Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Design principles of carbazole/dibenzothiophene derivatives as host material in modern efficient organic light-emitting diodes

Experimental details

General details: DSC was performed on a TA DSC 2010 unit at a heating rate of 10°C/min under a nitrogen atmosphere. TGA was performed on a TA SDT 2960 instrument at a heating rate of 10°C/min under a nitrogen atmosphere. Photoluminescence spectra were recorded with a luminescence spectrometer (Hitachi spectrophotometer, F-4600); 60 nm organic films were deposited on quartz by thermal vacuum deposition for the PL measurement. During the fluorescence measurement, photoluminescence excitation (PLE) spectrum was first recorded at the maximum of the PL spectrum, then the PL spectrum was measured at the maximum of the excitation spectrum; this process was repeated until the maxima of excitation and emission remained constant. The phosphorescence spectra were measured in frozen 2-methyltetrahydrofuran matrix at 77 K. Because the lifetime of fluorescence is shorter than that of phosphorescence, this is achieved by incorporating a delay between the exciting source and the sample during measurement. UV-Vis absorption spectra were recorded with a PerkinElmer lambda 900 spectrometer. 40 nm thin films were deposited on quartz glass substrate via thermal vacuum deposition for the measurement. The UPS setup used in this work was a KRATOSAXIS ULTRA DLD supplied by KRATOS Analytical. The instrument was incorporated in an ultra-high vacuum chamber at a base pressure of 10^{-9} mbar. The He-I excitation line (21.22 eV) of a He discharge lamp was used as a light source for excitation. 10 nm thin organic films deposited by thermal vacuum on ITO glass were used for UPS investigation.

OLEDs fabrication and measurement: in this work, all organic small molecule materials were deposited by thermal evaporation technique under high vacuum conditions between 4×10^{-6} and 1×10^{-6} mbar. The typical deposition rate for hole-transporting layer, emission layer and electron-transporting layer was 2 Å/s. For hole injection layer and electron injection layer, a low evaporation rate of 0.2-0.3 Å /s was used. The Al electrode was also prepared by thermal evaporation. During Al electrode deposition, a shadow mask was used to define the active area of the OLEDs (3 mm×3 mm= 0.09 cm^2) as well as the shape of the cathode. Thin PEIE film was prepared on ITO glass with a spin coater from Laurell Inc. PEIE (MW=70000g/mol) was dissolved in H_2O with a concentration of 35-40% when received from Sigma-Aldrich, then it was further diluted with 2-methoxyethanol to a weight concentration of 0.4%. The spin coating speed was ramped up to 5000 rpm in increments of 1000 rpm/s over 5 s. After this, the ITO/PEIE substrates were annealed at 100˚C on a hot plate for 10 min in ambient air. The thickness of the PEIE film was estimated to be around 10 nm [33]. Current-voltage-luminance characterizations of OLEDs were performed with a measurement robot. The electrical performance of OLEDs was characterized with an electrical source meter (SMU 2400, Keithley Inc.) which supplied a defined voltage *V* and detected the current *I* through the device. The spectrascan spectroradiometer (PR655, Photo Research Inc.) was used to record the emission spectra under different driving voltage. The external quantum efficiencies were calculated from the brightness, current density, and EL spectra, by assuming a Lambertian distribution.

Synthesis

The synthesis was straightforward with a classic Suzuku-Miyaura reaction and the synthesis route are illustrated in Scheme 1.

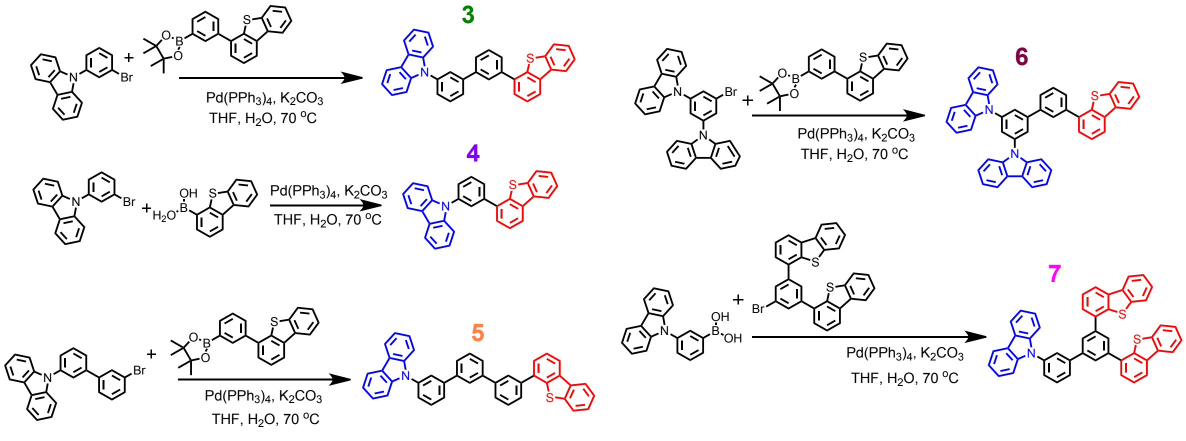
Compound **3**: 4-(3-bromophenyl) dibenzothiophene (1.00 g, 2.95 mmol), (3-(9H-carbazol-9-yl) phenyl) boronic acid (1.11 g, 3.87 mmol) were dissolved in tetrahydrofuran (THF)/2 M K2CO3 (45 ml, 3/1, v/v) in a Schlenk tube under argon, then the resulting mixture was refluxed for 12 h. After cooling to room temperature, the organic layer was collected and annealed to remove the solvent. The crude product was purified via column chromatography on silica gel with dichloromethane/petroleum (1/5, v/v) as eluent, followed by recrystallization from ethyl acetate/petroleum and vacuum sublimation successively. The final product was a white powder (1.10 g, 74.3 %). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 8.14-8.21 (m, 4H), 8.07 (t, J = 1.6 Hz, 1H), 7.92 (t, J = 1.6 Hz, 1H), 7.66-7.85 (m, 5H), 7.40-7.63 (m, 10H), 7.30 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 143.0, 141.5, 141.1, 140.9, 139.7, 138.8, 138.5, 136.8, 136.5, 136.0, 130.7, 130.6, 129.7, 127.9, 127.3, 127.1, 127.0, 126.4, 126.2, 126.0, 125.4, 124.7, 123.6, 122.9, 122.0, 120.9, 120.5, 120.2, 110.1. MS (EI): m/z 501.2 (M+). Anal. calcd for $C_{36}H_{23}NS$ (%): C 86.19, H 4.62, N 2.79; found: C 85.88, H 4.45, N 2.68.

Compound **4**: Dibenzothiophene-4-boronic acid (1.50g, 6.58 mmol), 9-(3-bromophenyl)-9H-carbazole (1.30g, 4.04 mmmol), and tetrakis (triphenylphosphine) palladium (0) 0.17g (5% molar ratio) were dissolved in THF/2 M K_2CO_3 (45 ml, 3/1, v/v) in a Schlenk tube under argon. The resulting mixture was refluxed for 12 h. After cooling to the room temperature, the organic layer was collected and annealed to remove the residual solvent. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum (1/5, v/v) as eluent, followed by recrystallization from ethyl acetate/petroleum and vacuum sublimation successively. The final product was a white powder (1.25 g, 72.9%). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 8.14-8.20 (m, 4H), 7.97 (b, 1H), 7.82-7.87 (m, 2H), 7.75 (t, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.53-7.61 (m, 4H), 7.43-7.50 (m, 4H), 7.32 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 142.7, 141.0, 139.6, 138.6, 138.4, 136.6, 136.1, 135.9, 130.5, 127.5, 127.2, 127.0, 126.7, 126.2, 125.4, 124.7, 123.7, 122.9, 122.0, 121.1, 120.6, 120.3, 110.1. MS (EI): m/z 425.1 (M+). Anal. calcd for $C_{30}H_{19}NS$ (%): C 84.67, H 4.50. N 3.29; found: C 84.34, H 4.42, N 3.28.

Compound **5**: 9-(3'-bromo-[1,1'-biphenyl]-3-yl)-9H-carbazole (1.20 g, 3.01 mmol), 2-(3-(dibenzothiophen-4-yl) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.39 g, 3.60 mmol) were dissolved in THF/2 M K_2CO_3 (45 ml, 3/1, v/v) in a Schlenk tube under argon. The resulting mixture was refluxed for 12 h. After cooling to the room temperature, the organic layer was collected and annealed to remove the residual solvent. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum (1/5, v/v) as eluent, followed by recrystallization from ethyl acetate/petroleum and vacuum sublimation successively. The final product was a white powder (1.05 g, 60.3%). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 8.14-8.20 (m, 4H), 8.04 (s, 1H), 7.95 (s, 1H), 7.88 (s, 1H), 7.53-7.79 (m, 12H), 7.35-7.51 (m, 6H), 7.29 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm):143.2, 142.0, 141.7, 141.4, 141.1, 141.0, 139.7, 138.8, 138.5, 137.0, 136.5, 136.0, 130.5, 129.7, 129.6, 127.6, 127.4, 127.1, 127.0, 126.5, 126.2, 126.0, 125.4, 124.6, 123.6, 122.8, 122.0, 120.8, 120.5, 120.2, 110.0. MS (EI): m/z 577.2 (M+). Anal. calcd for $C_{42}H_{27}NS$ (%): C 87.31, H 4.71, N 2.42; found: C 87.02, H 4.53, N 2.40.19, H 4.62, N 2.79.

Compound **6**: 9,9'-(5-bromo-1,3-phenylene) bis (9H-carbazole) (1.00 g, 2.05 mmol), 2-(3-(dibenzothiophen-4-yl) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.95 g, 2.46 mmol) were dissolved in THF/2 M K_2CO_3 (45 ml, 3/1, v/v) in a Schlenk tube under argon. The resulting mixture was refluxed for 12 h. After cooling to room temperature, the organic layer was collected and annealed to remove the residual solvent. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum (1/5, v/v) as eluent, followed by recrystallization from ethyl acetate/petroleum and vacuum sublimation successively. The final product was a white powder (0.86 g, 62.9%). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 8.16 (d, J = 8.0 Hz, 7H), 8.04 (d, J = 1.6 Hz, 2H), 7.75-7.86 (m, 4H), 7.62-7.67 (m, 5H), 7.54-7.57 (m, 2H), 7.42-7.49 (m, 6H), 7.32 (t, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 144.6, 141.8, 140.8, 140.1, 140.0, 139.6, 138.7, 136.6, 136.5, 135.9, 130.0, 128.5, 127.3, 127.1, 127.0, 126.5, 125.4, 124.7, 124.6, 124.1, 123.9, 122.9, 122.0, 121.0, 120.7, 120.6, 110.0. MS (EI): m/z 666.2 (M+). Anal. calcd for $C_{48}H_{30}N_2S$ (%): C 86.46, H 4.53, N 4.20; found: C 86.11, H 4.24, N 4.12.

Compound **7**: 4,4'-(5-bromo-1,3-phenylene) di-dibenzothiophene (0.5 g, 0.96 mmol), (3-(9H-carbazol-9-yl) phenyl) boronic acid (0.42 g, 1.46 mmol) were dissolved in THF/2 M K_2CO_3 (45 ml, 3/1, v/v) in a Schlenk tube under argon. The resulting mixture was refluxed for 12 h. After cooling to room temperature, the organic layer was collected and annealed to remove the residual solvent. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum (1/5, v/v) as eluent, followed by recrystallization from ethyl acetate/petroleum and vacuum sublimation successively. The final product was a white powder (0.40 g, 61.0%). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 8.10-8.22 (m, 9H), 8.02 (t, J = 1.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80-7.85 (m, 2H), 7.73 (t, J = 8.0 Hz, 1H), 7.51-7.67 (m, 7H), 7.43-7.50 (m, 4H), 7.40 (t, J = 8.4 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 142.8, 142.2, 141.5, 141.0, 139.7, 138.8, 138.7, 136.6, 136.5, 136.0, 130.7, 127.8, 127.3, 127.1, 126.8, 126.5, 126.4, 126.3, 126.1, 125.5, 124.7, 123.7, 122.9, 122.0, 121.1, 120.5, 120.2, 110.1. MS (EI): m/z 683.2 (M+). Anal. calcd for $C_{48}H_{29}NS_2$ (%): C 84.30, H 4.27, N 2.05; found: C 83.98, H 4.01, N 1.98.



Scheme 1. Synthesis of the carbazole/dibenzothiophene derivatives.

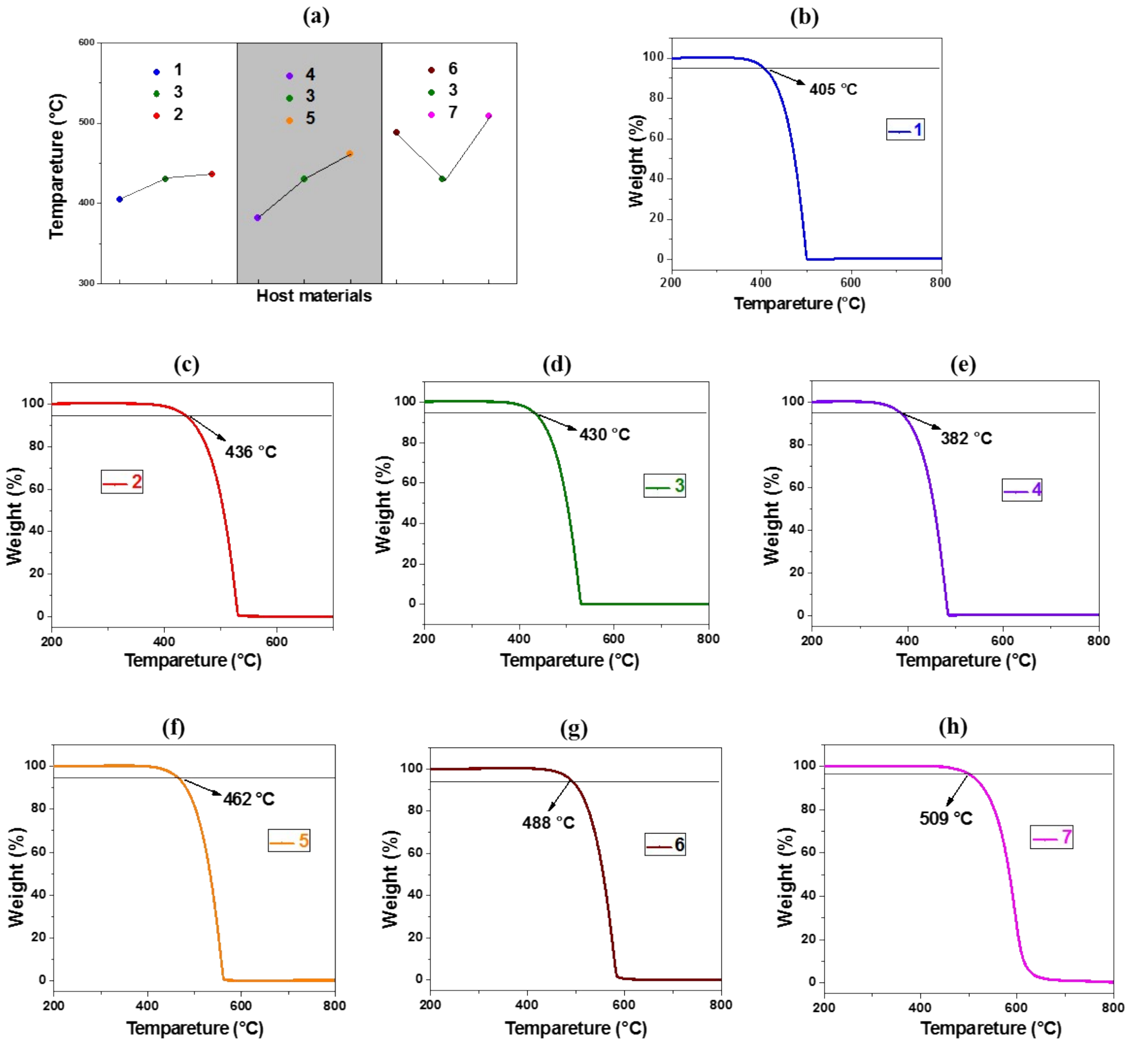


Figure S1. (a) Summary of decomposition temperatures recorded at a heating rate of 10˚C min^{-1}, (b)-(h): thermogravimetric analysis of compounds **1-7**, respectively.

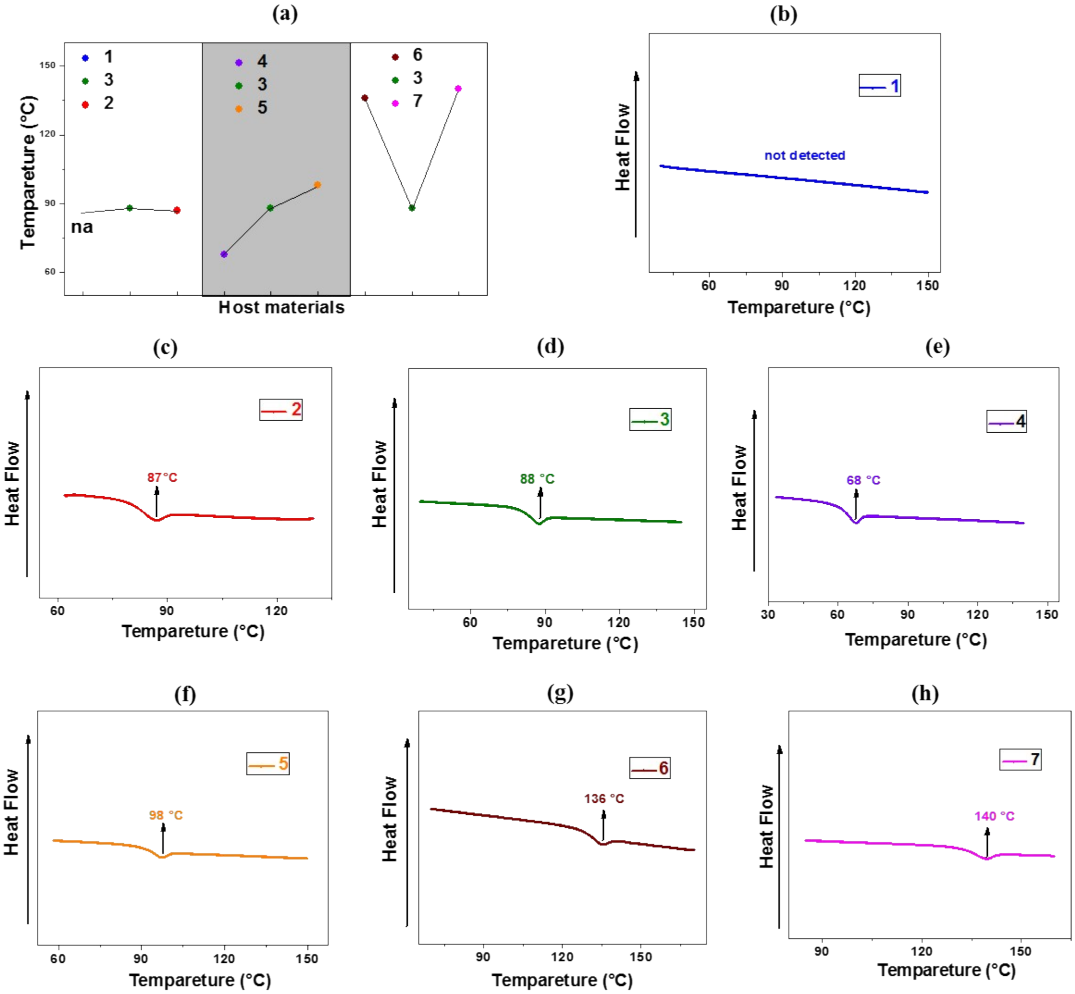


Figure S2. Summary of glass transition temperatures recorded at a heating rate of 10˚C min^{-1}; (b)-(h): differential scanning calorimetry curves of compounds **1-7**, respectively.

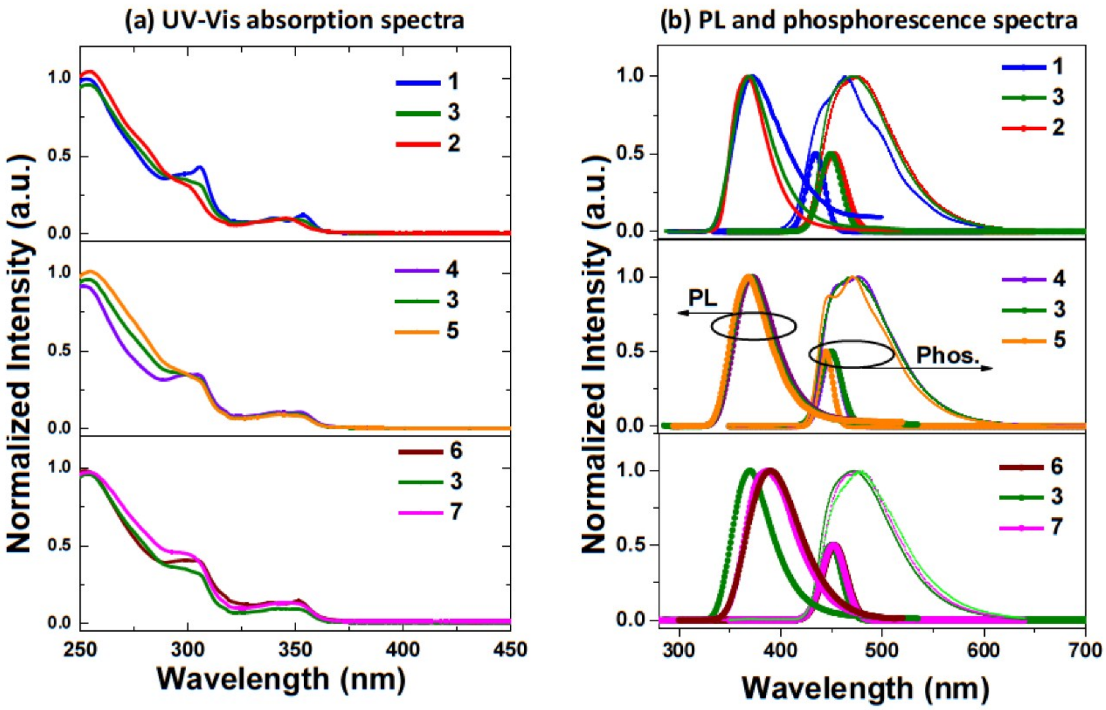


Figure S3. (a) Ultraviolet and visible absorption spectra of the host materials; (b) photoluminescence and phosphorescence spectra which were measured in frozen 2-MeTHF matrix at 77 K.

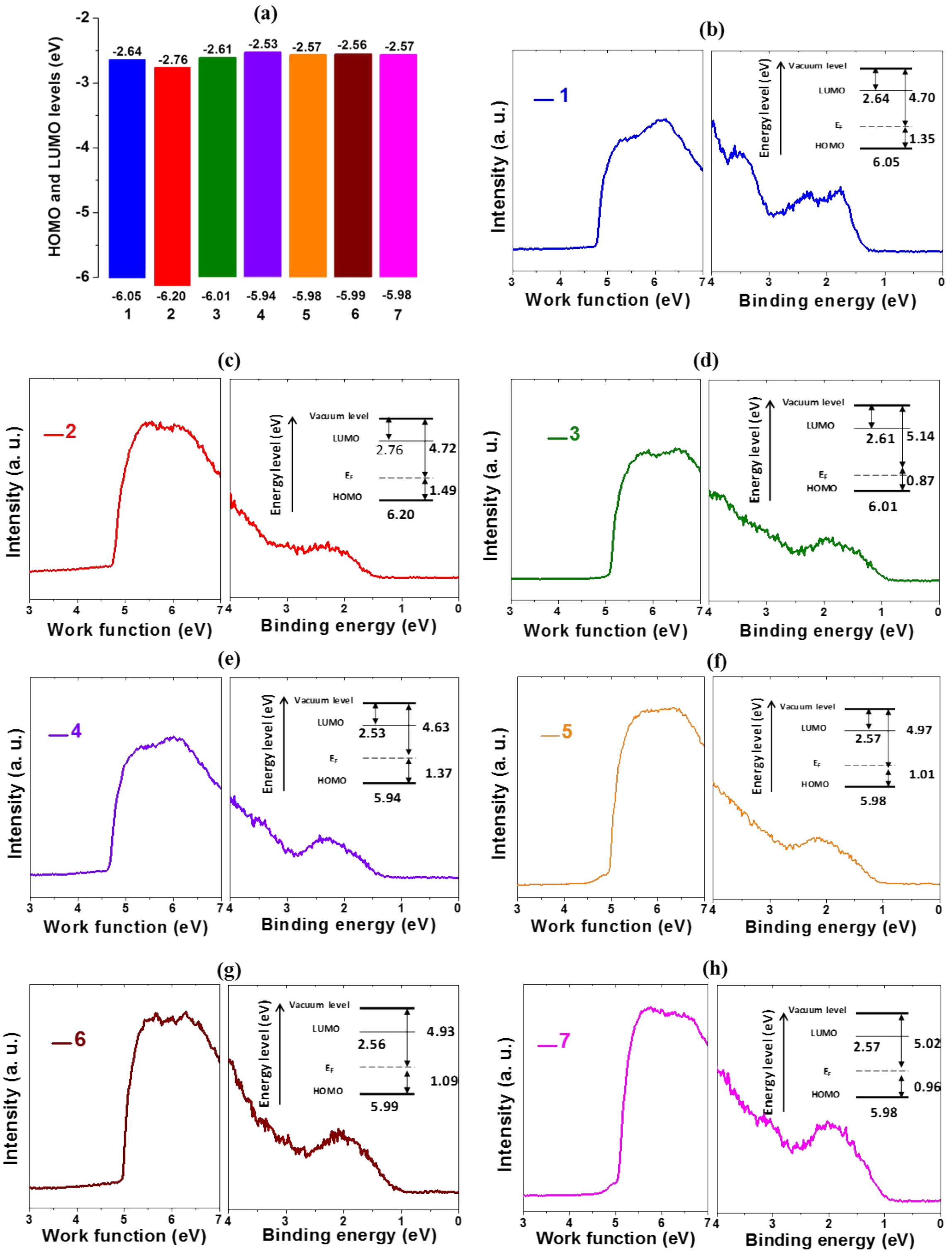


Figure S4. (a): Summary of energy levels, and (b)-(h): ultraviolet photoelectron spectroscopy spectra of compounds **1-7**, respectively.

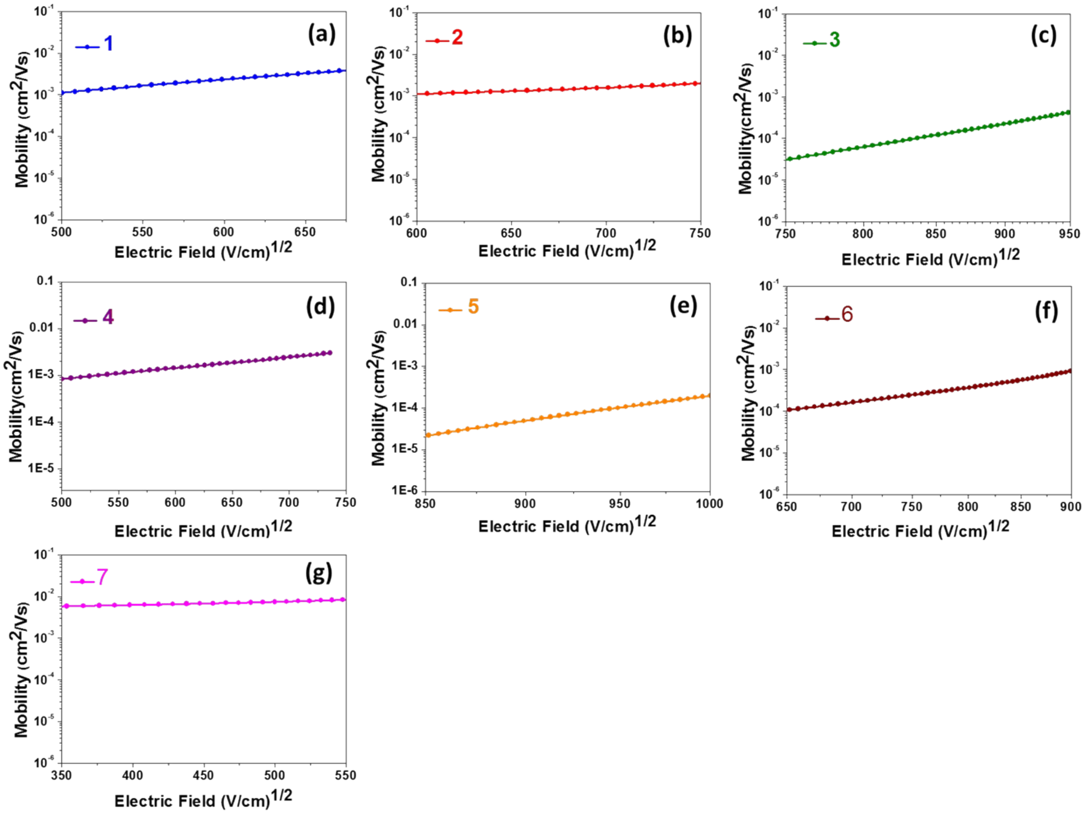


Figure S5. (a)-(g) Hole mobility-square root of electric field curves of compounds 1-7, respectively. Note: The hole-only device structure was ITO/MoO3/host/MoO3/Al.

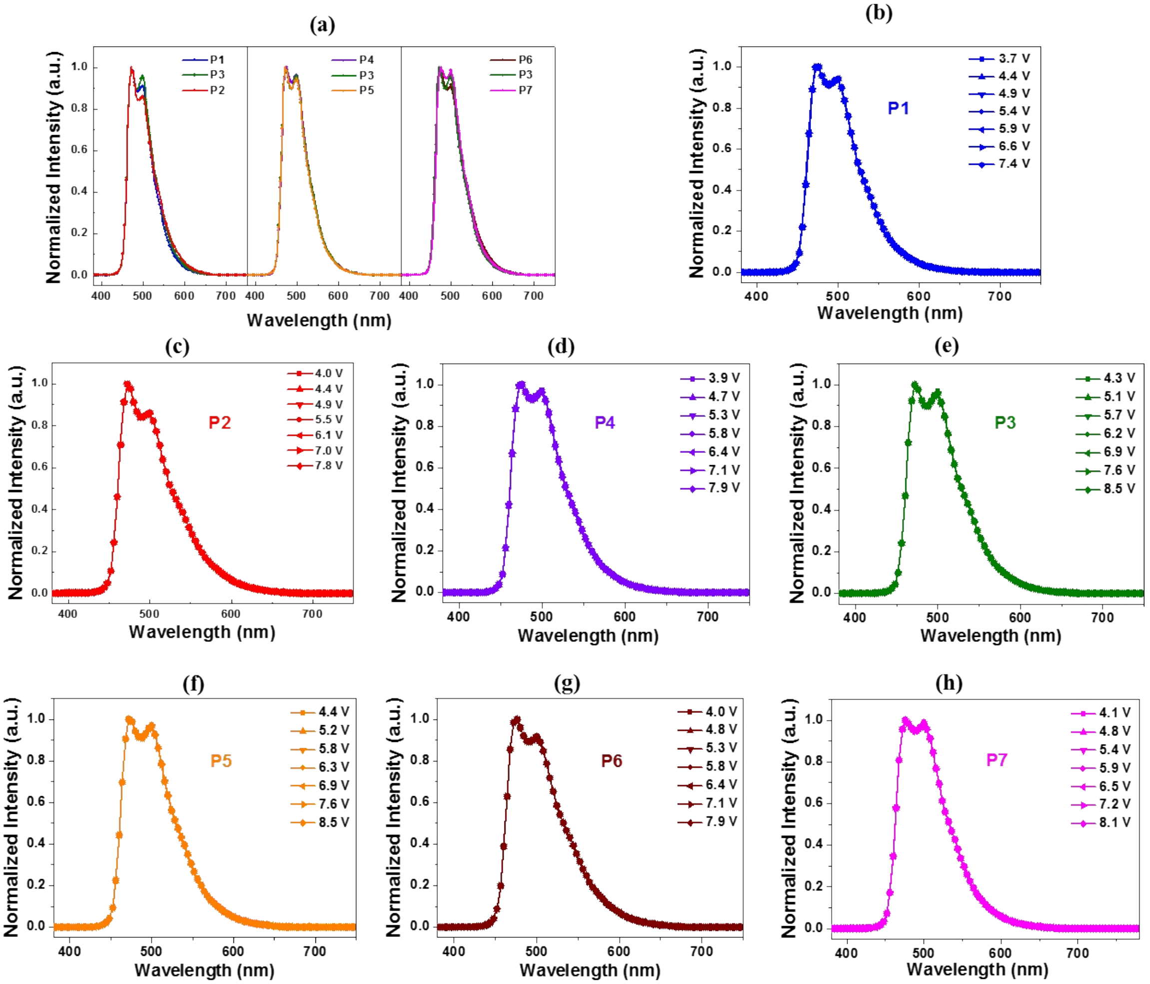


Figure S6. (a) Normalized electroluminescence spectra of PhOLEDs at 5 mA/cm^2; (b)-(h) normalized electroluminescence spectra of PhOLEDs at varied driving voltage (P1-P7, respectively).

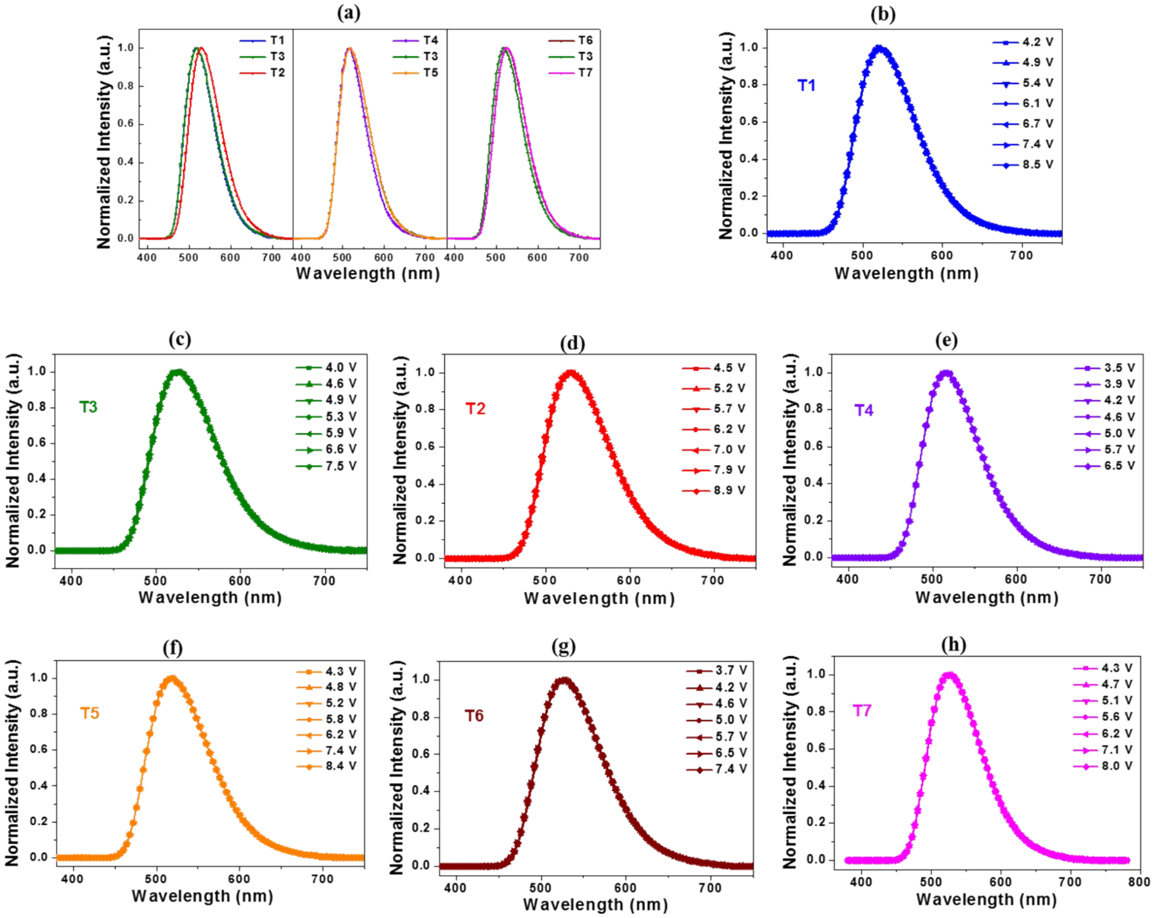


Figure S7. (a) Normalized electroluminescence spectra of TADF OLEDs at 5 mA/cm^2; (b)-(h) normalized electroluminescence spectra of TADF OLEDs at varied driving voltage (T1-T7, respectively).

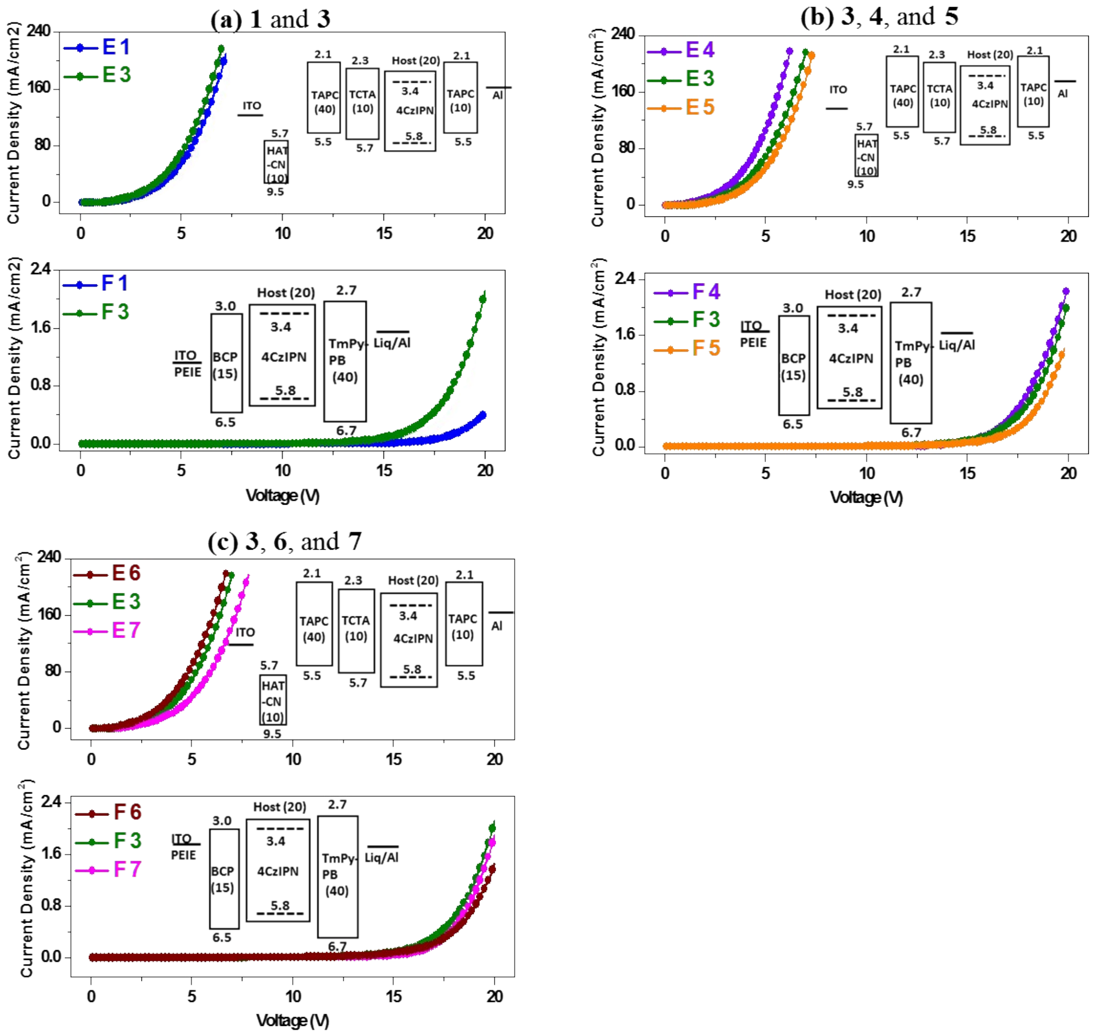


Figure S8. Current density-voltage characteristics of single-carrier-only (host:4CzIPN) devices. The hole-only device structure was ITO/MoO$_3$ (3.5 nm)/TAPC (40 nm)/host:4CzIPN (6 wt%, 20 nm)/TAPC (10 nm)/Al (120 nm) and the electron-only device structure was ITO/PEIE/BCP (15 nm)/host:4CzIPN (6 wt%, 20 nm)/TmPyPB (40 nm)/Liq (2.5 nm)/Al (120 nm). Note: For compound **2**, the low-lying HOMO level (6.2 eV) hindered the hole injection from the hole-transporting layer to the emitting layer due to the high energy barrier in the PhOLEDs, thus greatly reducing the device efficiencies, so E2 and F2 are not shown in Figure.