# **Supporting Information**

Suppressing Efficiency Roll-off of Orange-Red Thermally Activated Delayed Fluorescence Polymers based OLEDs via Copolymerizing Co-Hosts with Cascade Energy Levels

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# S1. Methods

### S1.1 Materials

All raw materials were procured from reputable commercial sources, including Bide Pharma Tech and Energy Chemical, and were utilized without additional purification unless specifically indicated. Toluene and tetrahydrofuran, obtained from Beijing Tongguang, were dried by refluxing over sodium for 24 hours to remove moisture. Anhydrous 1,4-dioxane was supplied by J&K Scientific. The host material 1,3-bis (carbazol-9-yl) benzene (mCP) and 1,1-Bis[(di-4-tolylamino) phenyl] cyclohexane (TAPC) used for doped films was purchased from Lumtec. Materials for device fabrication, including poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) 4083 (PEDOT: PSS), 1,3,5-tri[(3-pyridyl)-phen-3-yl] benzene (TmPyPB), and lithium fluoride (LiF), were purchased from Xi'an Polymer Light Technology Corp.

#### S1.2 Device fabrication and performance measurement

Commercially sourced indium tin oxide (ITO) glass substrates were ultrasonically cleaned using isopropanol, followed by deionized water, and subsequently dried in an oven at 120 °C. After undergoing hydrophilic treatment via UV ozone exposure for 6 minutes, a poly(3,4ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) aqueous solution was spincoated onto the ITO substrates at 2000 rpm. The substrates were then transferred into a glovebox and heat-treated at 120 °C to eliminate residual moisture. The mixed emissive layer solution, consisting of 3 mg of each polymer and 7 mg of 1,3-Bis(N-carbazolyl) benzene (mCP) and 1,1-Bis[(di-4-tolylamino) phenyl] cyclohexane (TAPC), dissolved in 1 mL of anhydrous chlorobenzene, was spin-coated onto the PEDOT: PSS films at 2000 rpm. Following a 15-minute heat treatment at 85 °C, the substrates were transferred into a deposition system. Under a vacuum of less than 10<sup>-5</sup> Pa, the remaining layers of the device were thermally evaporated. First, 1,3,5tri[(3-pyridyl)-phen-3-yl] benzene (TmPyPB) was deposited at a rate of 2.0 Å s<sup>-1</sup>, followed by the electron-injecting layer, lithium fluoride (LiF), which was deposited at a rate of 0.15 Å s<sup>-1</sup>. Finally, an aluminum electrode was evaporated at a rate of 1.0–3.0 Å s<sup>-1</sup>. The electroluminescence spectra and luminance of the OLED devices were measured using a PR670 spectrometer in conjunction with a Keithley 2400 source meter at room temperature.

## **S1.3 Characterization**

Nuclear magnetic resonance (NMR) spectra were acquired using a Bruker AVANCE III 400 spectrometer operating at 400 MHz. Both <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were performed with tetramethylsilane (TMS) as the internal standard. The <sup>1</sup>H NMR spectra are reported in terms of chemical shift, relative integral, multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant (*J* in Hz), and assignment.

Molecular masses were determined using mass spectrometry (ESI), with anhydrous dichloromethane as the solvent.

Ultraviolet-visible (UV-Vis) absorption spectra were recorded using a Hitachi U-2910 spectrophotometer under ambient conditions.

Photoluminescence (PL) spectra were measured with an Edinburgh Instruments FS-5 fluorescence spectrophotometer. Fluorescence decay of the doped films (30 wt% doped in 70 wt% mCP and TAPC) was recorded under vacuum conditions using the FS-5 spectrometer, equipped with a picosecond pulsed diode laser emitting at 375 nm. Temperature-dependent fluorescence decay measurements, ranging from 77 K to 300 K, were conducted under vacuum with the assistance of Oxford variable temperature accessories. The experimental activation energies ( $E_a^{RISC}$ ) were determined by fitting the temperature-dependent  $k_{RISC}$  data using Arrhenius equations:

$$lnk = \frac{-E_a}{RT} + lnA\#(S1)$$

The photoluminance quantum yields (PLQYs) of the doped films were measured on FS-5 with an integrating sphere ( $\varphi = 150$  mm).

The rate constants were determined using the following equations according to the literature<sup>1</sup>:

$$k_{PF} = \frac{\Phi_{PF}}{\tau_{PF}} \# (S2)$$
$$k_{DF} = \frac{\Phi_{DF}}{\tau_{DF}} \# (S3)$$
$$k_{ISC} = \frac{\Phi_{PF}}{\Phi_{DF}} k_{PF} \# (S4)$$

$$k_{RISC} = \frac{k_{DF}k_{PF}\Phi_{DF}}{k_{ISC} \Phi_{PF}} \# (S5)$$
  

$$k_{PF} = k_r^S + k_{nr}^S + k_{ISC} \# (S6)$$
  

$$k_r^S = \eta_{PF} \cdot k_{PF} \# (S7)$$
  

$$k_{nr}^S = k_{PF} - k_r^S - k_{ISC} \# (S8)$$

The PLQYs of the material in vacuum can be converted by integrating the steady state spectrum, and the PLQY in air<sup>2</sup>. The equation is as follows:

$$PLQY_{vac} = \frac{I_{vac}}{I_{air}} PLQY_{air} \#(S9)$$

In which,  $I_{vac}$  and  $I_{air}$  is the integrate of the steady state spectrum in vacuum and air atmospheres, respectively.

Cyclic voltammetry (CV) was performed at room temperature in nitrogen-purged acetonitrile using a CHI voltametric analyzer. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was employed as the supporting electrolyte. The conventional three-electrode setup comprised a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgNO<sub>3</sub> pseudo-reference electrode, with the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) redox couple serving as the external standard. Cyclic voltammograms were recorded at a scan rate of 100 mV s<sup>-1</sup>. The onset potential was determined by identifying the intersection of tangents drawn at the rising and background currents of the cyclic voltammogram. The HOMO and LUMO energy levels were calculated relative to the external Fc<sup>+</sup>/Fc standard in acetonitrile using the following formulas<sup>3</sup>:

$$E_{HOMO} = -\left(E_{(onset, ox vs Fc^+/Fc)} + 4.8\right) \#(S10)$$
$$E_{LUMO} = -\left(E_{(onset, red vs Fc^+/Fc)} + 4.8\right) \#(S11)$$

The morphologies of the doped films (30 wt% emitters in 70 wt% mCP) and (30 wt% emitters in 70 wt% TAPC) coated on quartz substrates were examined using atomic force microscopy (AFM) with an Agilent Technologies 5500 instrument in tapping mode. Differential scanning calorimetry (DSC) was conducted using a TA Q2000 calorimeter at a heating rate of 10 °C min<sup>-1</sup>, from 30 to 300 °C, under a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was performed on a METTLER TOLEDO TGA/DSC 1/1100SF instrument at a heating rate of 20 °C min<sup>-1</sup>, from 30 to 800 °C, also under a nitrogen atmosphere.

Gel permeation chromatography (GPC) analysis was carried out using a Waters 515-2410 system, with polystyrene standards as molecular weight references and tetrahydrofuran (THF) as the eluent.

#### **S1.4 Molecular simulation**

Density functional theory (DFT) calculations were conducted using Gaussian 09, employing the B3LYP functional with a 6-31G (d, p) basis set in the ground state. Based on the optimized geometries, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were determined. The excited state energy levels and properties were calculated using Gaussian 16 with the PBE1PBE/6-311G (d, p) basis set in time-dependent (TD) mode. To enhance the accuracy of singlet and triplet energy level calculations, the number of states was set to 10. Natural transition orbital (NTO) analysis was performed using Multiwfn 3.6, based on the Gaussian output<sup>4, 5</sup>, to assess the distributions of holes and electrons. The dominant nature of the transitions, whether charge transfer (CT) or locally excited (LE) states, was identified through the overlap integral of the primary contributing orbitals. To quantitatively analyze the impact of spin-orbit coupling (SOC), SOC matrix elements for the molecules were calculated using the ORCA 4.1.2 package<sup>6</sup> with the B3LYP/G TZVP method, considering five states in the computational analysis.

# **S2.** Energy level relationships of the backbone monomers.



**Figure S1.** (a) The spectra of carbazole (Cz), dibenzothiophene (DBT) and dibenzofuran (DBF) in dilute solutions. (b) The energy level diagram of the backbone units and emitting unit.

# **S3.** Materials synthesis

## **S3.1** Synthesis of monomers



Scheme S1. Synthesis routes of monomers.

### Synthesis of BP-PXZ (1):

BP-Br (0.34 mg, 0.95 mmol), 10H-Phenoxazine (0.23 mg, 1.15 mmol), palladium(II)acetate (10 mg, 0.05 mmol), 2-Dicyclohexylphosphine-2',4',6'-triisopropylbiphenyl (Xphos) (45 mg 0.095 mmol) and sodium tert-butoxide (384.4 mg, 4 mmol) were added to a 100 mL two-necked vial under an argon atmosphere. 10 mL toluene was injected sequentially as solvent. After stirring at 100 °C for 16 h, the reaction was cooled down to room temperature. Then the mixture was washed three times by saturated salt water and extracted by dichloromethane. The obtained solution was dried with anhydrous magnesium sulfate, then filtered, and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel using petroleum

ether/ dichloromethane (v/v = 1/1) as eluent to obtain BP-PXZ (1) as an orange solid (63% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.67 (d, *J* = 8.4 Hz, 1H), 9.48 (dd, *J* = 6.2, 3.4 Hz, 1H), 8.57 (d, *J* = 1.9 Hz, 1H), 8.49 (dd, *J* = 6.0, 3.5 Hz, 1H), 8.41 (dt, *J* = 6.0, 3.4 Hz, 2H), 7.93 – 7.90 (m, 2H), 7.80 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.74 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.6 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 2H), 6.61 (td, *J* = 7.7, 1.6 Hz, 2H), 6.09 (dd, *J* = 8.0, 1.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, THF-*d*<sub>8</sub>)  $\delta$  145.28, 143.59, 143.49, 136.25, 135.57, 131.64, 131.35, 131.26, 131.23, 130.59, 130.49, 129.53, 127.18, 124.90, 124.48, 122.60, 116.47, 114.67, 25.97. HRMS (ESI): m/z calculated for C<sub>32</sub>H<sub>19</sub>N<sub>3</sub>O [M]<sup>+</sup>: 461.1528; Found: 461.1537.

#### Synthesis of BP-PXZ-2Br (2):

BP-PXZ (0.973 g, 2.1 mmol) was dissolved in 20 mL anhydrous dichloromethane at 0 °C. The Nbromo succinimide (934.0 mg, 5.25 mmol) dissolved in 30 mL anhydrous dichloromethane was dropped into reaction at 0 °C with a constant pressure funnel in darkness. The reaction was quenched by water after stirring for overnight. Then the mixture was washed three times by water and extracted by dichloromethane. The obtained solution was dried with anhydrous magnesium sulfate, then filtered, and concentrated under reduced pressure. The crude product obtained was recrystallized with ethanol and chloroform, then dried under reduced pressure to obtain BP-PXZ-2Br (2) as an orange solid (40% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 8.4 Hz, 1H), 9.51 (dd, *J* = 6.0, 3.5 Hz, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 8.49 (dd, *J* = 6.1, 3.3 Hz, 1H), 8.47 – 8.38 (m, 2H), 7.98 – 7.89 (m, 2H), 7.83 (dt, *J* = 6.2, 3.5 Hz, 2H), 7.68 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 2H), 6.72 (dd, *J* = 8.6, 2.2 Hz, 2H), 5.93 (d, *J* = 8.6 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, THF-*d*<sub>8</sub>) δ 131.18, 130.26, 130.09, 127.14, 126.70, 126.36, 124.38, 119.13, 115.55, 66.91, 66.69, 24.85, 24.65.

HRMS (ESI): m/z calculated for C<sub>32</sub>H<sub>17</sub>Br<sub>2</sub>N<sub>3</sub>O [M]<sup>+</sup>: 618.9718; Found: 618.9718.

## Synthesis of DBT-2BO (3,7) (3):

A 500 mL two-necked vial was charged with 3,7-dibromodibenzo[b,d]thiophene (5.0 g, 14.6 mmol), bis(pinacolato)diboron (11.1 g, 43.8 mmol), potassium acetate (4.3 g, 43.8 mmol), and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (322 mg, 0.44 mmol) under an argon atmosphere. To this mixture, 150 mL of 1,4-dioxane was added as the solvent. The reaction

mixture was then stirred at 105 °C for 16 h. After cooling to room temperature, the reaction mixture was washed three times with saturated salt water and extracted using ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel, using a petroleum ether/ethyl acetate mixture (20:1 v/v) as the eluent, to yield a white solid. The crude product was further purified by recrystallization from ethanol and chloroform, followed by drying under reduced pressure to obtain DBT-2BO (3,7) as light-yellow needles (69% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 1.0 Hz, 1H), 7.97 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.79 (dd, *J* = 7.6, 0.9 Hz, 1H), 1.38 (s, 12H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 142.60, 135.24, 132.67, 128.70, 122.19, 84.09, 25.07. HRMS (ESI): m/z calculated for C<sub>24</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>S [M]<sup>+</sup>: 436.2051; Found 436.2146.

## Synthesis of DBT-2BO (2,8) (4):

The synthesis of DBT-2BO (2,8) follows the same procedure as that of DBT-2BO (3,7), with the exception that 2,8-dibromodibenzo[b,d]thiophene is used as the starting material. The resulting product, DBT-2BO (2,8) (4), was obtained as white needle crystals (65% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.52 (t, *J* = 0.9 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 1.41 (s, 12H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 142.48, 135.12, 132.56, 128.58, 122.07, 83.96, 24.96. HRMS (ESI): m/z calculated for C<sub>24</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>S [M]<sup>+</sup>: 436.2051; Found 436.2161.

## Synthesis of DBF-2BO (3,7) (5):

The synthesis of DBF-2BO (3,7) follows the same procedure as that of DBT-2BO (3,7), with the exception that 3,7-dibromodibenzofuran is used as the starting material. The resulting product, DBF-2BO (3,7) (5), was obtained as light-yellow needle crystals (65% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 1.0 Hz, 1H), 7.97 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.79 (dd, *J* = 7.6, 0.9 Hz, 1H), 1.38 (s, 12H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 156.14, 128.59, 126.49, 120.16, 117.74, 83.83, 24.74. HRMS (ESI): m/z calculated for C<sub>24</sub>H<sub>30</sub>B<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 421.2352; Found: 421.2361.

## Synthesis of DBF-2BO (2,8) (6):

The synthesis of DBF-2BO (2,8) follows the same procedure as that of DBT-2BO (2,8), with the exception that 2,8-dibromodibenzofuran is used as the starting material. The resulting product, DBF-2BO (2,8) (6), was obtained as white needle crystals (69% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.49 (t, *J* = 0.9 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 1.39 (s, 12H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.44, 133.75, 128.06, 123.85, 111.09, 83.87, 24.96. HRMS (ESI): m/z calculated for C<sub>24</sub>H<sub>30</sub>B<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 421.2352; Found: 421.2362.

### Synthesis of Cz-C20-2Br (7):

A stirred solution of 3,6-dibromo-9H-carbazole (5.0 g, 15.4 mmol) in dry N, Ndimethylformamide (50 mL) was treated with 60% sodium hydride dispersed in kerosene (1.0 g, 25 mmol) at 0 °C for 2 hours. Once the mixture reached room temperature, a diluted solution of 9-(bromomethyl) nonadecane (9.0 g, 25 mmol) was slowly added using a syringe, and the reaction was stirred for an additional 12 h. The reaction mixture was then poured into cold water and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel, using petroleum ether as the eluent, to obtain Cz-C20-2Br (5) as a colorless liquid (85% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.14 (d, *J* = 1.9 Hz, 2H), 7.56 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 4.08 (d, *J* = 7.5 Hz, 2H), 2.13 – 2.00 (m, 1H), 1.72 – 0.96 (m, 36H), 0.93 (td, *J* = 6.9, 3.9 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 139.89, 129.10, 123.53, 123.32, 112.06, 110.80, 48.13, 37.97, 32.06, 32.00, 31.98, 29.99, 29.73, 29.71, 29.63, 29.58, 29.47, 29.36, 26.68, 22.84, 22.79, 14.27, 14.26.

HRMS (ESI): m/z calculated for  $C_{32}H_{47}Br_2N [M+H]^+$ : 606.2128; Found 606.2120.

# S3.2 NMR and HRMS spectra of monomers



Figure S2. <sup>1</sup>H NMR spectrum of 1 in chloroform-*d*.



Figure S3. <sup>13</sup>C NMR spectrum of 1 in tetrahydrofuran- $d_8$ .



Figure S4. High-resolution mass spectrum of 1.



Figure S5. <sup>1</sup>H NMR spectrum of 2 in chloroform-*d*.



Figure S6. <sup>13</sup>C NMR spectrum of 2 in tetrahydrofuran- $d_8$ .



Figure S7. High-resolution mass spectrum of 2.



Figure S8. <sup>1</sup>H NMR spectrum of 3 in chloroform-*d*.



Figure S9. <sup>13</sup>C NMR spectrum of 3 in chloroform-*d*.



Figure S10. High-resolution mass spectrum of 3.



Figure S11. <sup>1</sup>H NMR spectrum of 4 in chloroform-*d*.



Figure S12. <sup>13</sup>C NMR spectrum of 4 in chloroform-*d*.



Figure S13. High-resolution mass spectrum of 4.



Figure S15. <sup>13</sup>C NMR spectrum of 5 in chloroform-*d*.



Figure S16. High-resolution mass spectrum of 5.



Figure S17. <sup>1</sup>H NMR spectrum of 6 in chloroform-*d*.



Figure S18. <sup>13</sup>C NMR spectrum of 6 in chloroform-d.



Figure S19. High-resolution mass spectrum of 6.



Figure S20. <sup>1</sup>H NMR spectrum of 7 in chloroform-*d*.



Figure S21. <sup>13</sup>C NMR spectrum of 7 in chloroform-d.



Figure S22. High-resolution mass spectrum of 7.

#### S3.3 Synthesis of pDBT37 series polymers



Scheme S2. Synthesis routes of pDBT37 series polymers.

The polymerization was conducted following standard procedures for palladium (II)-catalyzed Suzuki polycondensation. Under an argon atmosphere, a mixture containing BPPXZ-2Br (61.7 mg, 0.1 mmol for pDBT3710; 30.9 mg, 0.05 mmol for pDBT3705; 12.4 mg, 0.02 mmol for pDBT3702), Cz-C20-2Br (242.2 mg, 0.4 mmol for pDBT3710; 272.5 mg, 0.45 mmol for pDBT3705; 290.7 mg, 0.48 mmol for pDBT3702), DBT-2BO (3,7) (218.1 mg, 0.5 mmol), palladium (II) acetate (3 mg), tricyclohexylphosphine (PCy<sub>3</sub>) (6 mg), aqueous potassium carbonate (2 M, 5 mL), and tetraethylammonium hydroxide (Et<sub>4</sub>NOH) as an emulsifying base (0.5 mL) was added to a 100 mL Schlenk flask. Anhydrous THF (4 mL) was then introduced under argon. The mixture was stirred at 75 °C for 60 h, after which bromobenzene (0.5 mL) was added, and the reaction continued for another 12 h at 75 °C. Sodium diethyldithiocarbamate trihydrate (0.5 g) and deionized water (8 mL) were subsequently added, and the reaction mixture was stirred vigorously at 90 °C for 24 hours. After cooling to room temperature, the mixture was washed three times with saturated saltwater and extracted with dichloromethane. The resulting solution was dried using anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude

product was redissolved in THF and precipitated by adding it to a large amount of methanol. The precipitate was filtered, dried under vacuum, and further purified by Soxhlet extraction using n-hexane as the solvent. Finally, it was dried under vacuum to yield the pDBT37 series polymers. According to the <sup>1</sup>H NMR spectra of the polymers, the peak corresponding to the hydrogen atom in the TADF unit appeared at a chemical shift of 6.0-6.2 ppm, while the peak for the hydrogen atom in the carbazole unit appeared at 4.0-4.5 ppm, resulting in the formation of an orange-colored polymer.



Figure S23. <sup>1</sup>H NMR spectra of pDBT37 series polymers.

#### S3.4 Synthesis of pDBT28 series polymers



Scheme S3. Synthesis routes of pDBT28 series polymers.

The synthesis route of pDBT28 series polymers is the same as that of pDBT37 series, the difference is that the raw materials are changed to DBT-2BO (2,8).



Figure S24. <sup>1</sup>H NMR spectra of pDBT28 series polymers.

# S3.5 Synthesis of pDBF37 series polymers



Scheme S4. Synthesis routes of pDBF37 series polymers.

The synthesis route of pDBF37 series polymers is the same as that of pDBT37 series, the difference is that the raw materials are changed to DBT-2BO (3,7) to DBF-2BO (3,7).



Figure S25. <sup>1</sup>H NMR spectra of pDBF37 series polymers.

# S3.6 Synthesis of pBPPXZ-DBF28 series polymers



Scheme S5. Synthesis routes of pDBF28 series polymers.

Similarly, the synthesis route of pDBF37 series polymers is the same as that of pDBT37 series, the difference is that the raw materials are changed to DBT-2BO (2,8) to DBF-2BO (2,8).



Figure S26. <sup>1</sup>H NMR spectra of pDBF28 series polymers.

# S4. Supporting figures and tables



**Figure S27.** Gel permeation chromatography (GPC) curves of polymers. (a) pDBT series. (b) pDBF polymer series.

	$M_w^a$	M <sub>n</sub> <sup>b</sup>	PDI <sup>c</sup>	
pDBT3710	19407	12720	1.52	
pDBT3705	17658	11499	1.53	
pDBT3702	11020	6788	1.62	
pDBT2810	17704	12628	1.42	
pDBT2805	13943	8270	1.68	
pDBT2802	9138	6030	1.51	
pDBF3710	16106	7042	2.28	
pDBF3705	15238	11452	1.33	
pDBF3702	12857	6550	1.96	
pDBF2810	11081	5765	1.92	
pDBF2805	10626	6550	1.62	
pDBF2802	8385	5822	1.49	

Table S1. Gel permeation chromatography (GPC) data of polymers.

<sup>a</sup> Weight average molecular weight; <sup>b</sup> Number-average molecular weight; <sup>c</sup> Polymer dispersity index.



**Figure S28.** The differential scanning calorimetry characterizations of (a) pDBT37 series polymers; (b) pDBF37 series polymers; (c) pDBT28 series polymers and (d) pDBF28 series polymers. Thermal gravimetric analysis of (e) pDBT37 series polymers; (f) pDBT28 series polymers; (g) pDBF37 series polymers and (h) pDBF28 series polymers.



**Figure S29.** The isosurfaces of polymeric fragments from total SCF density mapped with ESP. (a) pDBT37 series polymers; (b) pDBF37 series polymers; (c) pDBT28 series polymers and (d) pDBF28 series polymers.



**Figure S30.** The cyclic voltammetry curves of (a) pDBT37 series polymers; (b) pDBT28 series polymers; (c) the external standard Fc<sup>+</sup>/Fc (the peak oxidation and reduction potentials are marked); (d) pDBF37 series polymers; (e) pDBF28 series polymers. (f) The corresponding energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the four series polymers.



Figure S31. Excited energy levels of the four series of polymers.



**Figure S32.** Energy level diagrams of excited states for the two series polymers (<sup>1</sup>CT denotes charge transfer singlet, <sup>3</sup>CT refers to charge transfer triplet, <sup>3</sup>LE indicates a locally excited triplet). The natural transition orbital analysis for typical fragments in both series polymer shows holes and electrons represented by blue and pink regions, respectively. The overlap integral between the hole and electron orbitals ( $\langle \psi_h \psi_e \rangle$ ) and spin-orbit coupling matrix elements for <sup>1</sup>CT and <sup>3</sup>CT ( $\langle ^{I}CT | \hat{H}_{SOC} | ^{3}CT \rangle$ , <sup>1</sup>CT and <sup>3</sup>LE ( $\langle ^{I}CT | \hat{H}_{SOC} | ^{3}LE \rangle$ ) are included.



**Figure S33.** Ultraviolet–visible absorption (Abs.) spectra (dotted line) and photoluminescence (PL) spectra (solid line) of (a) pDBT37 series polymers, (b) pDBT28 series polymers, (c) pDBF37 series polymers, (d) pDBF28 series polymers diluted in toluene.



**Figure S34.** The transient photoluminescence decay spectra in air and vacuum. (a) pDBT series and (b) pDBF series. The photoluminescence decays spectra were detected in the doped films (30 wt% emitters doped in mCP and TAPC) in vacuum.



**Figure S35.** (a) PLQYs of the doped polymers films (b) PLQYs of the 70 wt% pDBT3705 and (c) pDBF3705 doped films.



**Figure S36.** Steady-state photoluminescence (PL) spectroscopies in vacuum and air of (a) pDBT3702, (b) pDBT3705, (c) pDBT3710, (d) pDBT2802, (e) pDBT2805 and (f) pDBT2810.



**Figure S37.** Steady-state photoluminescence (PL) spectroscopies in vacuum and air of (a) pDBF3702, (b) pDBF3705, (c) pDBF3710, (d) pDBF2802, (e) pDBF2805 and (f) pDBF2810.



**Figure S38.** Temperature-dependent transient PL decay spectra in pure films of (a) pBDBT3702, (b) pDBT3710, (c) pDBT2802, (d) pDBT2805 and (e) pDBT2810.



**Figure S39.** Temperature-dependent transient PL decay spectra in pure films of (a) pDBF3702, (b) pDBF3710, (c) pDBF2802, (d) pDBF2805 and (e) pDBF2810.



**Figure S40.** The height images of the doped films detected by atomic force microscopy for (a) pDBT2802, (b) pDBT2805, (c) pDBT2810, (d) pDBT3702, (e) pDBT3705 and (f) pDBT3710. The root mean-square surface roughness (Ra) of the whole scanning area is shown in the images.



**Figure S41.** The height images of the doped films detected by atomic force microscopy for (a) pDBF2802, (b) pDBF2805, (c) pDBF2810, (d) pDBF3702, (e) pDBF3705 and (f) pDBF3710. The root mean-square surface roughness (Ra) of the whole scanning area is shown in the images.



**Figure S42.** (a)The electroluminescence spectra of pDBT series polymers (b) and pDBF series polymers (c). Curves of current density-voltage-luminance (*J-V-L*) of pDBT series polymers (d) and pDBF series polymers (e). EQE value versus luminance curves of pDBT series polymers (f) and pDBF series polymers.

**Table S2.** Spin-orbit coupling matrix elements (SOCMEs) between the lowest singlet excited state ( $S_1$ ) and the corresponding triplet excited state ( $T_n$ , n=0,1,2,3) for the four series polymers.

$< S_1   \hat{H}_{SOC}   T_n > / cm^{-1}$	1	2	3	4
pDBT37	0.031	0.155	0.041	0.031
pDBT28	0.060	0.140	0.022	0.017
pDBF37	0.022	0.156	0.041	0.031
pDBF28	0.024	0.156	0.017	0.014

	Tª [K]	τ <sub>p</sub> <sup>b</sup> [ns]	τ <sub>d</sub> c [μs]	<b>Φ</b> <sub>p</sub> <sup>d</sup> [%]	φ <sub>d</sub> e [%]	k <sub>RISC</sub> <sup>f</sup> [10 <sup>5</sup> s <sup>-1</sup> ]
	300	40.7	5.97	17.95	82.5	3.75
pDBT3710	200	56.6	6.51	31.77	68.83	1.63
	100	61.4	4.27	59.75	40.25	0.77
	77	63.3	4.90	65.10	34.90	0.53
	300	47.8	6.40	16.10	83.90	5.13
pDBT3705	200	49.4	6.46	28.71	71.29	2.42
	100	56.9	5.10	57.72	42.28	0.90
	77	57.6	4.94	62.65	37.35	0.76
	300	48.3	4.70	30.20	69.80	2.08
pDBT3702	200	37.6	6.34	39.68	60.32	1.08
	100	45.4	5.24	66.13	33.87	0.98
	77	45.4	3.70	76.24	23.76	0.61
	300	48.3	4.70	30.20	69.80	2.45
pDBT2810	200	58.6	5.27	43.90	56.10	1.21
-	100	64.9	2.83	68.12	31.92	0.82
	77	62.7	2.83	73.48	26.52	0.75
	300	48.6	5.34	24.64	75.36	2.01
pDBT2805	200	49.9	5.68	37.94	62.06	1.01
-	100	54.4	3.87	65.06	34.94	0.48
	77	58.6	3.61	70.54	29.46	0.40
	300	56.8	5.43	29.00	71.00	1.22
pDBT2802	200	58.4	5.45	45.09	55.91	0.62
	100	66.2	3.87	70.31	29.69	0.29
	77	69.5	3.89	73.03	26.97	0.25
	300	77.1	5.43	26.01	73.99	1.52
pDBF3710	200	39.0	6.07	45.65	54.35	0.56
	100	73.0	6.54	47.92	52.08	0.48
	77	46.2	3.87	72.82	27.18	0.28
	300	69.9	5.04	25.32	74.68	3.10
pDBF3705	200	49.7	6.25	29.14	70.86	2.06
	100	58.4	4.37	58.60	42.40	0.85
	77	58.5	4.75	64.86	35.14	0.60
	300	50.0	6.02	26.57	73.47	1.01
pDBF3702	200	82.3	1.98	57.81	42.19	0.81
	100	77.4	6.89	29.82	70.18	0.75
	77	55.6	6.55	41.78	58.22	0.46
	300	68.5	4.22	38.75	61.25	1.35
pDBF2810	200	58.6	5.27	43.90	56.10	0.87
1	100	64.9	2.83	68.10	31.10	0.58
	77	62 7	2.38	73 48	26 52	0.54
	300	57.0	4.99	42.15	57.85	0.97
pDBF2805	200	80.3	6.15	43.76	56.24	0.75
1	100	58.4	4.37	58.60	41.40	0.58

Table S3. Summary of photophysical properties of the polymers from 300 K to 77 K.

pDBF2802	77	46.2	3.87	72.28	27.18	0.35
	300	54.3	5.15	36.62	63.38	0.83
	200	78.2	6.25	35.85	64.15	0.71
	100	88.1	2.26	61.89	38.11	0.68
	77	57.5	3.31	81.96	18.06	0.16

<sup>a</sup> Temperature; <sup>b</sup> The lifetime of prompt fluorescence component; <sup>c</sup> The lifetime of delayed fluorescence component; <sup>d</sup> The ratio of prompt fluorescence (PF) component; <sup>e</sup> The ratio of delayed fluorescence component; <sup>f</sup> The rate constants of reverse intersystem crossing.

**Table S4.** The reported  $EQE_{max}$  and EQE at 500 cd m<sup>-2</sup> values of solution-processed OLEDs employing orange-red thermally activated delayed fluorescence polymers.

1,2,0,0		•	1 .		
	EQE <sub>max</sub>	EQE <sub>500</sub>	$\lambda$ (nm)	CIE	Ref.
pDBT3705	17.1	13.0	596	0.55, 0.44	This work
pDBF3705	14.2	3.8	582	0.54, 0.44	This work
pDBF2810	10.4	5.2	598	0.55, 0.44	This work
pDBT2810	9.3	5.5	608	0.57, 0.42	This work
PCzAB2Py10	5.6	10.3	581	0.50, 0.49	7
PTCz:mCP	6.5		590	0.51, 0.48	8
PFDMPE-R01	4.07	3.19	591	0.49, 0.42	9
PFSOTT2	19.4		592	0.51, 0.47	10
PSAQF20	24.1	4.9	608	0.48, 0.49	11
PCzAQC0.5	12.5	8.0	620	0.56, 0.42	12
PCzAQC0.5(5.4 k)	21.2	6.0	628	0.57, 0.42	13
PCzSOTAQ0.5	13.1		630	0.59, 0.39	14
PCzSOTAQ2	13.6		642	0.62, 0.37	14

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