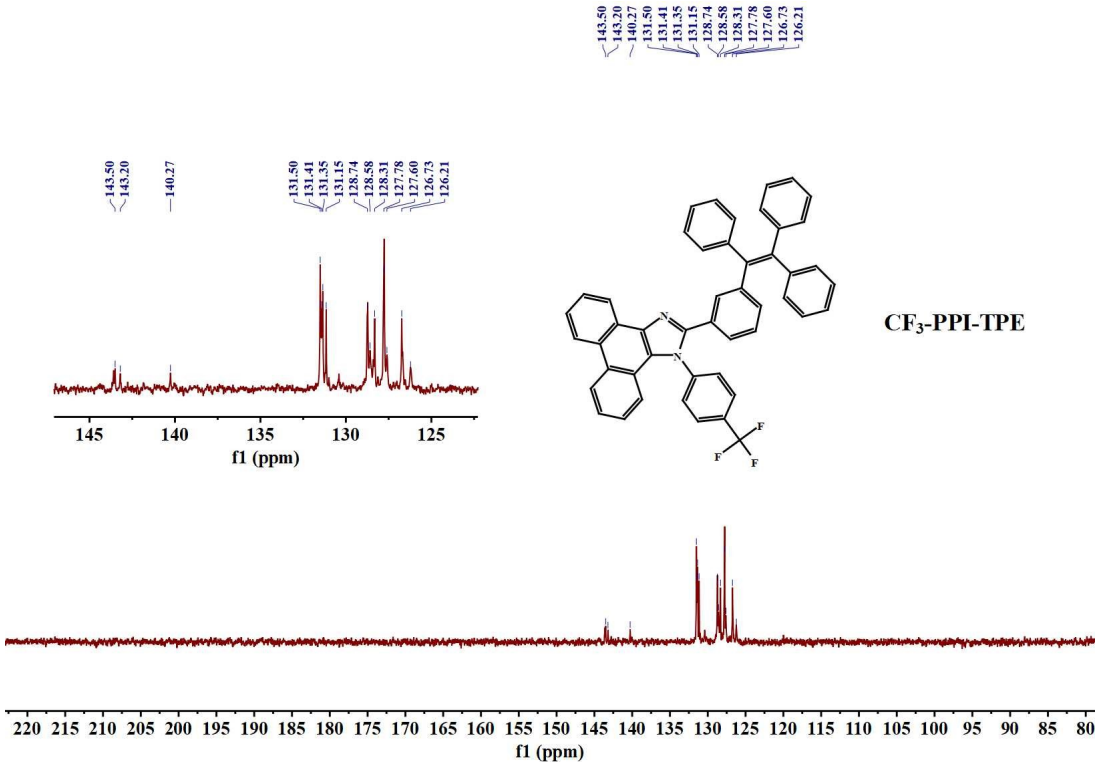


Figure S2. ^{13}C-NMR spectra of CF_3-PPI-TPE in $CDCl_3$

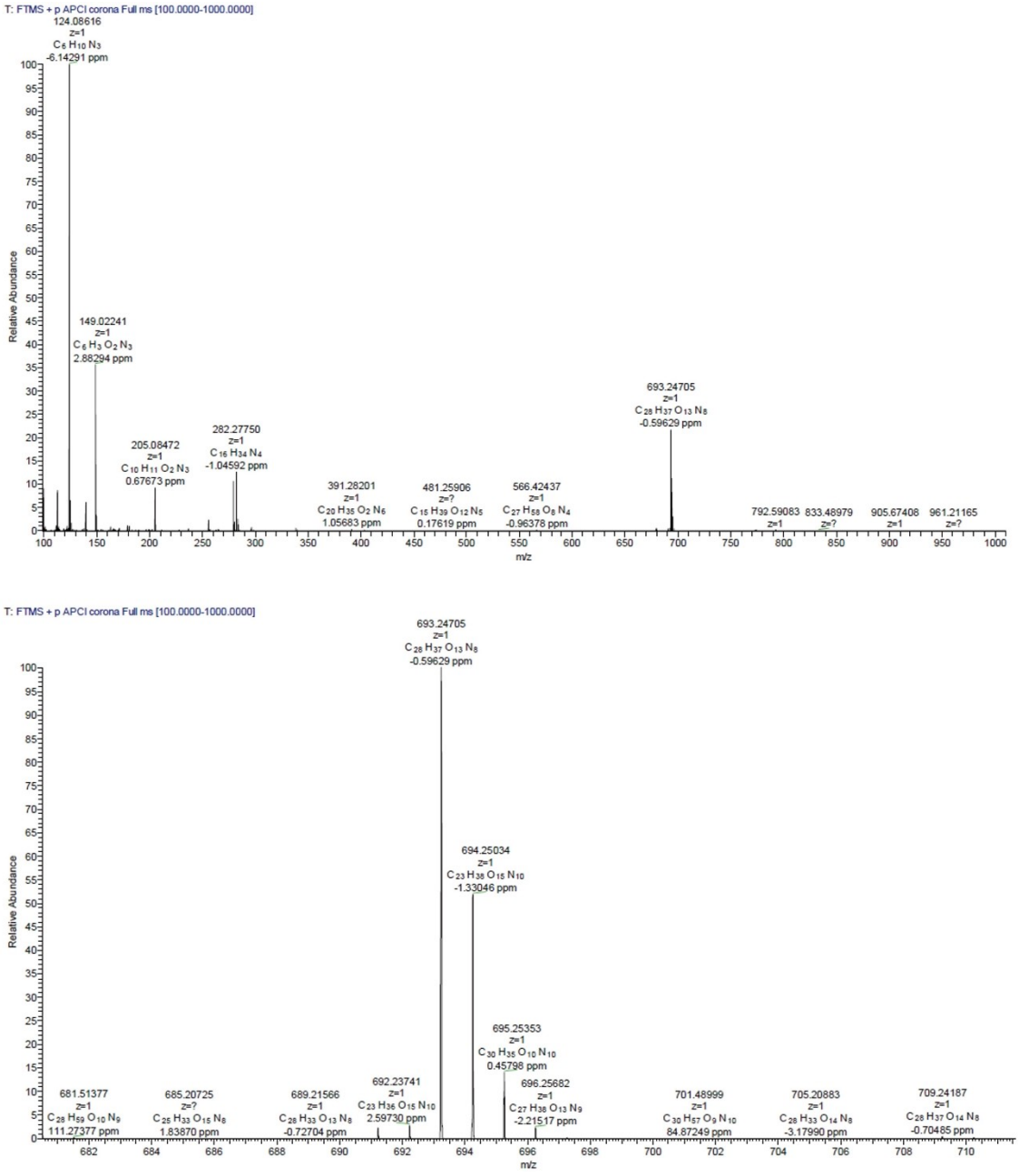


Figure S3. HRMS spectra of CF_3-PPI-TPE

Test results					
Detection mode	CHNS mode				
Detection date	250418				
Instrument model	Elemental UNICUBE				
Sample name	N (%)	C (%)	H (%)	S (%)	O (%)
CF_3-PPI-TPE	4.167	82.84	4.281	0.000	/

Figure S4. CHN elemental analysis of CF_3-PPI-TPE

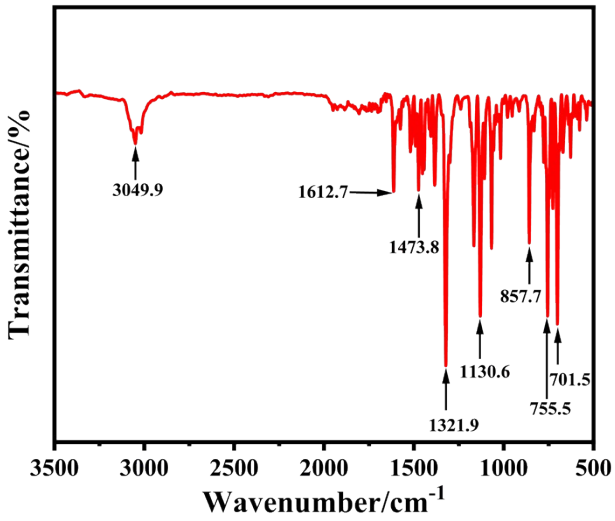


Figure S5. FT-IR spectrum of CF_3-PPI-TPE

4. Supplementary figures

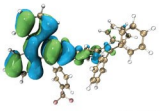
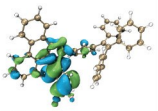
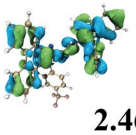
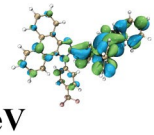
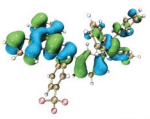
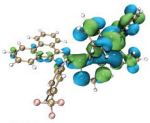
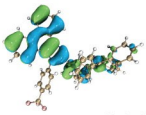
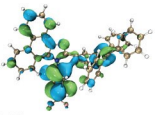
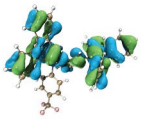
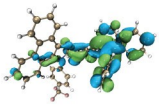
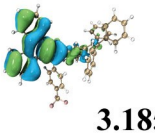
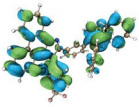
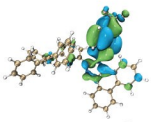
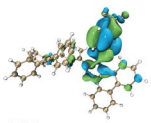
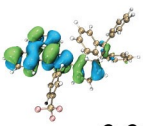
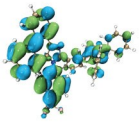
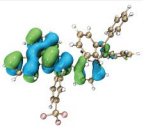
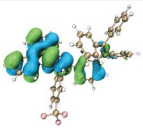
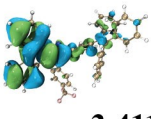
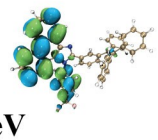
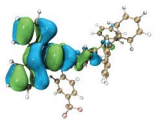
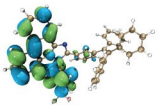
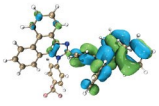
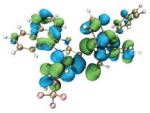
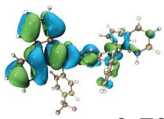
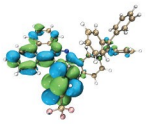
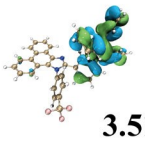
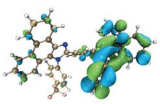
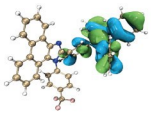
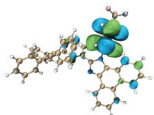
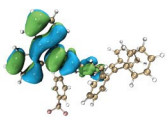
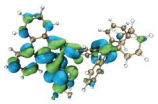
S_n	Hole	Particle	T_n	Hole	Particle
S_1		 3.3958 eV	T_1		 2.4671 eV
S_2		 3.5556 eV	T_2		 2.7550 eV
S_3		 3.6439 eV	T_3		 3.1856 eV
S_4		 3.6464 eV	T_4		 3.3222 eV
S_5		 3.7021 eV	T_5		 3.4114 eV
S_6		 3.7147 eV	T_6		 3.4955 eV
S_7		 3.7237 eV	T_7		 3.5199 eV
S_8		 3.7685 eV	T_8		 3.5637 eV

Figure S6. The natural transition orbitals (NTOs) of the singlet and triplet excited states for CF_3-PPI-TPE

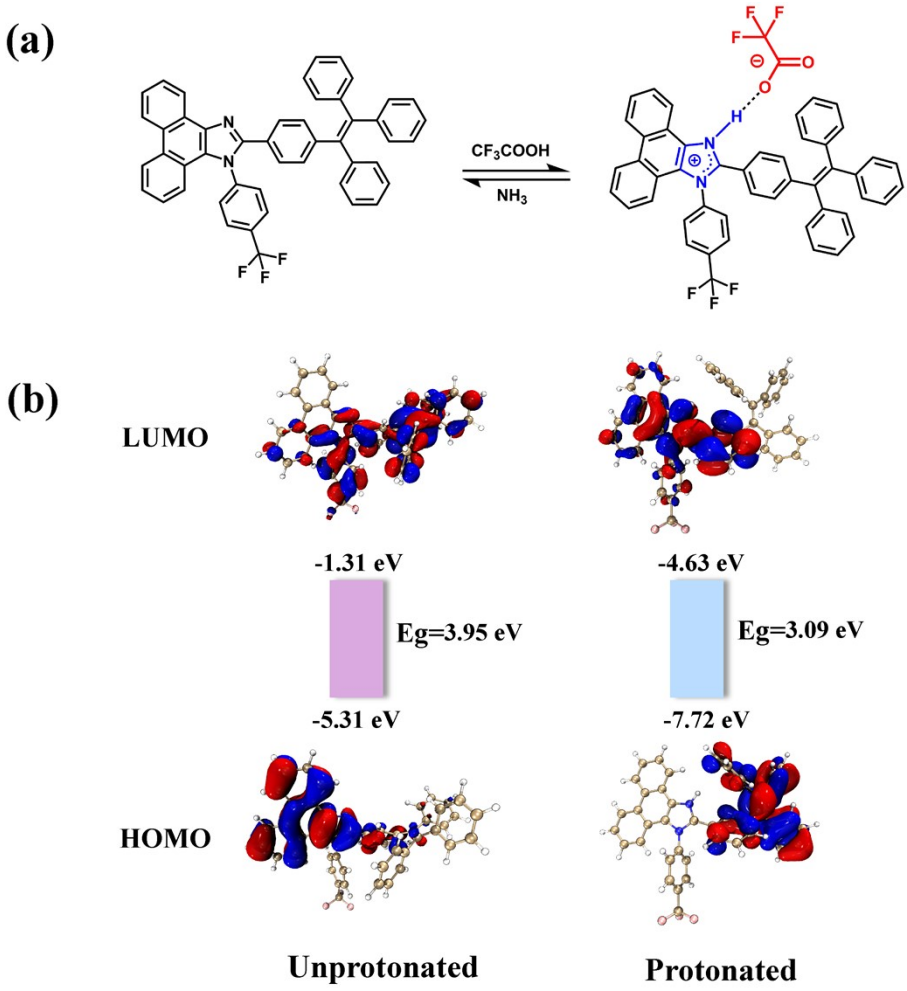


Figure S7. (a) Protonated PPI moiety with CF_3COOH. (b) The frontier molecular orbitals of the unprotonated and protonated of CF_3-PPI-TPE

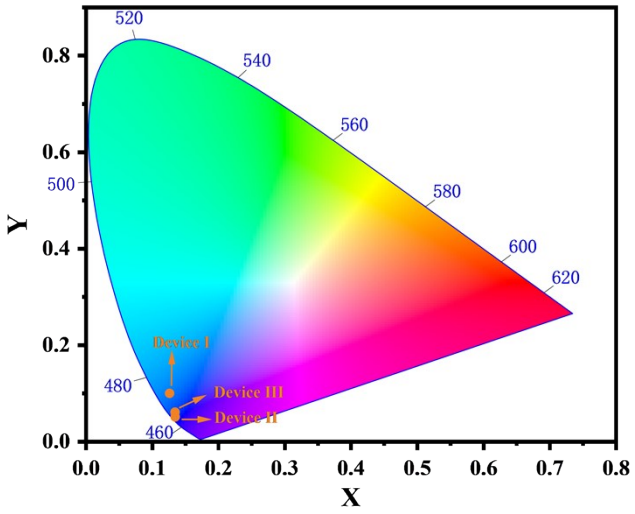


Figure S8. EL spectrum CIE coordinates of Device I, Device II and Device III.

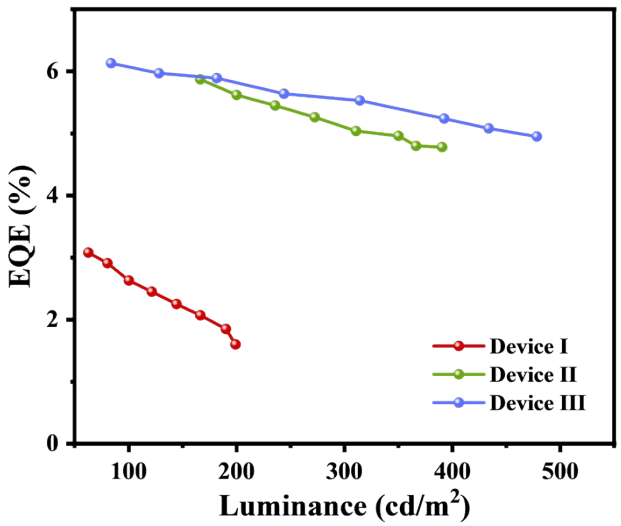


Figure S9. The external quantum efficiency-luminance plots of Device I, Device II and Device III.

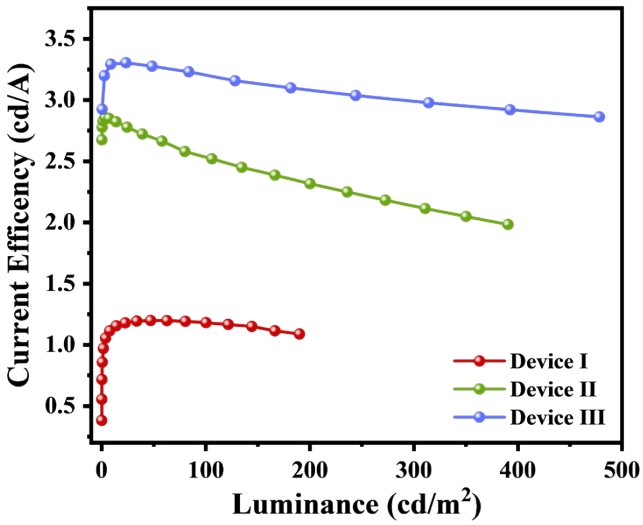


Figure S10. Current efficiency versus luminance curves of Device I, Device II and Device III.

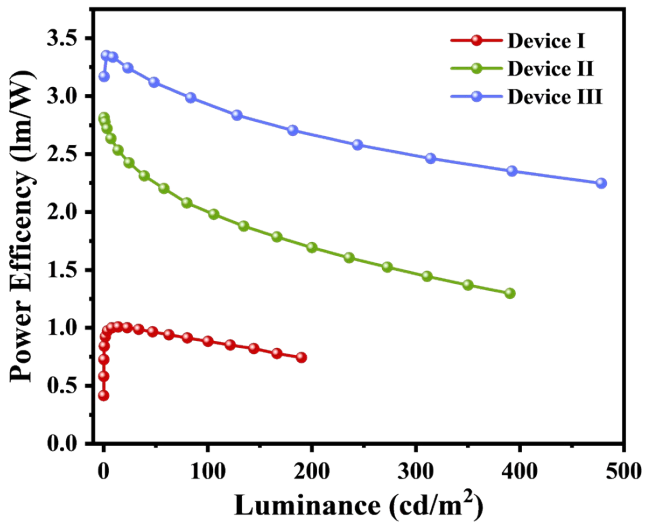


Figure S11. Power efficiency versus luminance curves of Device I, Device II and Device III

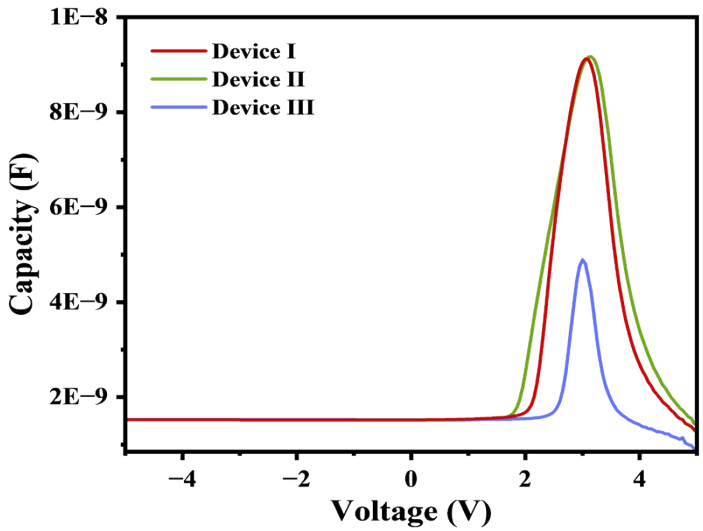


Figure S12. Capacitor Voltage Curves of Device I, Device II and Device III.

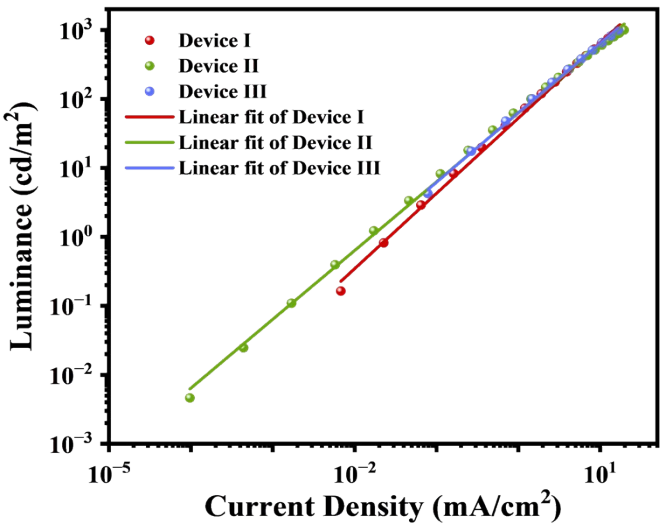


Figure S13. Luminance versus current density (symbol) and the fitted curve plot (line).

The Lippert-Mataga equation:

$$hc(v_a - v_f) = hc\left(v_a^0 - v_f^o\right) - \frac{2(\mu_e - \mu_g)^2}{a^3} f\ (\varepsilon, n) \qquad (1)$$

Among them, f is the orientational polarizability of the solvent. $v_a^0 - v_f^o$ corresponds to the Stokes shifts when f is zero. μ_e is the dipole moment of the solute molecule in the excited state. μ_g is the dipole moment of the solute molecule in the ground state. a is the solvent Onsager cavity radius, and ε and n are the solvent dielectric and the solvent refractive index, respectively. k is the slope of the $\Delta\nu$-Δf diagram, h is Planck's constant, c is the speed of light, M is the molar mass of the solute molecule, N is Avogadro's constant, and d is the solute molecule density (usually taken as 1 g/cm^3). μ_e and a can be calculated respectively as follows:

$$a = \sqrt[3]{\frac{3M}{4\pi N d}} \qquad (2)$$

$$(\mu_e - \mu_g) = \sqrt{\frac{khca^3}{2}} \qquad (3)$$

Table S1 Detailed absorption and emission peak positions of CF_3-PPI-TPE in different solvents.

Table S2 The energy difference between singlet and triplet excited states corresponding

Solvents	ε	n	f(ε,n)	CF_3-PPI-TPE		
				λ_a (nm)	λ_f (nm)	ν_a-ν_f (cm^{-1})
Toluene	2.38	1.494	0.014	342.5	415	5100.69
Dioxane	2.21	1.422	0.021	345.2	423	5328.05
Chloroform ($CHCl_3$)	4.81	1.443	0.149	344.5	432	5879.43
Ethyl ether	4.43	1.352	0.167	347.0	443	6245.08
Ethyl acetane (EA)	6.02	1.372	0.200	345.3	479	8083.49
Tetrahydrofuran (THF)	7.58	1.407	0.210	346.5	487	8326.15
Methylene chloride (DCM)	8.93	1.424	0.217	343.3	493	8845.07
Dimethyl formamide (DMF)	37	1.427	0.276	342.0	499	9199.69
Acetone	20.7	1.359	0.284	338.5	516	10162.25

spin orbital coupling (SOC, cm^{-1}) values for CF_3-PPI-TPE using B3LYP with TZVP

basis set.

Triplet/singlet state	T_1/S_1	T_2/S_1	T_3/S_1	T_4/S_1	T_5/S_1
SOC (cm^{-1})	0.33	0.53	0.09	0.63	0.66