# Supporting Information

# Butterfly-Shaped Tetrasubstituted Carbazole Derivatives as a New Class of Hosts for Highly Efficient Solution-processable Green Phosphorescent OLEDs

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***General Information.*** All solvents and materials were used as received from commercial suppliers without further purification. $^1$H NMR and $^{13}$C NMR spectra were measured on a Bruker-AF301 AT 400MHz spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Mass spectra were carried out on an a Bruker autoflex MALDITOF mass spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). PL spectra were recorded on Edinburgh instruments (FLSP920 spectrometers). Differential scanning calorimetry (DSC) was performed on a PE Instruments DSC 2920 unit at a heating rate of 10 ℃/min from 30 to 250℃ under nitrogen. Thermogravimetric analysis (TGA) was undertaken with a PerkinElmer Instruments (Pyris1 TGA). The thermal stability of the samples was determined by measuring their weight loss while heating at a rate of 10 ℃/min from 30 to 700 ℃ under a nitrogen atmosphere. Cyclic voltammetry measurements were carried out in a conventional three electrode cell using a Pt button working electrode of 2 mm in diameter, a platinum wire counter electrode, and an Ag/AgCl reference electrode on a computer- controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Reductions CV of all compounds were performed in dichloromethane containing 0.1 M tetrabutylammoniumhexafluorophosphate ($Bu_4NPF_6$) as the supporting electrolyte. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

***Computational Details.*** The geometrical and electronic properties were performed with the Amsterdam Density Functional (ADF) 2009.01 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) with the 6-31G(d) atomic basis set. Then the electronic structures were calculated at τ-HCTHhyb/6-311++ G(d,p)level. Molecular orbitals were visualized using ADFview.

***Device Fabrication and Measurement.*** In a general procedure, indium-tin oxide (ITO)-coated glass substrates were pre-cleaned carefully and treated by UV ozone for 5 min. 40 nm PEDOT: PSS aqueous solution was spin-coated onto the ITO substrate and baked at 150 □ for 20 min to remove the residual water. Then the substrates were transferred to glove box, where the emitting layers were spin-coated onto the PEDOT: PSS layer from 1,2-dichlorobenzene solution and annealed at 100 □ for 30 min. In evaporation chamber, 40 nm TPBI was evaporated at an evaporation rate of 1~2 Å/s under a pressure of $5\times10^{-6}$ Torr and the LiF/Al bilayer cathode was evaporated at evaporation rates of 0.2 and 10 Å/s for LiF and Al, respectively, under a pressure of $4\times10^{-5}$ Torr. The active area of the device was 9 $mm^2$. The current-voltage-brightness characteristics of the devices were characterized with Keithley 2400 source meter and a Keithley 2000 source multimeter equipped with a calibrated silicon photodiode.The electroluminescent spectra were collected with a PR655 Spectrophotometer. All measurements of the devices were carried out in ambient atmosphere without further encapsulations.

## *Synthesis Detail*

***Synthesis of 1,3,6,8-tetrabromo-9H-carbazole (1):*** Carbazole (1.67 g, 10.0 mmol) and $FeCl_3$ (81.1 mg, 0.5 mmol) were dissolved in 30 mL of $CHCl_3$, and then bromine (16.0 g, 100 mmol) was added in portions. The mixture was stirred at 100 ℃ for 24 h, then quenched with $NaHSO_3$ aqueous solution, the crude product was filtered as a pale solid, recrystallized with the mixture of ethanol and toluene to get white needle solid (1.92 g, 4.0 mmol). Yield: 40%. $^1$H-NMR ($CDCl_3$, 400 MHz,): δ (ppm) 8.32 (s, 1H), 8.05 (s, 2H), 7.75 (s, 2H).

***Synthesis of 1,3,6,8-tetrabromo-9-octyl-9H-carbazole (2):*** 1,3,6,8-tetrabromocarbazole (4.78, 10.0 mmol) and NaH (0.48 g, 20.0 mmol) were dissolved in 50 mL of DMF, and then 1-bromooctane (4.0 g, 20 mmol) was added slowly with syringe at nitrogen atmosphere, the mixture was stirred at 40 ℃ for about 4.0 h, the water was added and extracted with dichloromethane, the organic phase was washed with the distilled water, dried by anhydrous $NaSO_4$, and evaporated to dryness, the residue was recrystallized with $CH_2Cl_2$ and methanol to get white power. Yield: 98%. $^1$H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.02 (s, 2H), 7.77 (s, 2H), 5.10, (t, $J$ = 8.2 Hz, 2H), 1.80 ~ 1.77 (m, 2H), 1.42 ~ 1.25 (m, 10H), 0.86 (t, $J$ = 6.4 Hz, 3H).

***Synthesis of 9-octyl-1,3,6,8-tetra(2-(spirobifluorene))-9H-carbazole (TSPFCz):*** A mixture of 1,3,6,8- tetrabromo-9-octyl-9H-carbazole (**2**) (0.82 g, 1.38 mmol), 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.74 g, 6.2 mmol), $Pd(PPh_3)_4$ (240 mg, 0.2 mmol), 2.0 M $K_2CO_3$ (14 ml), toluene (100 ml) and ethanol (50 ml) was stirred at 100 □ for 24 h. Then the mixture was cooled to room temperature and saturated (sat.) ammonium chloride solution was added. The organic layer was extracted with $CH_2Cl_2$, and dried with $Na_2SO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel using $CH_2Cl_2$/hexane as the eluent to give white powder. Yield: 75%. $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.83 ~ 7.94(m, 19H), 7.63 (d, $J$ = 8.0 Hz, 2H), 7.36 ~ 7.41 (m, 13H), 7.06 ~ 7.15 (m, 12H), 6.94 (s, 2H), 6.75 (m, 10H), 6.69 (d, $J$ = 5.4 Hz 4H), 3.14 (w, 2H), 1.02 (w, 2H), 0.90 (t, *J* = 7.2 Hz 3H), 0.71 (m, 5H), 0.35 (w, 5H). $^{13}$C NMR: ($CDCl_3$, 100MHz): δ (ppm) 149.29, 149.15, 149.06, 148.81, 141.77, 141.42, 141.33, 140.71, 140.42, 139.93, 132.75, 129.04, 128.23, 127.90, 127.80, 127.63, 127.55, 127.25, 125.93, 124.19, 124.08, 123.85, 122.73, 120.13, 119.98, 119.86, 117.55, 66.05, 65.97, 45.74, 31.68, 28.77, 28.72, 25.81, 22.48, 14.06. MS (MALDI-TOF): calcd for $C_{120}H_{81}N$: 1535.6369, found, 1535.6358 $(M)^+$. Anal. calcd for $C_{120}H_{81}N$ (%): C 93.78, H 5.31, N 0.91; found: C 93.85, H 5.44, N 0.71.

***Synthesis of 1,3,6,8-tetra([1,1':3',1''-terphenyl]-5'-yl)-9-octyl-9H-carbazole (TTPhCz):*** The compound was synthesized in a similar way as **TSPFCZ** except using 2-([1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to instead 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Yield: 80%. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.60 (s, 2H), 8.0 (s, 4H), 7.76 ~ 7.86 (m, 18H), 7.68 (d, *J* = 8.0 Hz, 8H), 7.50 (t, *J* = 7.2 Hz, 8H), 7.36 ~ 7.42 (m, 16H), 3.69 (t, *J* = 7.2 Hz, 2H), 1.12 (s, 2H), 0.97 (t, *J* = 7.2 Hz, 2H), 0.78 (m, 2H), 0.73 (w, 5H), 0.56 (d, *J* = 7.2 Hz, 2H), 0.26 (s, 2H). $^{13}$C NMR: ($CDCl_3$, 100MHz): δ (ppm) 142.49, 141.62, 141.53, 141.37, 140.62, 139.19, 132.72, 128.89, 128.84, 128.73, 128.60, 127.62, 127.47, 127.33, 127.21, 127.14, 127.03, 125.93, 125.32, 125.10, 124.75, 118.08, 45.71, 31.54, 29.54, 29.06, 29.01, 26.21, 22.40, 13.98. MS (MALDI-TOF): calcd for $C_{92}H_{73}N$: 1192.5776,, found, 1192.5765 $(M)^+$. Anal. calcd for $C_{92}H_{73}N$ (%): C 92.66, H 6.17, N 1.17; found: C 92.54, H 6.44, N 1.02.

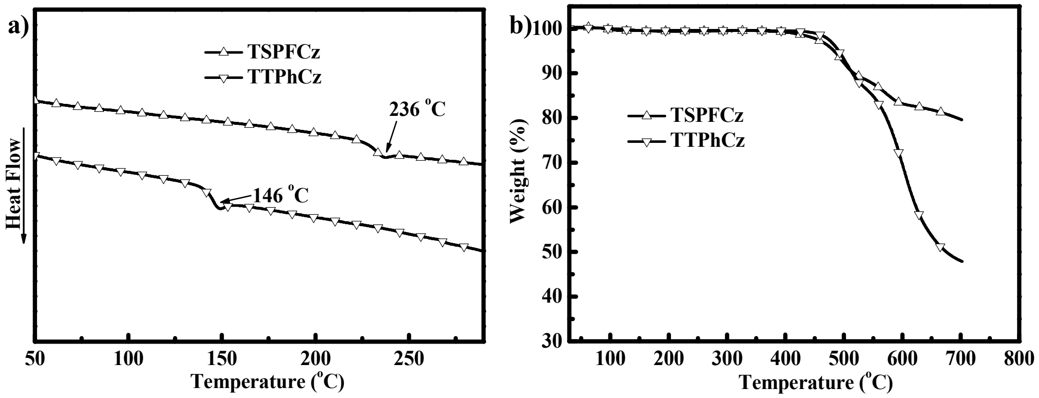
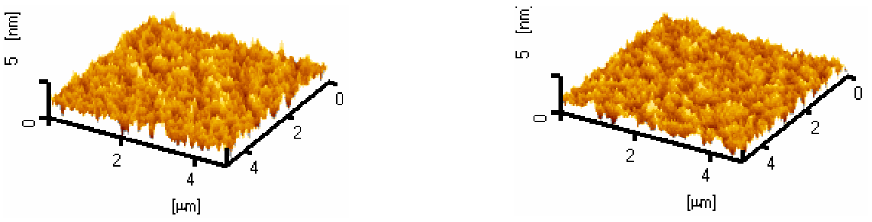


**Figure S1.** DSC (a) and TGA (b) curves of the compounds TSPFCz and TTPhCz



**TSPFCz** **TTPhCz**

**Figure S2.** AFM topographic images of **TSPFCz** and **TTPhCz**. The film were prepared through spin-coating from 1,2-dichlorobenzene solutions onto ITO/PEDOT:PSS.

**Table S1.** The photophysical, thermal and electrochemical properties of the compounds TSPFCz and TTPhCz

| Compounds | UV(nm)$^a$ | PL(nm)$^a$ | $E_g$ (eV)$^b$ | HOMO/LUMO (eV)$^c$ | | HOMO/LUMO (eV)$^d$ | | $E_T$ (eV)$^e$ | $T_g/T_d$ (℃)$^f$ |
|---|---|---|---|---|---|---|---|---|---|
| **TSPFCz** | 322/310 | 409 | 3.14 | -5.52 | -2.38 | -4.93 | -1.04 | 2.52 | 236/483 |
| **TTPhCz** | 369/302 | 395 | 3.26 | -5.54 | -2.28 | -5.20 | -1.03 | 2.73 | 146/487 |

$^a$Measured in toluene solution; $^b$Calculated from the onset of the absorption spectra; $^c$Measured from CV in $CH_2Cl_2$; $^d$Calculated from the DFT theory; $^e$Measured in 2-MeTHF at 77K; $^f$Measured by the DSC and TGA.

**Table S2.** Device performances of solution-processed phosphorescent organic light-emitting diodes.

| Device | host | $V_{on}$ (v)$^a$ | $L_{max}$[cd/m$^2$] (V at $L_{max}$, V) | $\eta_c{}^b$[cd/A] | $\eta_p{}^b$[lm/W] | EQE$^b$[%] | CIE [x, y]$^c$ |
|---|---|---|---|---|---|---|---|
| **A** | **TSPFCz** | 4.2 | 23786(12.4) | 36.1 | 23.1 | 10.3 | (0.31, 0.62) |
| **B** | **TTPhCz** | 4.0 | 32137(13.6) | 41.0 | 25.6 | 11.8 | (0.30, 0.62) |

$^a V_{on}$: the turn-on voltage at brightness of 1.0 cd/m$^2$; $L_{max}$ : the maximum luminance; V: the voltage at the maximum brightness; $\eta_c$: the maximum current efficiency; $\eta_p$: the maximum power efficiency; CIE[x, y]: the coordinate of the color; $^b$the maximum external quantum efficiency; $^c$Measured at the voltage of 8 V.

## $^{13}$CNMR and $^{1}$H NMR spectra of **TSPFCz** and **TTPhCz**

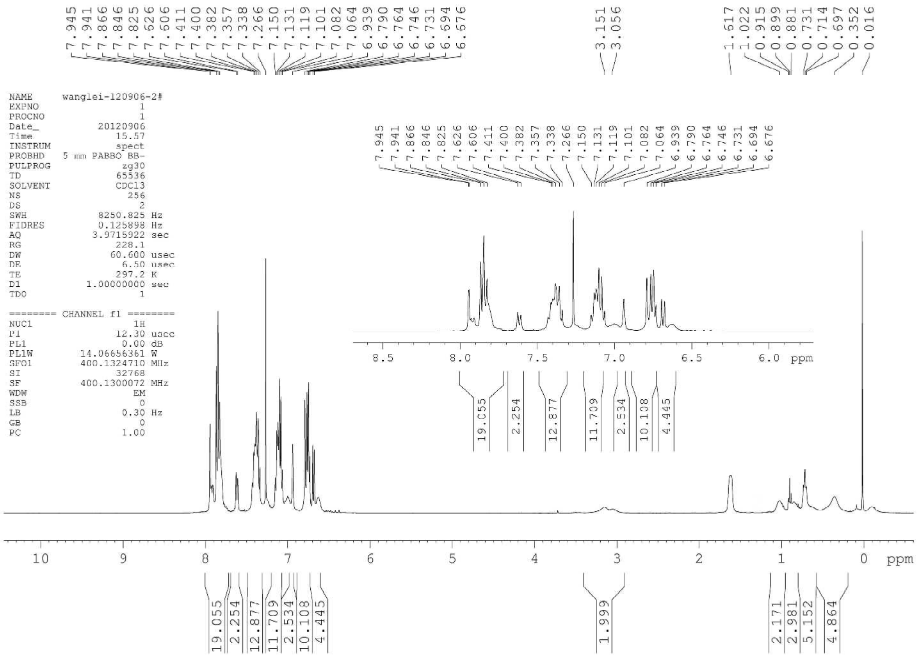


**Figure S3.** $^{1}$H NMR spectrum of **TSPFCz**

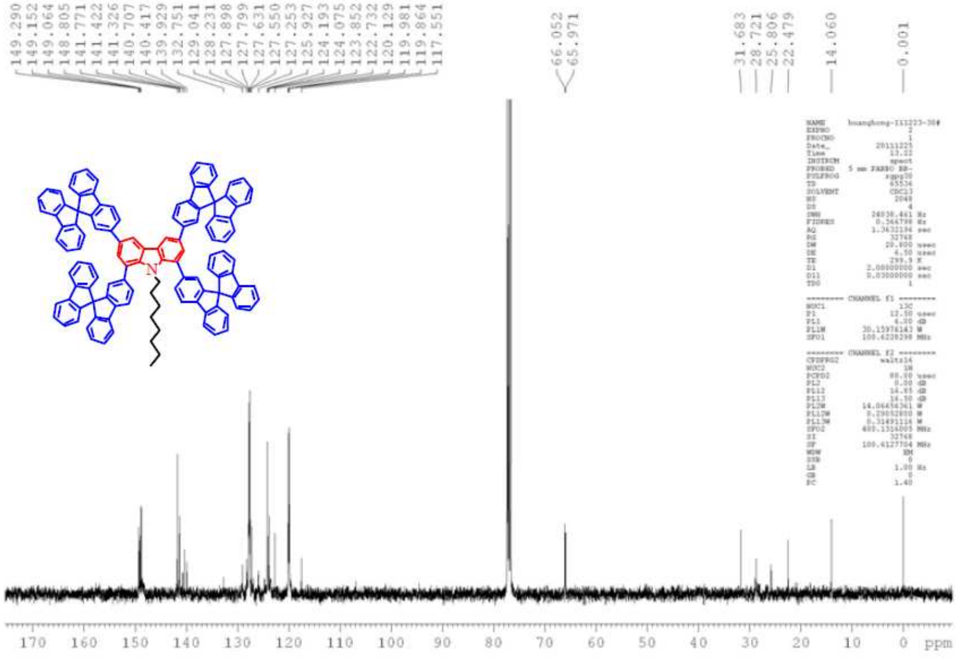


**Figure S4.** $^{13}$C NMR spectrum of **TSPFCz**

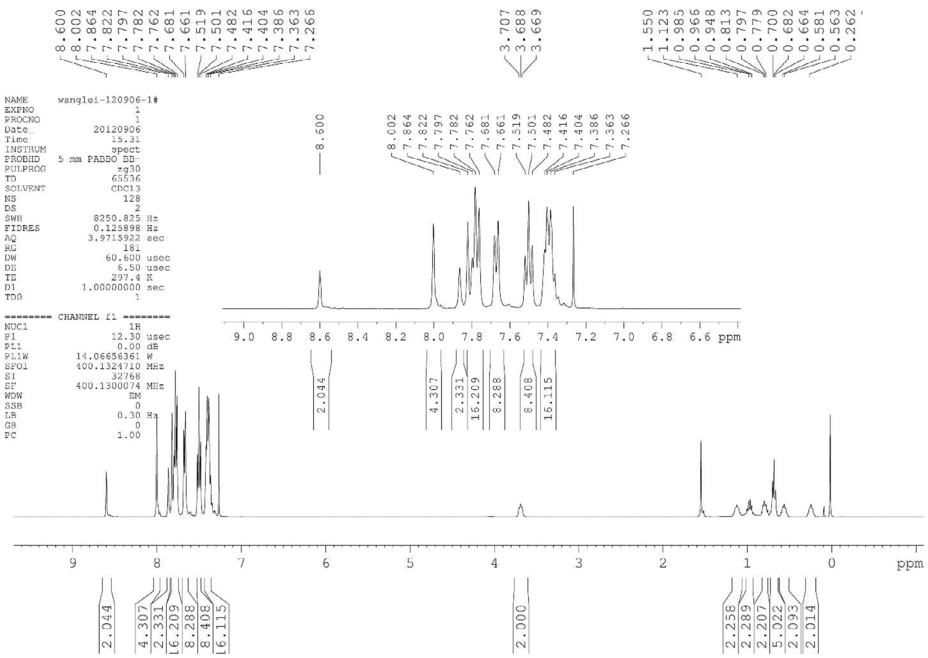


**Figure S5.** $^{1}$H NMR spectrum of **TTPhCz**

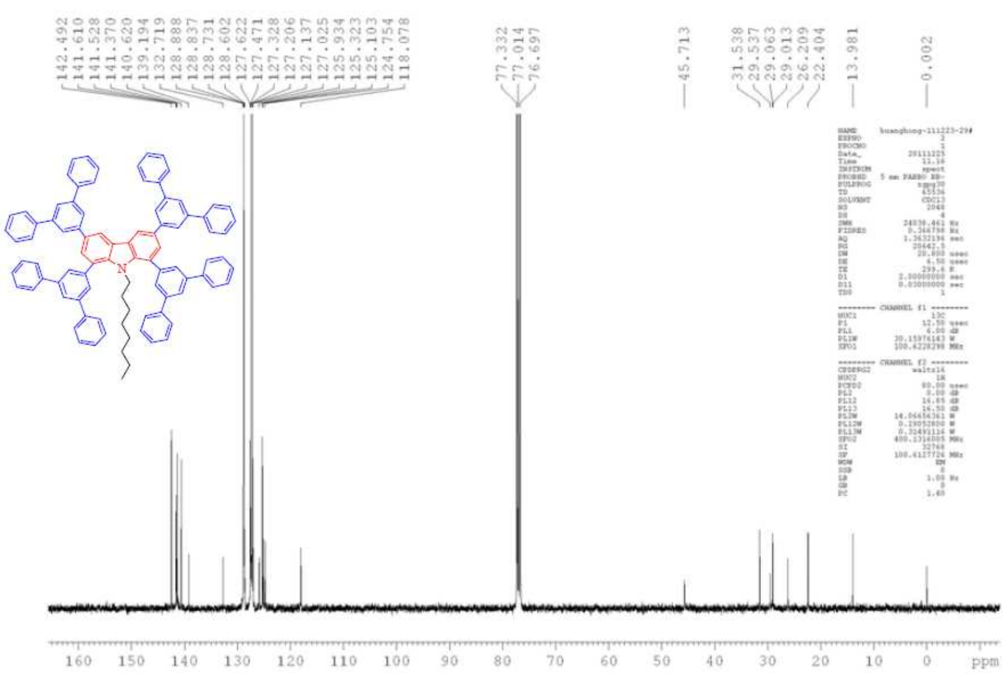


**Figure S6.** $^{13}$C NMR spectrum of **TTPhCz**