SUPPORTING INFORMATION

Contents

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Ⅰ. Experimental Procedures

1. Synthesis of 9-(4-(7-(4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-yl)phenyl)-9,9-dipropyl-9*H*-fluoren-2-yl)phenyl)-9*H*-carbazole (9-PCZCFTZ)

4-Bromobenzoyl chloride (10.00 g, 45.89 mmol), benzoyl hydrazide (6.20 g, 45.57 mmol) and triethylamine (8.00 mL) were dissolved in dichloromethane. The mixture was stirred at 20 ℃ temperature for 4 h, then washed with water and filtered with suction, then *N*'-benzoyl-4-bromobenzohydrazide (12.55 g, 87%) can be purified by recrystallization with ethanol. Aniline (5.60 mL, 60.00 mmol) and o-dichlorobenzene (60.00 mL) were added to a double-neck round-bottom bottle equipped with a reflux condenser, and PCl$_3$ (1.30 mL, 15.00 mmol) was added to the bottle in N$_2$ at 100 ℃ for 1 hour, and then N'-benzoyl-4-bromobenzohydrazide (3.20 g, 10.00 mmol) is added in reaction system, then heat up to 180 ℃ and stir for another 12 hours. After cooling, the reaction system was stirred in deionized water for 30 min, then filtered, and further purified by silica gel column chromatography to obtain white powder 3-(4-bromophenyl)-4,5-diphenyl-4*H*-1,2,4-triazole at a yield of 76% (TZ-Br). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 – 7.37 (m, 7H), 7.34 (t, J = 7.5 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.13 (d, J = 7.6 Hz, 2H).

TZ-Br (2.63 g, 7.00 mmol), Bis(pinacolato)diboron (2.13 g, 8.40 mmol), Pd (dppf) Cl$_2$ (0.15 g, 0.20 mmol) and KOAc (2.06 g, 21.00 mmol) were added to the two-port flask under nitrogen protection. Add 1, 4-dioxane (30.00 mL) to the mixture. The solution was stirred and refluxed at 100 ℃ for 12 hours. After the reaction cooling to room temperature, the mixture was slowly extracted with water and dichloromethane. The water in the organic phase of the system is dried with anhydrous magnesium sulfate and filtered. After the solvent was evaporated, the given residue was purified by silica gel column chromatography. Petroleum ether/ethyl acetate (2/1 v/v) was used as eluent to obtain a white solid (TZ-B, 2.51 g, 86% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 (dd, J = 7.9, 3.1 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.27 (m, 2H), 7.16 – 7.10 (m, 2H), 1.33 (d, J = 2.7 Hz, 7H).

4-(9*H*-carbazol-9-yl)phenylboronic acid (PCT-B, 0.85 g, 2.96 mmol), 2,7-dibromo-9,9-dipropyl-9*H*-fluorene (CF, 1.00 g, 2.46 mmol), and K$_2$CO$_3$ (0.51 g, 3.69 mmol) were soluble in tetrahydrofuran (THF) and water (THF: H$_2$O = 50.00 mL: 10.00 mL), and dropped quickly into Pd(PPh$_3$)$_4$ (0.09 g, 0.07 mmol) at 90 ℃ for 24 hours under N$_2$ in a closed system. The excess THF was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane 3 times, and then 9-(4-(7-bromo-9,9-dipropyl-9*H*-fluoren-2-yl)phenyl)-9*H*-carbazole (PCZCF-Br, 1.05 g, yield 80%) can be pruified by column chromatography with petroleum ether and dichloromethane. And then, a mixture of PCZCF-Br (1.14 g, 2.00 mmol), 3,4-diphenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4*H*-1,2,4-triazole (TZ-B, 1.02 g, 2.40 mmol), K$_2$CO$_3$ (0.41 g, 3.00 mmol), THF (50.00 mL), and water (10.00 mL), with Pd(PPh$_3$)$_4$ (0.07 g, 0.06 mmol) acting as catalyst was refluxed at 90 ℃ for 24 hours under an argon atmosphere in a closed system. The excess THF was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane, the organic phase was dried by MgSO$_4$ and filtered, then 9-PCZCFTZ (1.30 g) can be purified by column chromatography with pure dichloromethane with yield of 82%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 (dd, J = 7.9, 3.2 Hz, 1H), 7.91 (dd, J = 8.4, 3.8 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.80 – 7.77 (m, 1H), 7.70 – 7.66 (m, 1H), 7.64 – 7.61 (m, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.53 (m, 1H), 7.52 – 7.41 (m, 6H), 7.37 (t, J = 7.3 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.23 (d, J = 8.5 Hz, 4H), 2.08 – 2.00 (m, 3H), 0.81 – 0.68 (m, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 153.95 (s), 153.57 (s), 150.90 (d, *J* = 9.4 Hz), 141.61 (s), 139.90 (s), 139.57 (d, *J* = 16.0 Hz), 139.23 (s), 138.31 (s), 138.00 (s), 135.79 (s), 134.41 (s), 129.06 (s), 128.67 (d, *J* = 6.0 Hz), 128.01 (d, *J* = 28.3 Hz), 127.85 (s), 127.49 (d, *J* = 13.6 Hz), 126.95 (s), 126.36 (s), 126.03 (d, *J* = 7.2 Hz), 125.07 (d, *J* = 19.6 Hz), 124.68 (s), 122.46 (s), 120.43 (d, *J* = 19.9 Hz), 119.36 (s), 119.11 (d, *J* = 26.5 Hz), 108.85 (s), 76.19 (d, *J* = 29.5 Hz), 75.97 (d, *J* = 22.3 Hz), 75.80 (s), 75.19 (s), 54.61 (s), 41.87 (s), 17.45 (s), 16.34 (s), 13.55 (s). MALDI-TOF MS (mass *m/z*): calcd for C$_{57}$H$_{46}$N$_4$, 787.3801; found, 787.3810 [M$^+$].

2. Synthesis of 3-(7-(4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-yl)phenyl)-9,9-dipropyl-9*H*-fluoren-2-yl)-9-phenyl-9*H*-carbazole (3-PCZCFTZ)

(9-phenyl-9*H*-carbazol-3-yl)boronic acid (3-PCZ-B, 0.90 g, 3.13 mmol), 2,7-dibromo-9,9-dipropyl-9*H*-fluorene (CF, 1.00 g , 2.46 mmol), and K$_2$CO$_3$ (0.50 g, 3.61 mmol) were soluble in tetrahydrofuran (THF, 50.00 mL) and water (10.00 mL), and dropped into Pd(PPh$_3$)$_4$ (0.11 g, 0.09 mmol) at 90 ℃ for 24 hours under N$_2$. The excess THF was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane, and then 3-(7-bromo-9,9-dipropyl-9*H*-fluoren-2-yl)-9-phenyl-9*H*-carbazole (3-PCZCF-Br, 1.09 g, yield 82%) can be pruified by column chromatography with petroleum ether and dichloromethane. And then, a mixture of 3-PCZCF-Br (1.14 g, 2.00 mmol), 3,4-diphenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4*H*-1,2,4-triazole (TZ-B, 1.02 g, 2.40 mmol), K$_2$CO$_3$ (0.41 g, 3.00 mmol), THF: water = 50.00 mL: 10.00 mL and Pd(PPh$_3$)$_4$ (0.07 g, 0.06 mmol) acting as catalyst was refluxed at 90 ℃ for 24 hours under an argon atmospherein a closed system. Then the mixture was washed with water and dichloromethane, the organic phase was dried by MgSO$_4$ and filtered, then 3-PCZCFTZ (1.20 g) can be purified by column chromatography with petroleum ether and dichloromethane, with yield of 78%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.41 (d, J = 4.5 Hz, 1H), 8.24 (dd, J = 8.0, 3.6 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.74 – 7.67 (m, 1H), 7.66 – 7.59 (m, 2H), 7.58 – 7.52 (m, 2H), 7.52 – 7.42 (m, 7H), 7.36 (t, J = 7.5 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.24 – 7.21 (m, 4H), 2.05 (dt, J = 11.9, 5.0 Hz, 2H), 0.84 – 0.67 (m, 5H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 154.91 (s), 154.59 (s), 151.79 (d, J = 2.8 Hz), 142.74 (s), 141.41 (s), 141.21 (s), 140.86 (s), 140.38 (s), 139.12 (s), 138.57 (s), 137.69 (s), 135.40 (s), 133.86 (s), 130.00 (d, J = 14.2 Hz), 129.66 (d, J = 6.3 Hz), 129.10 (s), 128.85 (s), 128.42 (s), 127.95 (s), 127.55 (s), 127.05 (d, J = 6.3 Hz), 126.42 – 125.94 (m), 125.57 (d, J = 11.7 Hz), 123.97 (s), 123.51 (s), 121.74 (s), 121.30 (s), 120.45 (s), 120.24 – 119.90 (m), 118.79 (s), 110.00 (d, J = 11.3 Hz), 77.28 (s), 77.03 (s), 76.77 (s), 55.54 (s), 42.89 (s), 17.34 (s), 14.55 (s). MALDI-TOF MS (mass *m/z*): calcd for C$_{57}$H$_{46}$N$_4$, 787.3801; found, 787.3816 [M$^+$].

SUPPORTING INFORMATION

Ⅱ. General Methods

NMR spectra were recorded on a Mercury 500 spectrometer. Elemental analysis was recorded on a Carlo Erba 1106 Elemental Analyzer.

The DFT calculations were carried out with the Gaussian 09 B.01 Package at the level of M062X/6-31+G(d,p). And Natural transition orbitals (NTOs) calculations were obtained on Multiwfn program. The influence of solvent environment on the optical property of **9-PCZCFTZ** and **3-PCZCFTZ** can be understood using the Lippert-Mataga equation, which can describe the interactions between the solvent and the dipole moment of solute.

UV-vis absorption spectra were measured on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were measured on a Hitachi F-4600 spectrophotometer.

In Thermal stabilities, the dates of thermal gravimetric analysis (TGA) are from Perkin-Elmer thermal analysis system with the temperature of 50-800 °C under a heating rate of 10 °C /min and the nitrogen atmosphere. The dates of Differential scanning calorimetry (DSC) are from NETZSCH (DSC-204) instrument with the temperature of 50-350 °C at a heating rate of 10 °C /min and a nitrogen flow rate of 80 mL/min.

The single crystals of the two molecules are obtained from the trichloromethane/ethanol mixed solvent. Single-crystal X-ray diffraction data were collected by Rigaku RAXIS-PRID diffractometer.

Cyclic voltammetry (CV) analysis of the materials was recorded on a three-electrode cell with tetra-n-butyl-ammonium hexafluorophosphate (TBAPF6, 0.1 m in acetonitrile) as the supporting electrolyte. Two platinum wires were used as counter electrode and reference electrode. The scan rate is 100 mV/s, and all the potentials were corrected to the ferrocene/ferrocene $^+$ (Fe/Fe $^+$) standard under room temperature. The oxidation curve is obtained by dissolving the product and electrolyte in dichloromethane (DCM), and the reduction curve is obtained in *N,N*-Dimethylformamide (DMF).

ITO-coated glass with a sheet resistance of 15-20 Ω square^{-1} was used as the substrate. Before device fabrication, the ITO glass substrates were cleaned with acetone, Hellmanex^{TM} III and deionized water, dried 45 mins and 3 times, the substrates were treated 7 minutes by oxygen flow rate of 20 Pa to improve the hole injection ability of ITO. Finally transferred to a vacuum deposition system with a pressure of < 1.6×10^{-4} Pa. The OLEDs of the two materials were fabricated the structure of ITO/PEDOT: PSS (40 nm)/TCTA (20 nm)/emissive materials (20 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm), where poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) used as a hole-injecting layer is a water-soluble conductive polymer with good performance, thicker TCTA (4,4′,4″-tri-9-carbazolytriphenylamine) is as a hole transport layer and electron blocking layer, the 2,2′2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) serves as the electron-transporting layer and hole-blocking layer. The hole-only and electron-only OLEDs of the two materials were fabricated the structure of Device Ⅰ: ITO/HATCN (20 nm)/EML (80 nm)/HATCN (20 nm) /Al (100 nm), and ITO/LiF (1 nm)/TPBi (10 nm)/EMLs (80 nm)/LiF (1 nm)/Al (100 nm), in which 2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexaazatriphe-nylene (HATCN) has the function of hole injection and electron blocking, while TPBi has the function of electron injection and hole blocking. The current–voltage–brightness characteristics were measured by using a Keithley source measurement unit (Keithley 2450 and LS-160), EL spectra were measured with Flame-S (Serial Number: FLMS16791, Range: >350 nm). *EQE*s were calculated from the luminance, current density, and EL spectrum, all the results were measured in the forward-viewing direction without using any light out-coupling technique. According to equation following (**Formula S1**).

$$EQE = \frac{\pi \cdot L \cdot e}{683 \cdot I \cdot h \cdot c} \cdot \frac{\int_{380}^{780} I(\lambda) \cdot \lambda \cdot d\lambda}{\int_{380}^{780} I(\lambda) \cdot K(\lambda) \cdot d\lambda}$$

(S1)

where *L* (cd m^{-2}) is the total luminance of device, *I* (A) is the current flowing into the EL device, λ (nm) is EL wavelength, *I(λ)* is the relative EL intensity at each wavelength and obtained by measuring the EL spectrum, *K(λ)* is the Commision International de L'Eclairage chromaticity (CIE) standard photopic efficiency function, *e* is the charge of an electron, *h* is the Planck's constant, *c* is the velocity of light.

The efficiency roll-offs of blue OLED device were calculated from maximum *EQE* and the *EQE* at luminescence of 1000 cd m^{-2}. According to equation following (**Formula S2**):

$$\eta = \frac{EQE_{max} - EQE_{1000}}{EQE_{max}}$$

(S2)

The space-charge-limited current (SCLC) method is utilized in this study for the determination of mobility. The SCLC characteristics can be described by the following Mott–Gurney equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{E^2}{L}$$

(S3)

where ε_0 is the free-space permittivity (8.85 × 10^{-14} C V^{-1} cm^{-1}), ε_r is the relative dielectric constant (assumed to be 3.0 for organic semiconductors), E is the electric field, and L is the thickness of emitters. In general, the carrier mobility (μ) of organic semiconductors depends on the electric field (E), which can be expressed via the Poole–Frenkel formula:

$$\mu = \mu_0 \exp\left(\gamma\sqrt{E}\right)$$

(S4)

where γ is the Poole–Frenkel factor and μ_0 is the zero-field mobility. According to **Formula S3** and **S4**, the current density (J) of the SCLC region can be further expressed as:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0\frac{V^2}{L^3}\exp\left(0.891\gamma\sqrt{\frac{V}{L}}\right)$$

(S5)

By fitting the *J–V* curves in the SCLC region to **Formula S5**, the μ_0 and γ values are obtained, thus generating the field-dependent carrier mobility according to **Formula S4**.

Ⅲ. Supplementary Figures
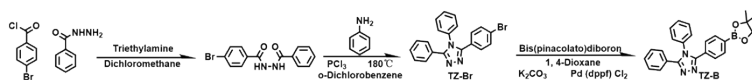
Figure S1. The synthesis route of the **TZ-B**.
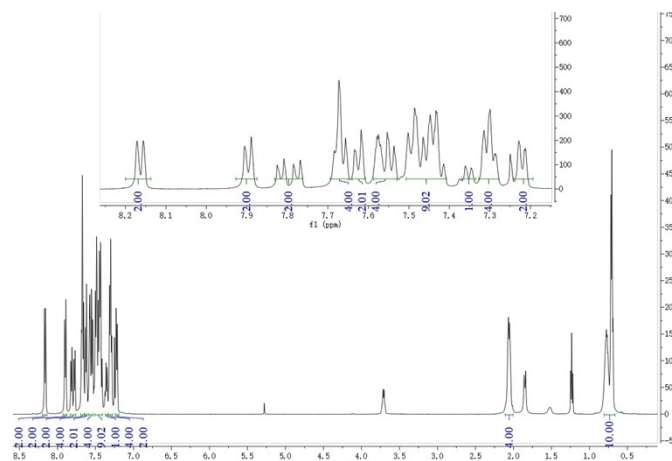
Figure S2. ^{1}H-NMR Spectrum of **9-PCZCFTZ** in CDCl$_3$.
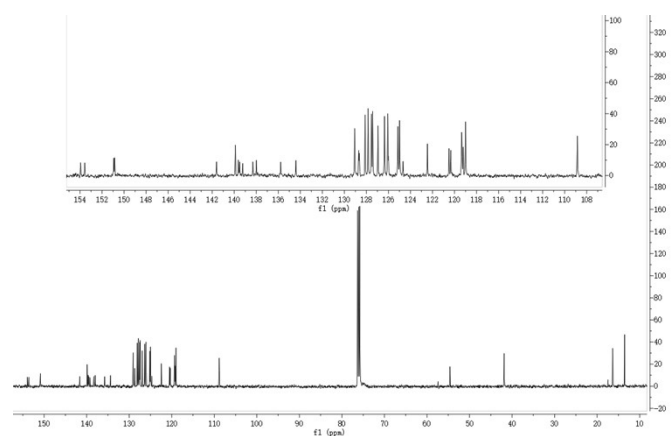
Figure S3. ^{13}C-NMR Spectrum of **9-PCZCFTZ** in CDCl$_3$.
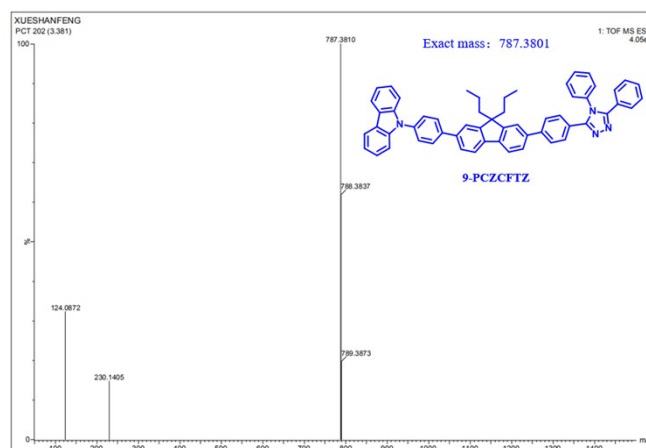
Figure S4. Mass Spectrum (M$^+$H$^+$) of **9-PCZCFTZ**.

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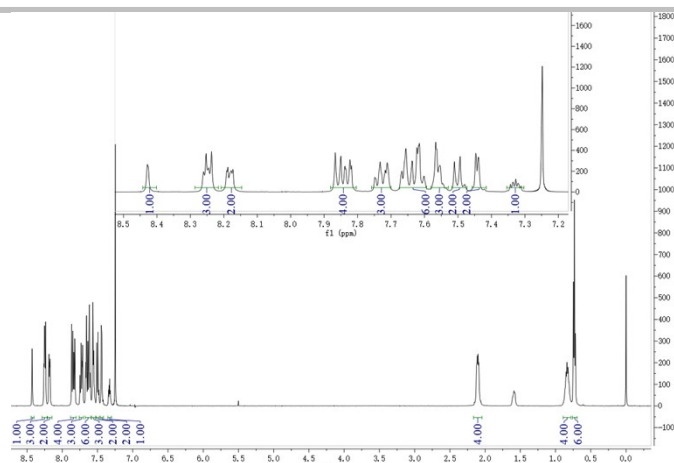
Figure S5. ^{1}H-NMR Spectrum of **3-PCZCFTZ** in CDCl$_3$.
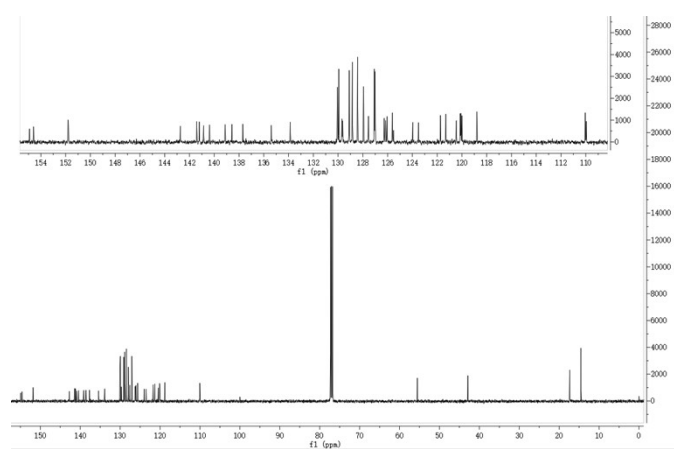
Figure S6. ^{13}C-NMR Spectrum of **3-PCZCFTZ** in CDCl$_3$.
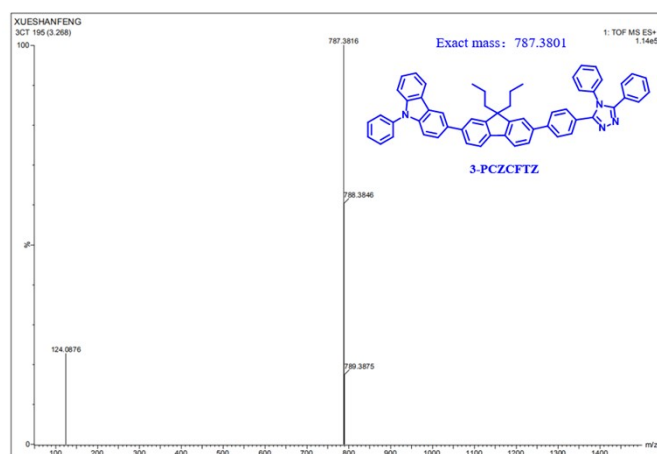
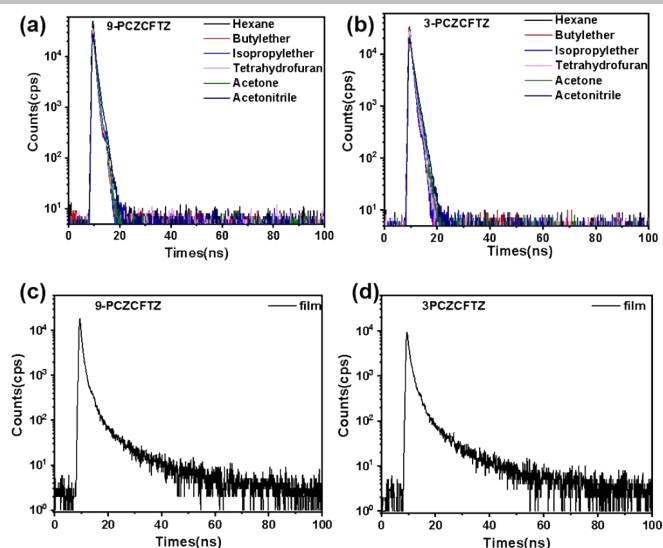**Figure S7**. Mass Spectrum (M[+]H^{+}) of **3-PCZCFTZ**.

Figure S8. The transient PL decay spectra of the two molecules in different solvents (a, b) and film states (c, d).
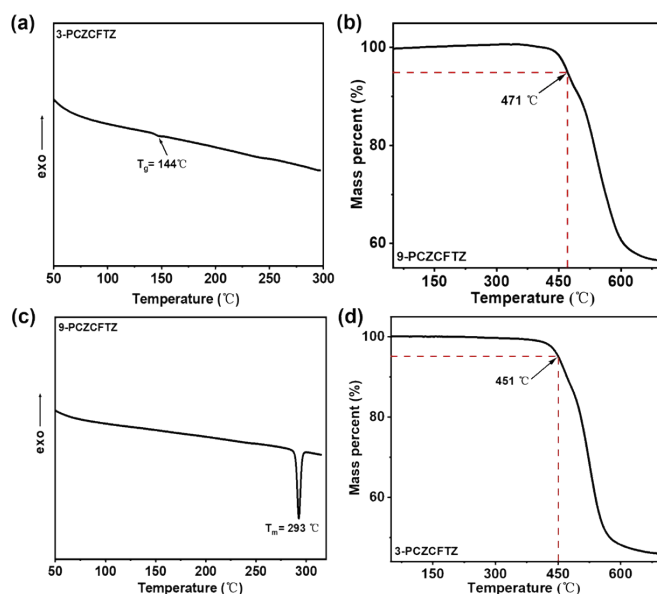

Figure S9. (a), (c) are the differential scanning calorimetry (DSC) curves of the two molecules. (b), (d) are the thermogravimetric analysis (TGA) curves of the two molecules. T_d is temperature of 5% weight loss.
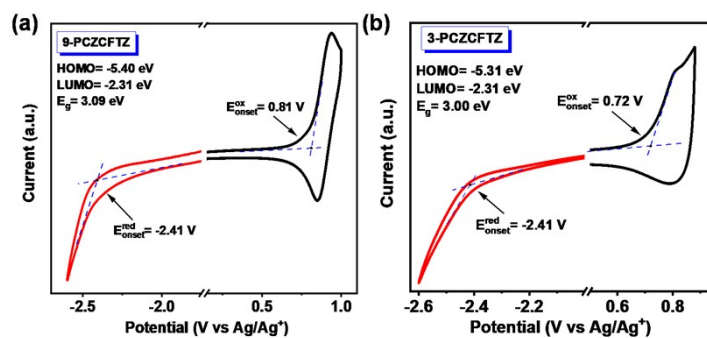

Figure S10. The cyclic voltammetry curve of the two molecules in dichloromethane solution (oxidation section) and DMF solution (reduction section).
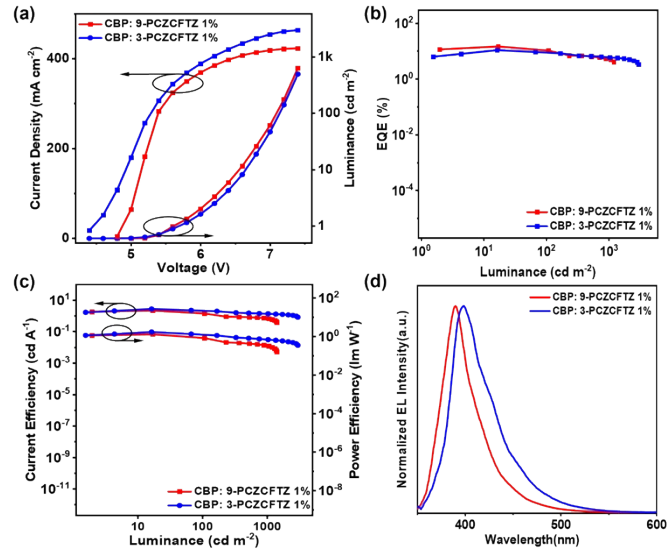
Figure S11. Doped OLEDs performances of the two D-π-A materials. (a) current density-voltage-luminance curves, (b) *EQE*-luminance curves, (c) current efficiency-luminance-power efficiency curves, (d) The EL spectra curves.
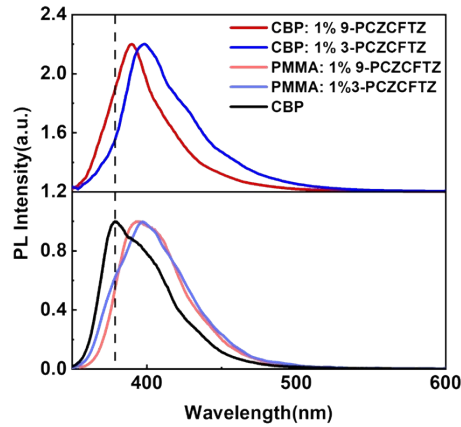

Figure S12. The photoluminescence (PL) spectra of the doped film and pure CBP films.
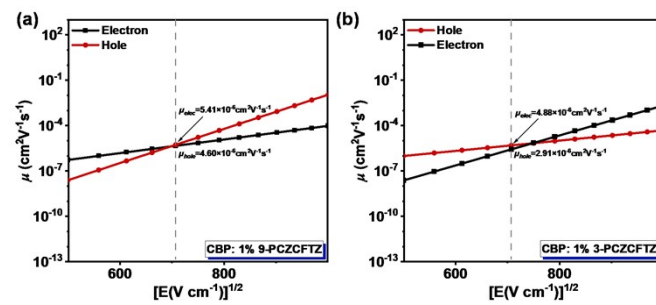

Figure S13. *The estimated hole and electron mobilities of the doped film under different electric fields. The configuration of hole-only device: ITO/HATCN (20 nm)/CBP:1%EML (80 nm)/HATCN (20 nm) /Al (100 nm). The configuration of electron-only device: ITO/LiF (1 nm)/TPBi (10 nm)/CBP:1%EML (80 nm)/LiF (1 nm)/Al (100).*

SUPPORTING INFORMATION

Ⅳ. Supplementary Tables

Table S1. The carrier mobilities and thermal properties of the two materials.

Molecules	Hole mobility [a] [$cm^2 V^{-1} s^{-1}$]	Electron mobility [b] [$cm^2 V^{-1} s^{-1}$]	T_g [c] [°C]	T_m [d] [°C]	T_d [e] [°C]
9-PCZCFTZ	1.07×10^{-6}	1.11×10^{-5}	-	293	471
3-PCZCFTZ	5.49×10^{-7}	2.33×10^{-5}	144	-	443

[a] [b] Carrier mobility under electric field of 5.0×10^5 V cm^{-1}; [c] T_g: Glass transition temperatures; [d] T_m: Melting temperatures; [e] T_d: Temperature of 5% weight loss.

Table S2. The single crystal data of the two molecules.

Compound	**9-PCZCFTZ**	**3-PCZCFTZ**
Chemical formula	C57H46N4	C57H46N4
Formula weight	787.38	787.38
Crystal system	Triclinic	Triclinic
a/Å	10.315 (19)	10.419 (4)
b/ Å	12.254 (16)	10.639 (4)
c/ Å	20.687 (14)	23.685 (9)
α/°	79.983 (7)	93.232 (8)
β/°	82.962 (10)	102.281 (8)
γ/°	71.165 (15)	112.408 (7)
Unit cell volume/ Å3	2431.0 (6)	2344.1 (17)
Temperature/K	296 K	100 K
Space group	P-1	P-1
Z	2	2
Density (calculated) /g cm^{-3}	1.119	1.284
F(000)	868	948
Theta range for data collection	2.16 to 19.61	2.15 to 27.43
Index ranges	-12<=h<=8, -14<=k<=14, -24<=l<=16	-12<=h<=12, -12<=k<=11, -25<=l<=28
Reflections measured	11630	11692
Independent reflections	8314	8154
$Rint$	0.0523	0.0712
Completeness to theta = 72.13°	0.970	0.986
Data / restraints / parameters	8314 / 6 / 571	8154 / 186 / 588
Goodness-of-fit on F^2	1.062	1.058
Final R_1 values ($I > 2\sigma(I)$)	0.1107	0.1255
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2692	0.3279
Final R_1 values (all data)	0.2219	0.2081
Final $wR(F^2)$ values (all data)	0.3146	0.3596
CCDC number	2176493	2176856