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Electronic Supplementary Information

Aggregation-Induced Emission Polymers for High Performance PLEDs with Low Efficiency Roll-off

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General Information

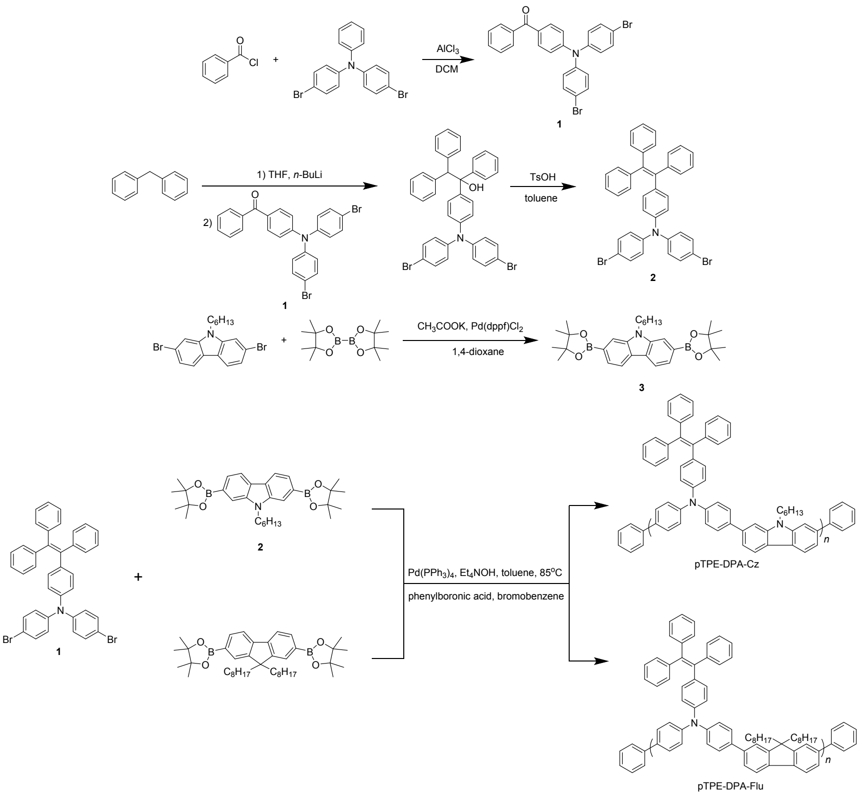
All solvents and reagents were purchased and used as received without further purification,unless otherwise mentioned. The weight-average molecular weights (M_w) and polydispersities (M_w/M_n) were measured using a Waters Advanced Polymer Chromatography (APC) system equipped with aphoto-diode array (PDA) detector. A set of monodisperse polystyrenes covering the molecular weight range from 10^3 to 10^7 were utilized as standards and THF was used as the eluent at aflow rate of 0.5 mL min^{-1}. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Advance 500 MHz NMR spectrometerusing $CDCl_3$or CD_2Cl_2as the solvent at room temperature. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449 F3 at a heating rate of 20 °Cmin^{-1} under a nitrogen flow. The thermal transition temperature was investigated by differential scanning calorimetry(DSC) using a NETZSCH DSC-204(F1) instrument under dry nitrogen at a heating rate of 10 °Cmin^{-1}. UV-vis absorption spectrum was measured on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. PL quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Cyclic voltammogram was measured in a solution of tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in dichloromethane (DCM), using Hg/Hg_2Cl_2 and platinum wire as reference and counter electrode, respectively, at a scant rate of 0.1 V s^{-1}. A platinum electrode coated with thin molecule film was used as the working electrode.Time-dependent density functional theory (TD-DFT) calculations were performed on Gaussian09 package. The ground state (S_0) geometries were optimized with the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6-31G(d)basis sets[1].

Synthesis and Characterization

4-(Bis(4-bromophenyl)amino)benzophnone **(1)**. Compound **1** was prepared from 4,4'-dibromotriphenylamine (4.03 g, 10 mmol), benzoyl chloride (1.41 g, 10 mmol) and aluminium chloride (1.40 g, 10.5 mmol) in dichloromethane (DCM, 60 mL). The reaction mixture was stirred overnight. Afterward, alarge amount of cold water was added to quench the reactionand the mixture was then extracted with DCM. The organic phase was washed with water and dried over magnesium sulfate. After filtration and solvent evaporation, the cured product was purified by column chromatography on silica gel (PE/DCM, 1:1 v/v), and **1** was obtained as yellowish solid in 90% yield (4.56 g).^{1}H NMR (500 MHz, CD_2Cl_2) δ(ppm): 7.76-7.74 (m, 2H), 7.71-7.69 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.43 (m, 6H), 7.06-7.02 (m, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ(ppm): 196.06, 152.17, 146.79, 139.51, 134.02, 133.14, 132.16, 130.88, 129.48, 128.44, 121.92, 118.60.

4-(Bis(4-bromophenyl)amino)tetraphenylethene **(2)**. To a solution of diphenylmethane (2.66 g, 5.25 mmol) in dry THF (60 mL) was added 5 mmol of *n*-butyllithium solution (2.5 M in hexane) at 0 °C under nitrogen. The resultant solution containing diphenylmethyllithium was stirred at 0 °C and 5 mmol of **1** was then added. The reaction mixture was allowed to warm to room temperature and stirred for additional 6 h. Then, the reaction was quenched by adding anaqueous solution of ammonium chloride. The organic layer was extracted with DCM three times. The resultant organic layers were combined, washed with water and dried over anhydrous magnesium sulfate. After solvent evaporation, the crude intermediate containing excess diphenylmethane was dissolved in about 50mL of toluene in a 100 mL two-necked round bottom flask equipped with a condenser. A catalytic amount of *p*-toluenesulphonic acid (TsOH) was then added and the mixture was heated to reflux.

After being cooled to room temperature, the organic layer was washed with 25 mL of 10% aqueous sodium bicarbonate solution twice and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the cured product was purified by column chromatography on silica gel (PE/DCM, 2:1 v/v), and **2** was obtained as yellowish solid in 84% yield (2.77 g). ^{1}H NMR (500 MHz, CD_2Cl_2) δ(ppm): 7.35-7.32 (m, 4H), 7.17-7.09 (m, 11H), 7.06-7.03 (m, 4H), 6.93-6.88 (m, 6H), 6.78 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ(ppm): 146.94, 145.63, 144.46, 144.24, 144.01, 132.88, 132.76, 131.77, 128.22, 128.19, 128.14, 127.04, 126.98, 126.95, 125.94, 124.07, 115.78.



Scheme S1. Synthetic route of pTPE-DPA-Cz and pTPE-DPA-Flu.

9-Hexyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole **(3)**. 2,7-dibromo-9-hexyl-9*H*-carbazole (4.09 g, 10 mmol), bis(pinacolato)diboron (5.59 g, 22 mmol) and potassium acetate (4.91 g, 50 mmol) were dissolved in dry dioxane (100 mL) under nitrogen. Pd(dppf)Cl_2 (413 mg, 0.5 mmol) was added and the mixture was stirred at 80 °C for 6 h. The reaction mixture was cooled to room temperature and water (200 mL) was added. The aqueous layer was extracted with AcOEt (100 mL). The organic phase was washed with brine (100 mL × 2) and dried over anhydrous Na_2SO_4. After filtration and solvent evaporation, this crude product was purified by column chromatography on silica gel (PE/DCM, 2:3 v/v), and **3** was obtained as white solid in 46% yield (2.31 g). ^1H NMR (500 MHz, $CDCl_3$) δ(ppm): 8.13-8.11 (m, 2H), 7.88 (s, 2H), 7.69-7.66 (m, 2H), 4.39 (t, J = 7.5 Hz, 2H), 1.90-1.86 (m, 2H), 1.40 (s, 24H), 1.37-1.25 (m, 6H), 0.90-0.87 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ(ppm): 140.57, 125.18, 124.95, 120.14, 115.38, 83.91, 83.63, 42.96, 31.73, 29.31, 26.93, 25.15, 22.74, 14.20.

Synthesis of pTPE-DPA-Cz.

4-(Bis(4-bromophenyl)amino)tetraphenylethene **2** (164.4 mg, 0.25 mmol), 9-hexyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole **3** (125.8 mg, 0.25 mmol), and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) were dissolved in toluene (5 mL) under nitrogen. Then tetraethyl ammonium hydroxide aqueous solution (1 mL, 25wt%) was added in one portion, and the mixture was heated to 85 °C with the reaction being continued for 48 h. Phenylboronicacid (305 mg, 2.5 mmol) was added and allowed to react for 12 h and then bromobenzene (785 mg, 5 mmol) was added in one portion and left to react for additional 12 h. The reaction mixture was cooled to room temperature and precipitated in methanol. The crude polymer was purified by Soxhlet extraction in methanol and acetone. After purification, the polymer was dissolved in THF, precipitated in methanol. After filtration, the product was dried at 60 °C in the vacuum oven for 10 h, a yellow-green solid was obtained in 60% yield (112 mg). ^1H NMR (500 MHz, CD_2Cl_2) δ(ppm): 8.14-8.12 (m, 2H), 7.77-7.62 (m, 6H), 7.52-7.46 (m, 3H), 7.24-7.07 (m, 18H), 6.99-6.93 (m, 4H), 4.40 (s, 2H), 1.99-1.89 (m, 2H), 1.49-1.24 (m, 6H), 0.88 (t, J = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ(ppm): 146.80, 145.94, 144.18, 143.98, 143.80, 141.76, 140.89, 138.54, 136.56, 132.34, 131.42, 128.28, 127.78, 126.58, 124.46, 123.41, 121.72, 120.61, 118.33, 106.86, 43.22, 31.78, 29.11, 27.14, 22.74, 13.95.

Synthesis of pTPE-DPA-Flu.

4-(Bis(4-bromophenyl)amino)tetraphenylethene **2** (164.4 mg, 0.25 mmol), 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (160.6 mg, 0.25 mmol), and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) were dissolved in toluene (5 mL) under nitrogen. Then tetraethyl ammonium hydroxide aqueous solution (1 mL, 25wt%) was added in one portion, and the mixture was heated to 85 °C with the reaction being continued for 48 h. Phenylboronicacid (305 mg, 2.5 mmol) was added and allowed to react for 12 h and then bromobenzene (785 mg, 5 mmol) was added in one portion and left to react for additional 12 h. The purification procedures were similar with those of the synthesis of pTPE-DPA-Cz, a yellow-green solid was obtainedin 68 % yield (151 mg).^{1}H NMR (500 MHz, CD_2Cl_2) δ(ppm):7.82-7.74 (m, 2H), 7.63-7.54 (m, 8H), 7.24-7.01 (m, 19H), 6.98-6.88 (m, 4H), 2.08 (t, J = 9.5 Hz, 4H), 1.25-1.09 (m, 20H), 0.83-0.72 (m, 10H).^{13}C NMR (125 MHz, CD_2Cl_2) δ(ppm): 153.06, 147.98, 147.05, 145.35, 145.16, 144.96, 142.03, 141.11, 140.65, 139.88, 137.15, 133.51, 132.59, 130.05, 129.04, 128.94, 128.38, 127.75, 126.75, 125.56, 124.56, 122.32, 121.22, 56.58, 41.70, 33.09, 31.31, 30.52, 25.19, 23.91, 15.15.

PLED Fabrication and Characterization

Before devices fabrication, 180 nm indium tin oxide (ITO) pre-coated glass substrates were cleaned in an ultrasonic detergent bath for 2 h, followed by ultrasonic de-ionized water bath for 30 min, then dried by compressed N_2 flow and oven baking at 120 °C for 1 h. The substrates were further cleaned by UV/ozone for 15 min. Then, PEDOT:PSS was spin-coated onto cleaned ITO surface with a condition of 3000 rpm for 30s to achieve a thickness of 50 nm. And the substrates were further baked at 150 °C for 15 min to remove the residual solvent. Afterward, they were moved into a glove box with N_2 atmosphere. The emitting layer was spin-coated according to the device configuration requirement. Here, solutions of pTPE-DPA-Cz(5, 10 and 30 wt%) doped in CBP with a concentration of 20 mg mL^{-1} in chlorobenzene were spin-coated under 2000 rpm for 45s to get films which had thickness of 55 nm, while solutions of pTPE-DPA-Flu achieved films with the thickness of 60 nm under the same conditions of pTPE-DPA-Cz. And the non-doped pTPE-DPA-Cz and pTPE-

DPA-Flu were dissolved in chlorobenzene with a concentration of 20 mg mL^{-1}, then they were spin-coated under 3500 and 2000 rpm for 45 s to get films with the thickness of 60 and 40 nm, respectively. The emitting layers were dried at 120 °C for 15 min to remove the residual solvent. Finally, the substrates were transferred into vacuum chamber under 1×10^{-4} Pa. An electron-transporting layer (TmPyPB) with the thickness of 40 nm was deposited onto EML with a rate of 1-2 Å s^{-1}, an electron-injecting layer (LiF) with the thickness of 1 nm was deposited onto TmPyPB with a rate of 0.1~0.2 Å s^{-1}. At last, a cathode (Al) with the thickness of 120 nm was deposited onto LiF with a rate of 2-5 Å s^{-1}. The emission area of the devices is 4 × 4 mm^2. Current density-luminance-voltage characteristics were taken by Keithley 2400 and Konica Minolta chromameter CS-200, respectively. And EL spectra were collected by an optical analyzer, FlAME-S-VIS-NIR. External quantum efficiencies were calculated by assuming that the devices were according with Lambertian light sources. All the device characterization steps were carried out at room temperature under ambient laboratory conditions without encapsulation except spectrum collection process.

Table S1. Polymerization results and electrochemical properties of polymers.

	Yield (%)	M_w^{a} (g mol^{-1})	M_w/M_n^{a}	T_d^{b} (°C)	T_g^{c} （°C）	E_{HOMO}^{d} (eV)	E_{LUMO}^{e} (eV)
pTPE-DPA-Cz	60	19 000	1.47	510	193	-5.56	-2.62
pTPE-DPA-Flu	68	24 000	1.62	442	152	-5.49	-2.57

^{a}Determined by APC in THF on the basis of a linear polystyrene calibration. ^{b}The T_d of the polymers detected by the TGA ata heating rate of 20 °C min^{-1} under nitrogen. ^{c}The T_g of the polymers detected by the DSC at a heating rate of 10 °C min^{-1} under nitrogen. ^{d}$E_{HOMO} = -(E_{onset(ox)} + 4.8)$ eV. ^{e}$E_{LUMO} = (E_{HOMO} + E_g^{opt})$ eV.

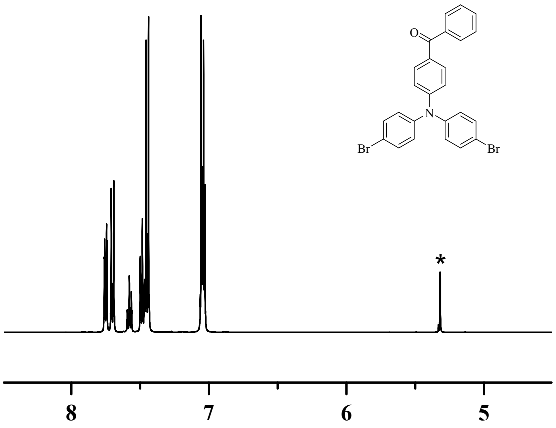


Figure S1. The ^{1}H NMR spectrum of compound **1** in CD_2Cl_2. The solvent peak is marked with asterisk.

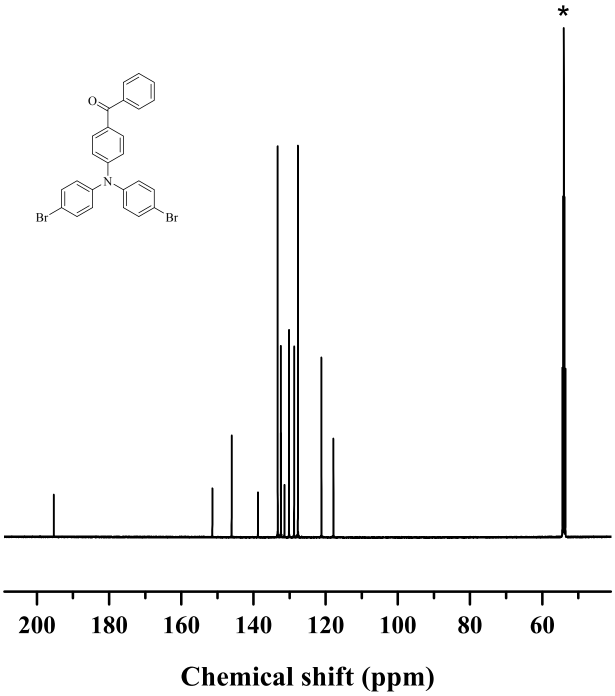


Figure S2. The ^{13}C NMR spectrum of compound **1** in CD_2Cl_2. The solvent peaks are marked with asterisk.

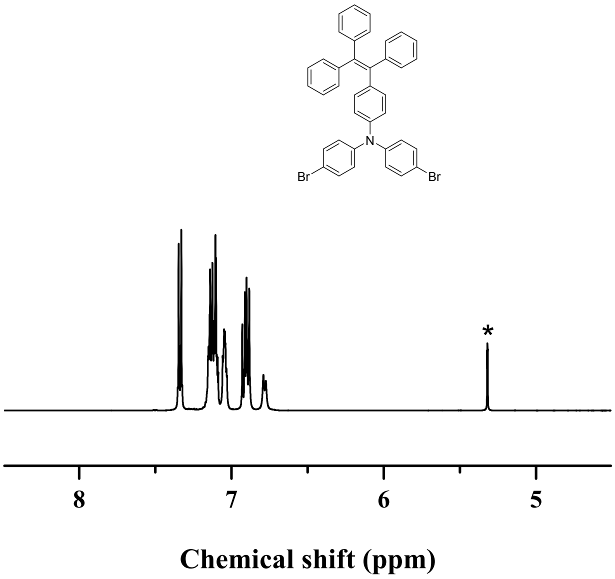


Figure S3. The ^{1}H NMR spectrum of compound **2** in CD_2Cl_2. The solvent peak is marked with asterisk.

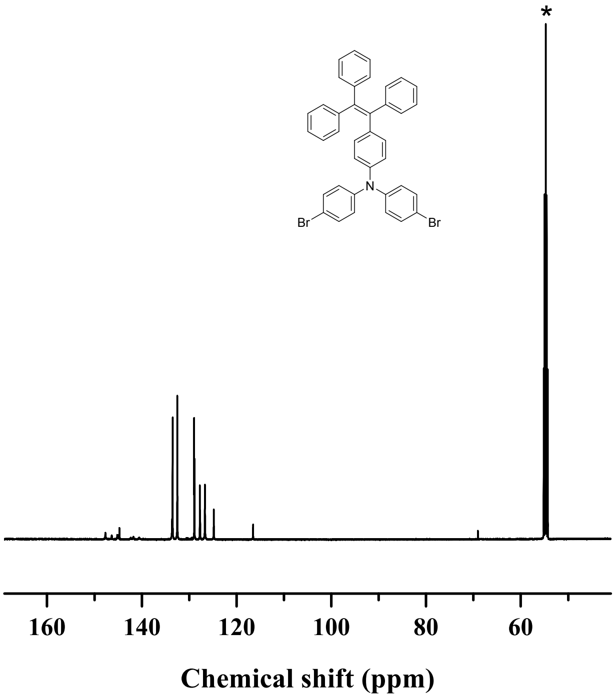


Figure S4. The ^{13}C NMR spectrum of compound **2** in CD_2Cl_2. The solvent peaks are marked with asterisk.

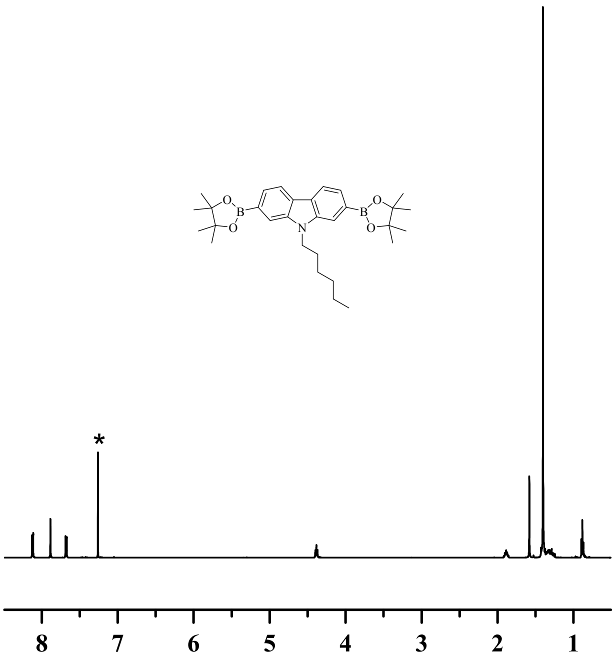


Figure S5. The ^{1}H NMR spectrum of compound **3** in $CDCl_3$. The solvent peak is marked with asterisk.

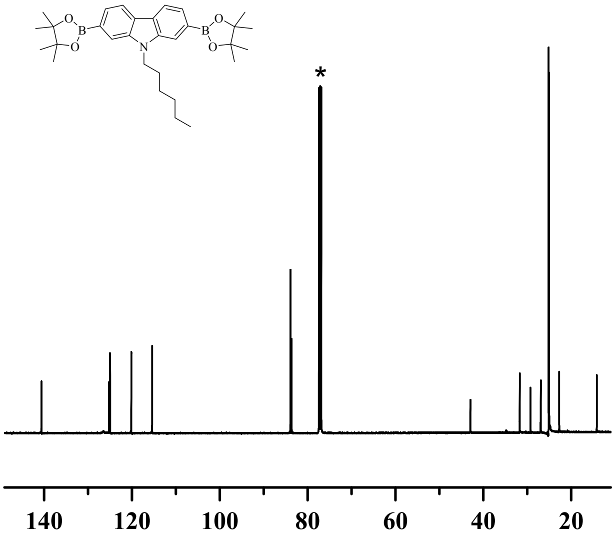


Figure S6. The ^{13}C NMR spectrum of compound **3** in $CDCl_3$. The solvent peaks are marked with asterisk.

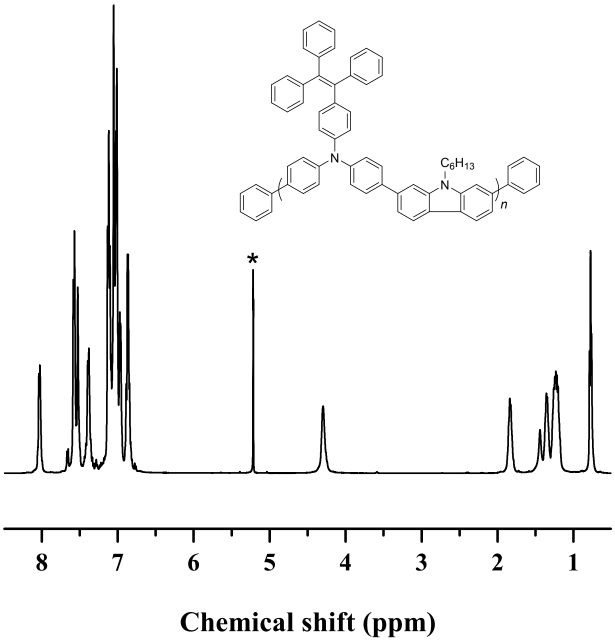


Figure S7. The ^{1}H NMR spectrum of pTPE-DPA-Cz in CD_2Cl_2. The solvent peak is marked with asterisk.

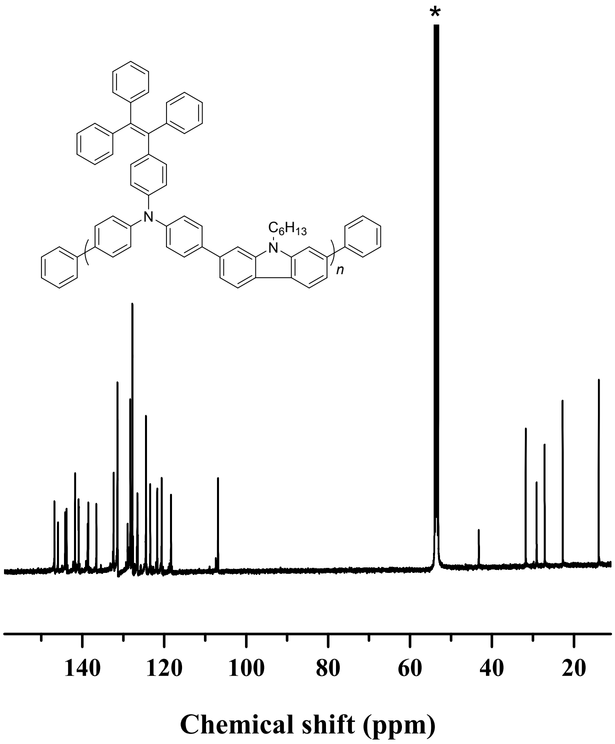


Figure S8. The ^{13}C NMR spectrum of pTPE-DPA-Cz in CD_2Cl_2. The solvent peaks are marked with asterisk.

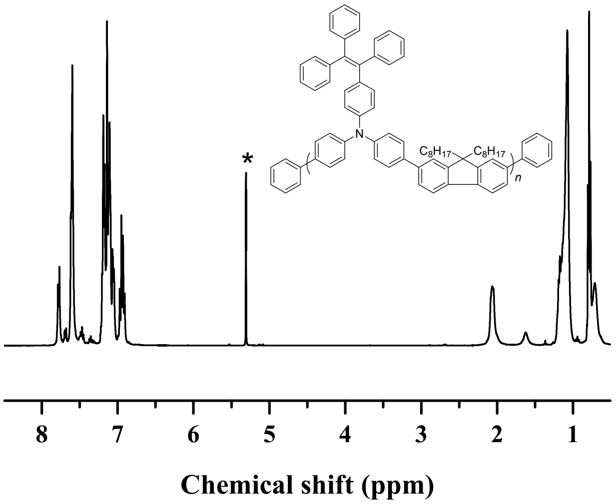


Figure S9. The ^{1}H NMR spectrum of pTPE-DPA-Flu in CD_2Cl_2. The solvent peak is marked with asterisk.

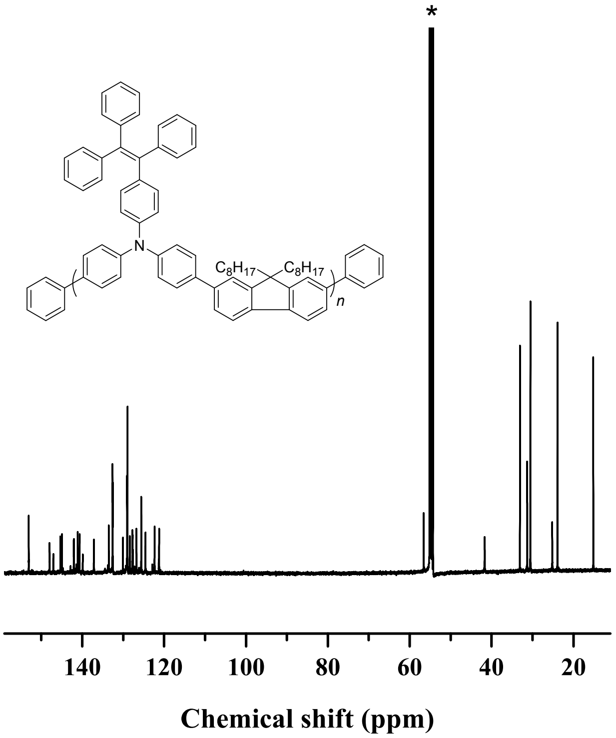


Figure S10. The ^{13}C NMR spectrum of pTPE-DPA-Flu in CD_2Cl_2. The solvent peaks are marked with asterisk.

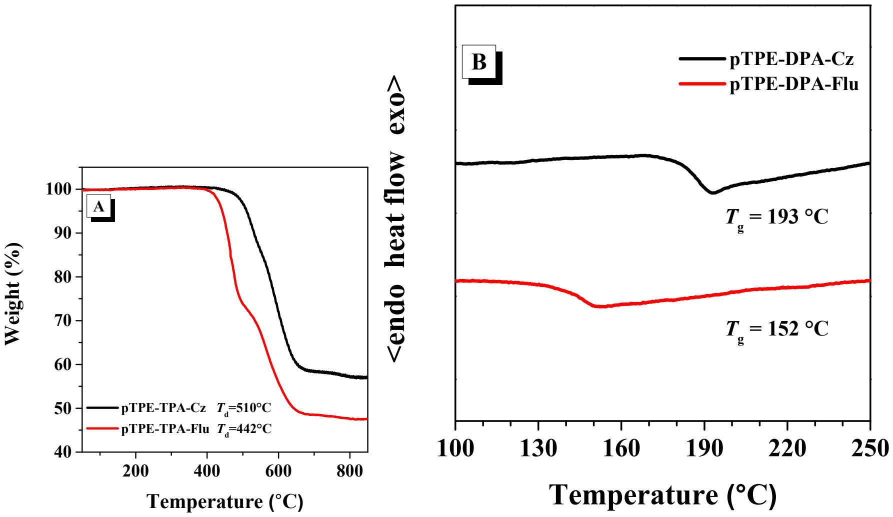


Figure S11. (A) TGA and (B) DSC thermograms of pTPE-DPA-Cz and pTPE-DPA-Flu recorded under nitrogen at a heating rate of (A) 20 °C min^{-1} and (B) 10 °C min^{-1}.

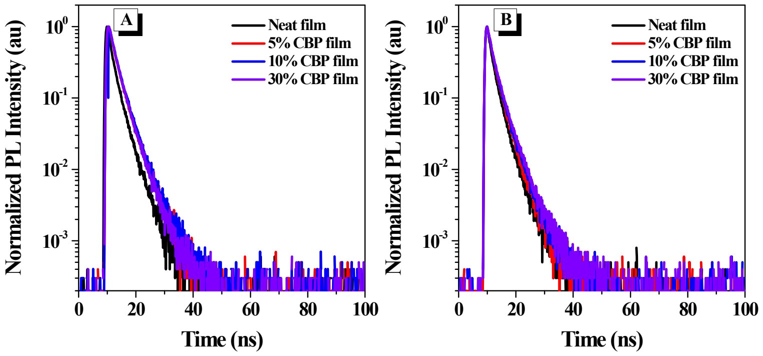


Figure S12. PL transient spectra of (A) pTPE-DPA-Cz and (B) pTPE-DPA-Flu at 300k. The nondoped and doped films (CBP as the matrix) were deposited on quartz substrates.

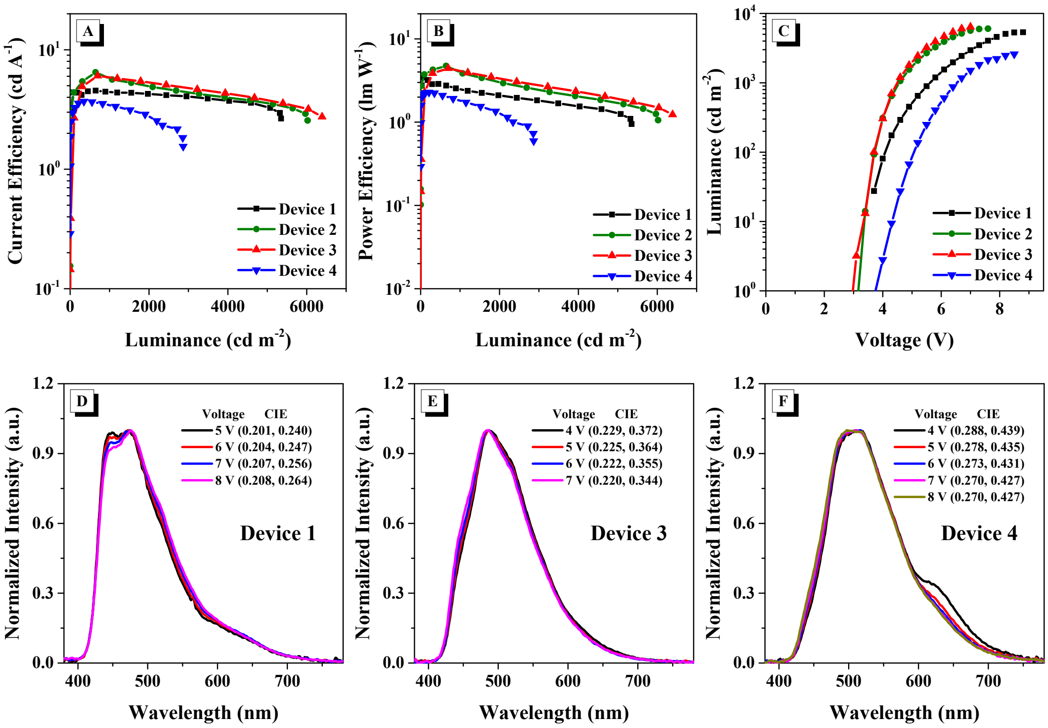


Figure S13. (A) Current efficiency as a function of luminance for devices 1-4. (B) Power efficiency as a function of luminance for devices 1-4. (C) Luminance as a function of voltage for devices 1-4. (D), (E) and (F) Normalized EL spectra at different voltages of devices 1, 3 and 4, respectively.

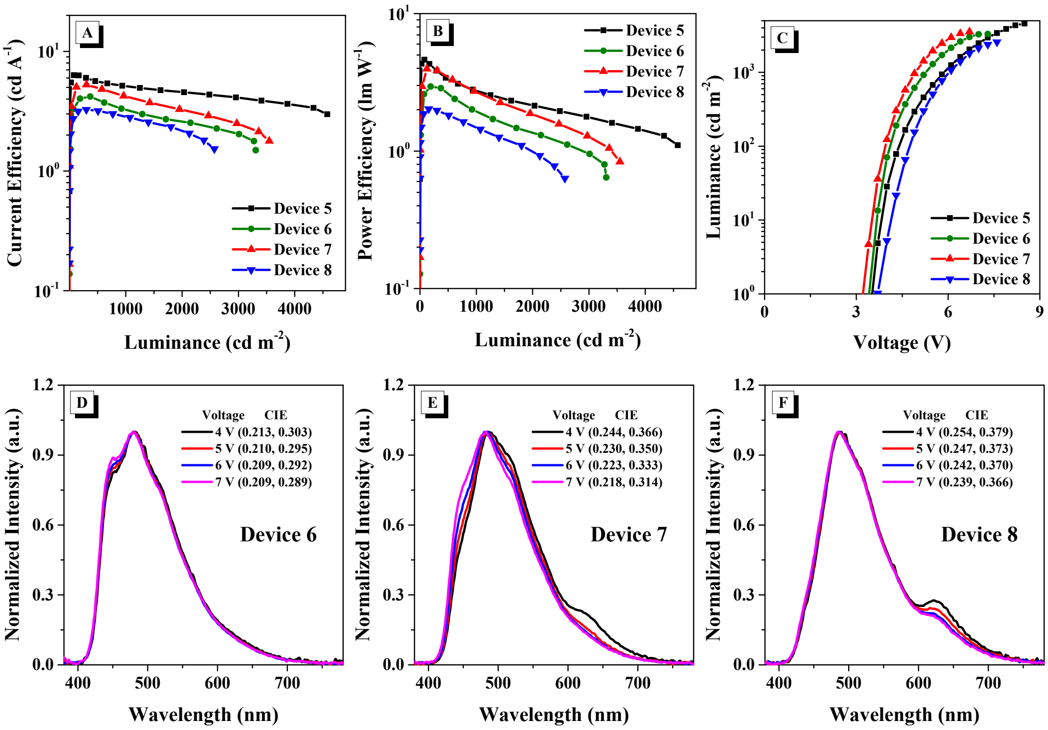


Figure S14. (A) Current efficiency as a function of luminance for devices 5-8. (B) Power efficiency as a function of luminance for devices 5-8. (C) Luminance as a function of voltage for devices 5-8. (D), (E) and (F) Normalized EL spectra at different voltages of devices 6, 7 and 8, respectively.

References

1 (a) J. Fan, L. Lin, C.-K. Wang, *J. Mater. Chem. C.*, 2017, 5; (b) X. Cai, X. Li, G. Xie, Z. He, K. Gao, K. Liu, D. Chen, Y. Cao, S.-J. Su, *Chem. Sci.*, 2016,7, 4264.