

Supporting Information

The Inductive-Effect of Electron Withdrawing Trifluoromethyl for Thermally Activated Delayed Fluorescence: Tunable Emission from *Tetra-* to *Penta-* Carbazole Derivatives in Solution Processed Blue OLEDs

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Experimental section

General Information

¹H NMR spectra was measured on a MECUYR-VX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. Mass spectra were measured on Bruker autoflex matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF). UV-vis absorption spectra were recorded on a Shimadzu UV-1750 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The PL quantum yields and the transient lifetime were measured in toluene solution using the Edinburgh FLS-920 Instruments. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min⁻¹ from 0 to 300°C under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min⁻¹ from 25 to 600°C. Cyclic voltammetry (CV) was measured in nitrogen-purged dichloromethane for oxidation scan, with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal

standard. Cyclic voltammograms were obtained at scan rate of 100 mV s⁻¹. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

Computational Details

To estimate the frontier molecular orbitals, density functional theory (DFT) calculations were performed. The ground-state geometries were optimized with Gaussian 09 software¹ using the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation) functional and 6-31G(d) basis set. Molecular orbitals were visualized using Gaussview. The highest occupied and lowest unoccupied natural transition orbitals (HONTO and LUNTO) of T₁ and S₁ were both simulated at the wB97XD/6-311G(d,p) level.

Device Fabrication and Measurements

OLEDs were prepared on a patterned indium tin oxide (ITO) glass layer, ITO glass substrates were ultrasonically cleaned with detergent, alcohol and acetone, deionized water and then dried at 120°C in a vacuum oven. After ultraviolet (UV)-ozone treating for 4 min, a ~ 40 nm PEDOT:PSS was spin coated on the ITO substrate and dried at 120°C in a vacuum oven for 15 min to remove residue solvent. Afterwards, the emissive layers (EMLs) of mCP or 4CzCF₃Ph: 5CzCF₃Ph (10 wt%, ~ 40 nm) were spin-coated on top of PEDOT:PSS from chloroform and then annealed using a hot plate at 80°C for 20 min to extract residual solvent. Following that, the samples were transferred into a thermal evaporator chamber. Then TmPyPB (60 nm), LiF (0.8 nm), and Al (100 nm) were deposited by thermal evaporation under a pressure of 5×10⁻⁴ Pa, respectively. The active area of the device is 13.5 mm². The luminance-current-voltage characteristics of the devices were recorded using a combination of a

Keithley source-meter (model 2602) and a calibrated luminance meter. Electroluminescence (EL) spectra and Commission International de l'Eclairage (CIE) coordinates were obtained using a spectra-scan PR655 spectrophotometer. The thickness of the organic films was measured with a spectroscopic ellipsometry (α -SE, J.A. Wollam Co. Inc.). All the measurements were carried out at room temperature under ambient conditions.

Synthesis

2,3,5,6-tetra(9H-carbazol-9-yl)trifluoromethylbenzene (4CzCF₃Ph).

A mixture of carbazole (1.0 g, 6.0 mmol), 2, 3, 5, 6-Tetrafluorobenzotrifluoride (0.30 g, 1.4 mmol), and K₂CO₃ (1.9 g, 13.6 mmol) in dimethyl sulfoxide (DMSO) (10 mL) was stirred at 150 °C for 12 h under an N₂ atmosphere. After cooling to room temperature, the mixture was poured into water, filtered, and then purified by column chromatography over silica gel with CH₂Cl₂/petroleum ether as the eluent to afford a white solid (0.56 g, Yield: 80%). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.33 (s, 1H), 7.77 (t, 7H, J = 6.0 Hz), 7.41-7.07(m, 25H). ¹³C NMR (75 MHz, CDCl₃): δ ppm 142.0, 141.4, 139.1, 126.8, 126.7, 125.2, 125.1, 122.0, 121.4, 111.6, 111.0. MALDI-TOF Mass (m/z): calcd for C₅₅H₃₃F₃N₄: 806.27; found: 806.04. ; Anal. Calcd. For C₅₅H₃₃F₃N₄: C 81.87, H 4.12, N 6.94%; found: C 81.95, H 4.09, N 6.88%.

2,3,4,5,6-tetra(9H-carbazol-9-yl)trifluoromethylbenzene (5CzCF₃Ph).

5CzCF₃Ph was prepared according to a similar procedure to 4CzCF₃Ph, by using octafluorotoluene to take replace of 2,3,5,6-tetrafluorobenzotrifluoride as the starting material. Yield: 40%. ¹H NMR (CDCl₃, 300 MHz): δ ppm 7.67 (d, 4H, J = 3.0 Hz), 7.42 (t, 3H, J = 3.0 Hz), 7.32(s, 4H), 7.27-7.13(m, 18H), 6.77-6.66 (m, 11H); ¹³C NMR was unavailable due to low solubility of the compound. MALDI-TOF Mass (m/z): calcd for C₆₇H₄₀F₃N₅: 971.32; found: 971.27; Anal. Calcd. For C₆₇H₄₀F₃N₅: C 82.78, H 4.15, N 7.20 %; found: C 82.51, H 4.02, N 6.89 %.

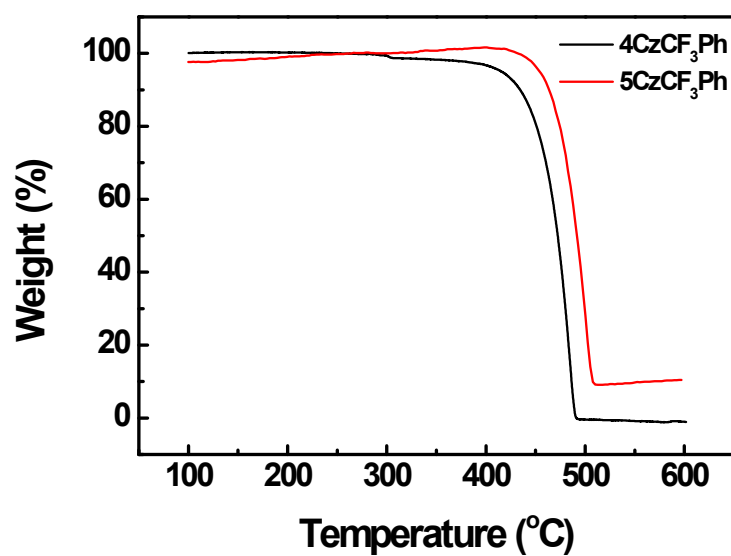


Fig. S1. TGA curves for 4CzCF₃Ph and 5CzCF₃Ph.

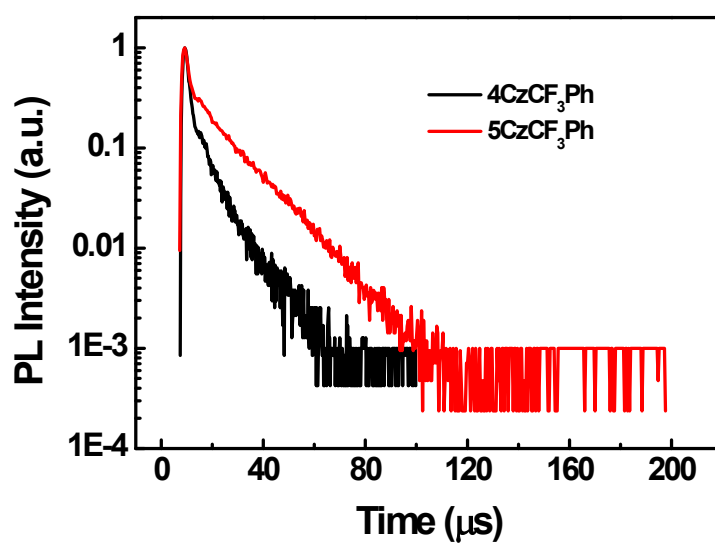


Fig. S2 Fluorescence emission lifetime for 4CzCF₃Ph and 5CzCF₃Ph in degassed toluene solution.

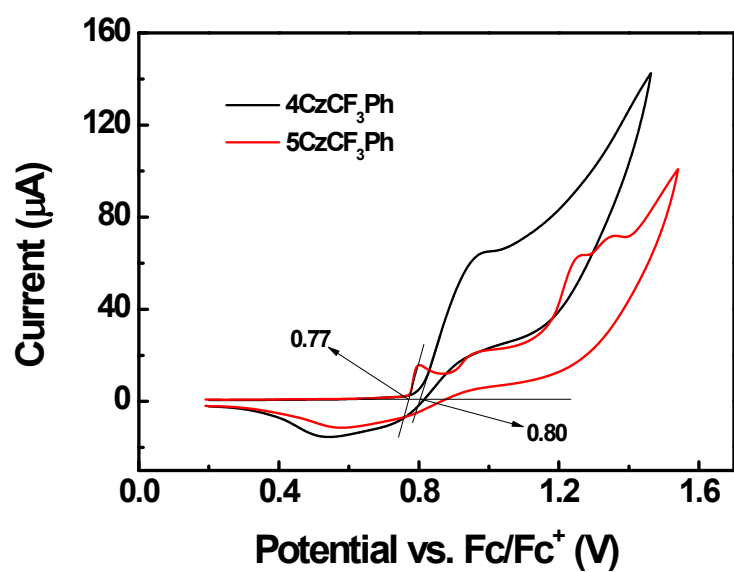


Fig. S3 The cyclic voltammograms for $4\text{CzCF}_3\text{Ph}$ and $5\text{CzCF}_3\text{Ph}$ in DCM.

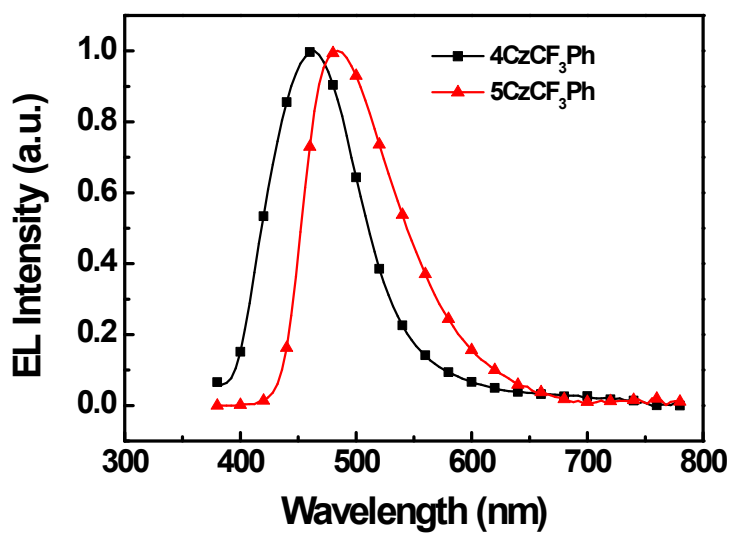


Fig. S4 Normalized electroluminescent (EL) spectra of devices based on $4\text{CzCF}_3\text{Ph}$ and $5\text{CzCF}_3\text{Ph}$.

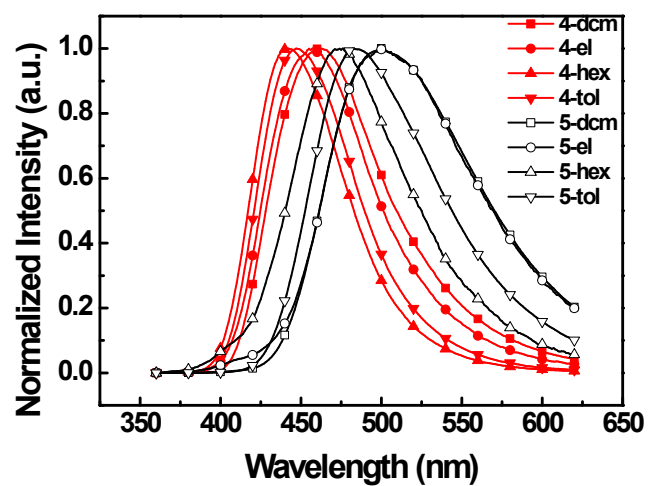


Fig. S5 PL spectra of the TADF emitters in solution with different polarity.(dcm: dichloromethane; el: ethyl alcohol; hex: hexane; tol: toluene)