

Supplementary Information for

Cohosts with efficient host-to-emitter energy transfer for stable blue phosphorescent organic light-emitting diodes

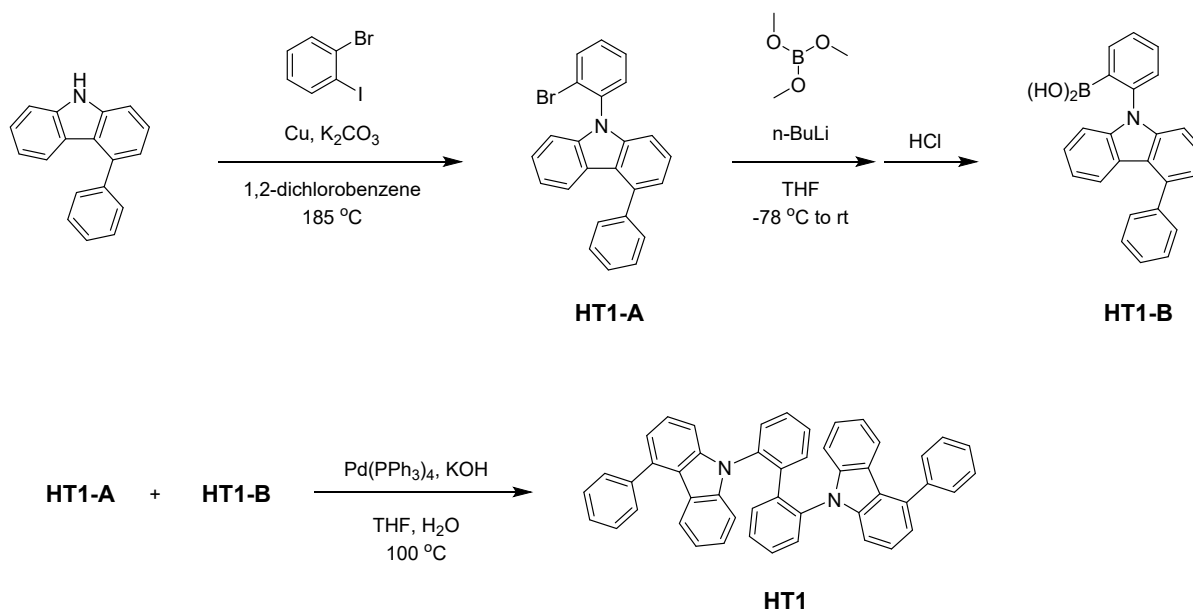
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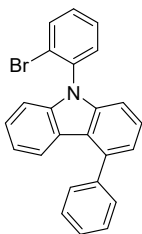
1. Synthesis and characterization of component hosts

¹H NMR and ¹³C NMR spectra were recorded on a Bruker ASCEND 500 at 500 MHz using CD₂Cl₂ and Acetone-d₆ as the solvent. The LCMS-IT-TOF was recorded using a Shimadzu spectrometer. The Ultraviolet–Visible (UV-Vis) spectra was obtained by means of a Varian model UV-Vis-NIR spectrophotometer 5000 and the fluorescence spectra were measured on a HITACHI F7000 spectrometer for the solution states. The UV-Vis absorption and solution PL emission spectra of host materials were obtained from dilute tetrahydrofuran solution (1×10^{-5} M), while the triplet energy values of the host materials were obtained from the photoluminescence spectra at 77 K using liquid nitrogen. The differential scanning calorimeter (DSC) measurements was performed on a TA Instruments Q2000 under nitrogen at a heating rate of 10 °C min⁻¹ from room temperature to 400 °C to to measure the glass transition temperature (T_g). Thermogravimetric-differential thermal analyzer (TG-DTA) were done on a TA Instruments Q5000 under flowing nitrogen at a heating rate of 10 °C min⁻¹ from room temperature to 600 °C at 1,013 Pa and measured with NETZSCH TG-DTA 2000 SE-HV from room temperature to 500 °C at 10 Pa.



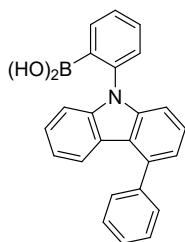
Scheme S1. Synthetic route of **HT1** host

9-(2-bromophenyl)-4-phenyl-9H-carbazole (**HT1-A**)



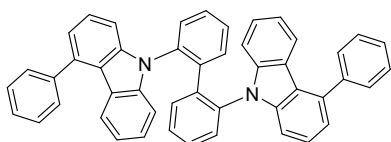
4-phenyl-9H-carbazole (20.0 g, 82.2 mmol), 1-bromo-2-iodobenzene (30.2 g, 106 mmol), potassium carbonate (K_2CO_3 , 45.4 g, 329 mmol) and Cu powder (13.1 g, 206 mmol) were dissolved in anhydrous o-dichlorobenzene (330 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h at 185 °C. After allowing it to cool to ambient temperature, the reaction mixture was filtered and washed with dichloromethane. The organic layer was evaporated with a rotary evaporator. The crude product was purified by column chromatography by dichloromethane/n-hexane (1/5) and the dried under vacuum to give **HT1-A** (19.5 g, 60 % yield).

(2-(4-phenyl-9H-carbazol-9-yl)phenyl)boronic acid (HT1-B)



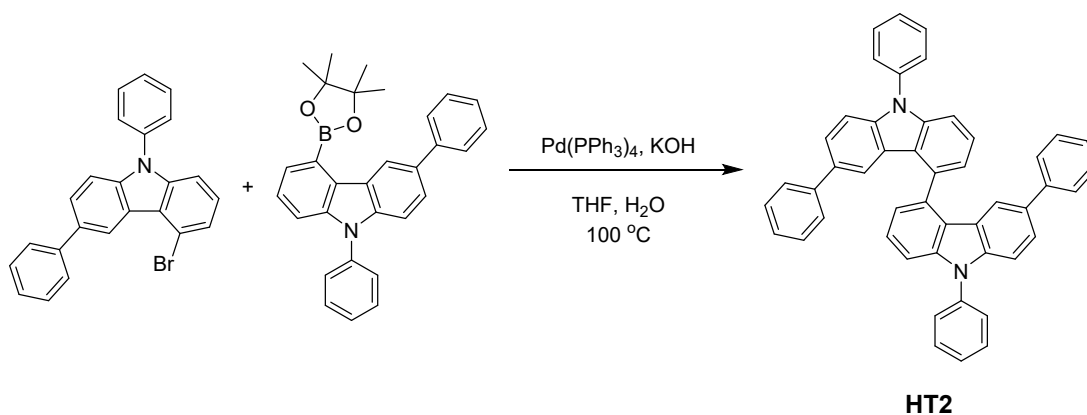
To a stirred solution of 9-(2-bromophenyl)-4-phenyl-9H-carbazole (**HT1-A**) (11.0g, 27.6 mmol) in anhydrous tetrahydrofuran (THF, 115 mL) was slowly added *n*-BuLi (20.7 mL, 1.6 M in hexane solution, 0.33.1 mmol) at -78°C. After stirring for 90 min at -78°C, trimethyl borate (6.16 mL, 104 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 20 h. The reaction mixture was quenched with 3M HCl solution (200 mL) and stirred for additional 1 h. The mixture was diluted with ethyl acetate, and washed with water. The organic layer was dried over anhydrous MgSO₄ and evaporated with a rotary evaporator. To the residue was added *n*-hexane and precipitate was collected to yield 7.0 g (70% yield) of (**HT1-B**).

2,2'-bis(4-phenyl-9H-carbazol-9-yl)-1,1'-biphenyl (HT1)



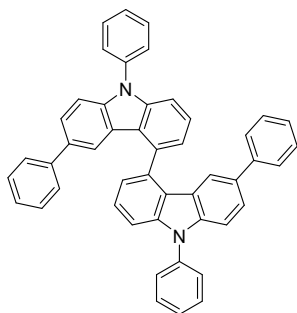
A mixture of 9-(2-bromophenyl)-4-phenyl-9H-carbazole (**HT1-A**) (3.80 g, 10.5 mmol), (2-(4-phenyl-9H-carbazol-9-yl)phenyl)boronic acid (**HT1-B**) (4.58 g, 11.5 mmol), potassium hydroxide (KOH, 4.70 g, 56.1 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 2.42 g, 2.09 mmol, 20 mol %) in tetrahydrofuran (THF, 50 mL) and water (50 mL) was refluxed for 24 h. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/*n*-hexane (1/4), and 3.30 g (50% yield) of 2,2'-bis(4-

phenyl-9H-carbazol-9-yl)-1,1'-biphenyl (**HT1**) was obtained a white solid. ^1H NMR (500 MHz, CD_2Cl_2): δ 8.01 (br. d, J = 7.0 Hz, 2H), 7.64 (td, J = 7.7, 1.2 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.32~7.44 (overlapped m, 14H), 7.07 (d, J = 7.8 Hz, 2H), 6.80~7.20 (br. m, 8H), 5.9~6.1 (br. m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 142.0 (br), 141.1 (br), 138.7, 138.5, 136.6, 134.5, 129.7, 129.1 (br), 128.9, 128.8, 127.8, 127.3, 125.5, 123.9, 123.6, 120.2 (br), 120.0(br), 119.3, 110.7 (br), 108.4 (br); LCMS-IT-TOF: 637.27 [(M + H) $^+$]. Anal. Calcd. for $\text{C}_{48}\text{H}_{32}\text{N}_2$: C, 90.54; H, 5.07; N, 4.40. Found : C, 90.4; H, 5.1; N, 4.5



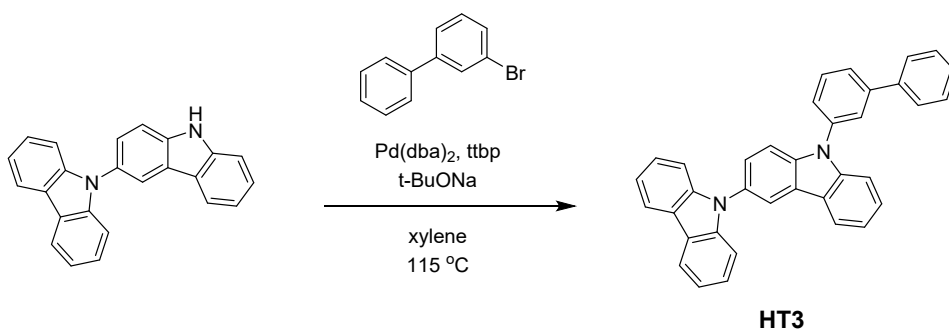
Scheme S2. Synthetic route of **HT2** host

6,6',9,9'-tetraphenyl-9H,9'H-4,4'-bicarbazole (**HT2**)



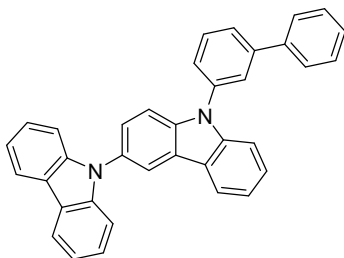
A mixture of 5-bromo-3,9-diphenyl-9H-carbazole (8.29 g, 20.8 mmol), 3,9-diphenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (12.05 g, 27.1 mmol), potassium hydroxide (KOH, 9.34 g, 166.46 mmol) and

tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, 2.40 g, 2.1 mmol, 10 mol %) in tetrahydrofuran (THF, 52 mL) and water(52 mL) was refluxed for 24 h. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane (1/2), and 7.2 g (54 % yield) of 6,6',9,9'-tetraphenyl-9H,9'H-4,4'-bicarbazole (**HT2**) was obtained a white solid. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.69~7.74 (overlapped m, 8H), 7.56~7.65 (overlapped m, 6H), 7.47~7.49 (overlapped m, 4H), 7.42 (d, $J = 8.6$ Hz, 2H), 7.20~7.23 (m, 4H), 7.15~7.18 (m, 2H), 7.06 (d, $J = 1.4$ Hz, 2H), 6.99~7.02 (m, 4H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 142.2, 142.1, 141.3, 138.2, 136.4, 133.1, 130.6, 129.0, 128.3, 127.9, 127.2, 126.9, 126.7, 125.5, 124.1, 122.2, 122.0, 121.3, 110.2, 110.0; LCMS-IT-TOF: 637.27 [(M + H) $^+$]. Anal. Calcd. for $\text{C}_{48}\text{H}_{32}\text{N}_2$: C, 90.54; H, 5.07; N, 4.40. Found : C, 90.5; H, 5.1; N, 4.4

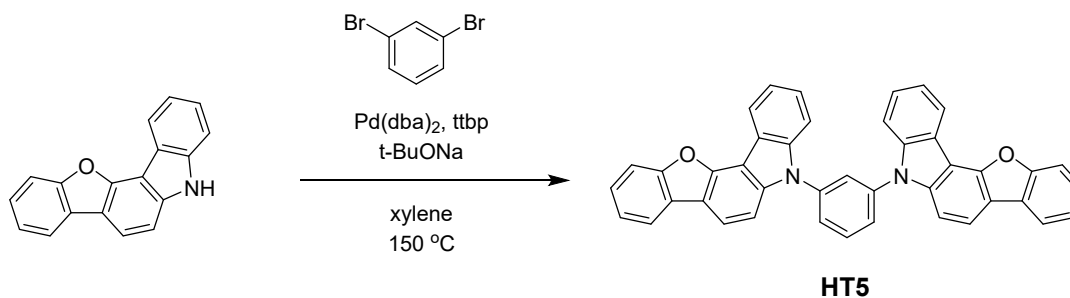


Scheme S3. Synthetic route of **HT3** host

9-([1,1'-biphenyl]-3-yl)-9H-3,9'-bicarbazole (**HT3**)

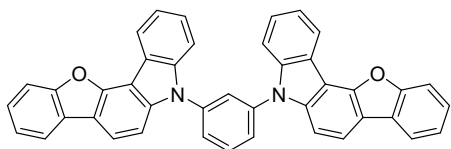


A mixture of 9H-3,9'-bicarbazole (13.0 g, 40.3 mmol), 3-bromo-1,1'-biphenyl (9.07 mL, 48.4 mmol), sodium-tert-butoxide (t-BuONa, 7.75 g, 80.7 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd(dba)₂, 2.32 g, 4.03 mmol, 10 mol %) and tri-tert-butylphosphine (TTBP, 4.04 mL, 50% in xylene solution, 8.06 mmol, 20 mol%) in 130 mL of anhydrous xylene was refluxed under nitrogen for 18 h. After cooling to ambient temperature, the solvents were evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane eluent (1/4) and recrystallized from dichloromethane/n-hexane was obtained. (14.2 g, 73 % yield); ¹H NMR (500 MHz, Acetone-d₆): δ 8.47 (d, *J* = 1.1 Hz, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.25 (dt, *J* = 7.8, 0.8 Hz, 2H), 8.03 (t, *J* = 1.8 Hz, 1H), 7.91 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.84~7.88 (overlapped m, 3H), 7.74~7.78 (overlapped m, 2H), 7.64 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.51~7.55 (overlapped m, 3H), 7.40~7.45 (overlapped m, 5H), 7.36 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 7.29 (ddd, *J* = 7.9, 6.3, 1.8 Hz, 2H); ¹³C NMR (126 MHz, Acetone-d₆): δ 144.1, 142.7, 142.5, 140.9, 140.8, 138.9, 131.7, 130.9, 130.0, 128.9, 128.0, 127.9, 127.4, 126.9, 126.8, 126.4, 126.3, 125.4, 124.0, 124.0, 121.9, 121.4, 121.2, 120.6, 120.4, 112.0, 111.1, 110.7; LCMS-IT-TOF: 485.19 [(M + H)⁺]. Anal. Calcd. for C₃₆H₂₄N₂: C, 89.23; H, 4.99; N, 5.78. Found : C, 88.7; H, 5.0; N, 5.8

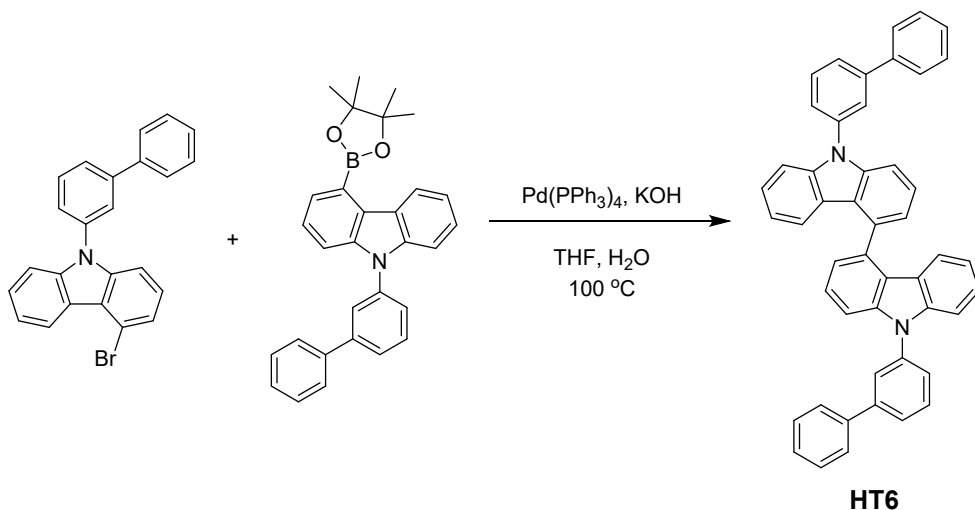


Scheme S4. Synthetic route of **HT5** host

1,3-bis(5H-benzofuro[3,2-c]carbazol-5-yl)benzene (HT5)

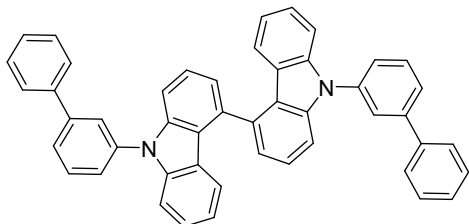


A mixture of 5*H*-benzofuro[3,4-*c*]carbazole (16.39 g, 63.7 mmol), 1,3-dibromobenzene (6.01 g, 25.5 mmol), sodium-*tert*-butoxide (t-BuONa, 9.80 g, 101.9 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd(dba)₂, 1.47 g, 2.6 mmol, 10 mol%) and tri-*tert*-butylphosphine (TTBP, 2.06 g, 50% in xylene solution, 5.1 mmol, 20 mol%) in 160 mL of anhydrous *o*-xylene was refluxed under nitrogen for 18 h. After allowing it to cool to ambient temperature, to the reaction mixture was added methanol (1.5 L) and the precipitate was collected. The resulting solid was dissolved in hot toluene (1.0 L) and filtered through silica gel pad and evaporated with a rotary evaporator. The product was purified by recrystallized from toluene was obtained. (7.10 g, 47 % yield); ¹H NMR (500 MHz, CD₂Cl₂): δ 8.56 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.02 (dd, *J* = 7.5, 0.7 Hz, 2H), 7.96~7.99 (overlapped m, 1+1H), 7.85 (dd, *J* = 7.8, 2.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.54 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.44~7.49 (m, 4H), 7.41 (td, *J* = 7.6, 0.9 Hz, 2H); ¹³C NMR (126 MHz, CD₂Cl₂): δ 156.9, 151.7, 141.8, 141.0, 139.9, 132.1, 127.2, 126.6, 126.4, 126.1, 125.5, 123.6, 123.2, 121.7, 121.6, 120.4, 118.8, 117.4, 112.2, 110.4, 109.4, 160.1; LCMS-IT-TOF: 589.18 [(*M* + *H*)⁺]. Anal. Calcd. for C₄₂H₂₄N₂O₂: C, 85.70; H, 4.11; N, 4.76; O, 5.44. Found : C, 85.0; H, 4.1; N, 4.8; O, 5.7



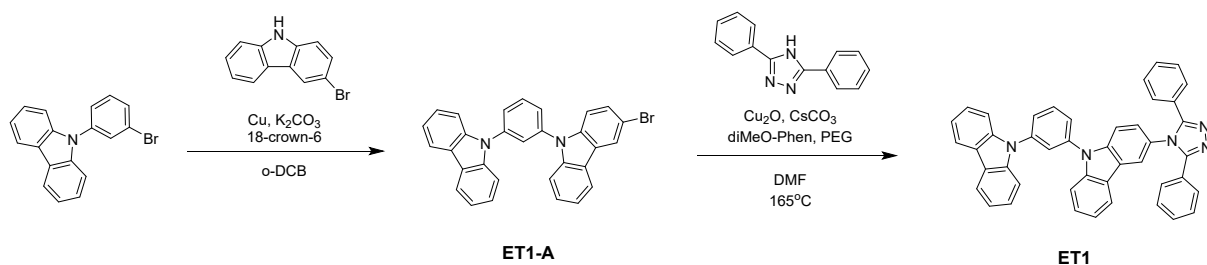
Scheme S5. Synthetic route of **HT6** host

9,9'-di([1,1'-biphenyl]-3-yl)-9H,9'H-4,4'-bicarbazole (HT6)



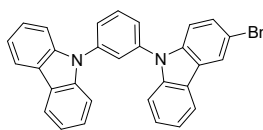
A mixture of 9-([1,1'-biphenyl]-3-yl)-4-bromo-9H-carbazole (8.29 g, 20.8 mmol), 9-([1,1'-biphenyl]-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (12.05 g, 27.1 mmol), potassium hydroxide (KOH, 9.34 g, 166.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 2.40 g, 2.1 mmol, 10 mol %) in tetrahydrofuran (THF, 52 mL) and water(52 mL) was refluxed for 24 h. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane (1/2), and 7.2 g (54 % yield) of 9,9'-di([1,1'-biphenyl]-3-yl)-9H,9'H-4,4'-bicarbazole (**HT6**) was obtained a white solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.94 (br. s, 2H), 7.72~7.81 (m, 8H), 7.66~7.71 (br. d, 2H), 7.65 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.61 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 4H), 7.40~7.45 (overlapped m, 2+2H), 7.37 (dd, *J* = 7.0, 1.1 Hz, 2H), 7.26 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.81 (td, *J* = 8.0, 0.8 Hz, 2H); ¹³C NMR (126 MHz, CD₂Cl₂): δ 143.7, 141.9, 141.7, 140.7, 138.8, 136.4, 131.0, 129.5, 128.4, 127.7, 126.8, 126.7, 126.5, 126.5, 126.3, 123.7, 122.6, 122.0, 121.9, 120.2, 110.1, 109.7; LCMS-IT-TOF: 637.26 [(M + H)⁺]. Anal. Calcd. for C₄₈H₃₂N₂: C, 90.54; H, 5.07; N, 4.40. Found : C, 90.1; H, 5.1; N,

4.4



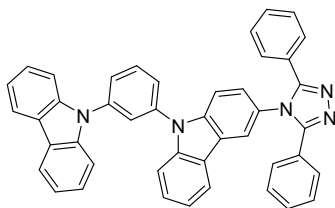
Scheme S6. Synthetic route of **ET1** host

9-(3-(9H-Carbazol-9-yl)phenyl)-3-bromo-9H-carbazole (ET1-A)



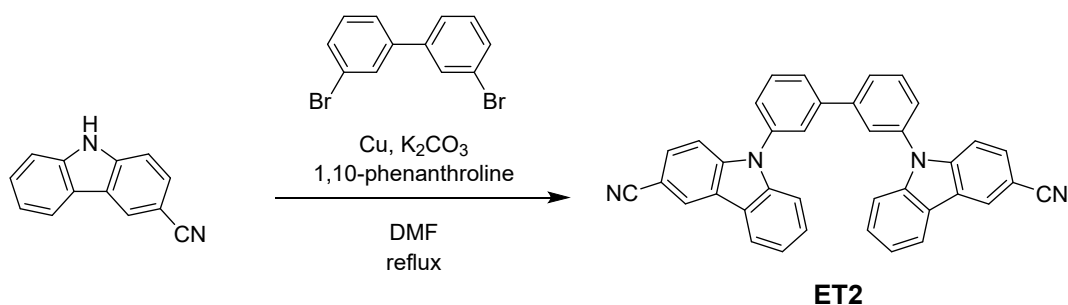
9-(3-Bromophenyl)-9Hcarbazole (0.31 g, 1.0 mmol), 3-bromo-9H-carbazole (0.20 g, 0.8 mmol), potassium carbonate (K_2CO_3 , 0.44 g, 3.3 mmol), Cu powder (0.1 g, 1.6 mmol) and dibenzo 18-crown-6 (0.02 g, 0.1 mmol) were dissolved in anhydrous o-dichlorobenzene (o-DCB) under nitrogen atmosphere. The reaction mixture was stirred for 12 h at 100 °C. The mixture was diluted with dichloromethane and washed with distilled water (100 mL) three times. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product, which was purified by column chromatography by n-hexane. The final white powdery product was obtained in 90% yield.

9-(3-(9H-Carbazol-9-yl)phenyl)-3-(3,5-diphenyl-4H-1,2,4-triazol-4-yl)-9H-carbazole (ET1)



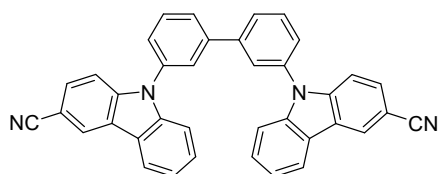
3,5-Diphenyl-4H-1,2,4-triazole (11.80g, 53.3 mmol), 9-(3-(9H-carbazol-9-yl)phenyl)-3-bromo-9H-carbazole (**ET1-A**) (20.00g, 41.0 mmol), 4,7-dimethoxy-1,10-phenanthroline (1.48 g, 6.2 mmol), cesium carbonate ($CsCO_3$, 18.72 g, 57.5

mmol), polyethylene glycol (PEG, 10.00 g, 20.5 mmol) and copper(I) oxide (Cu_2O , 0.294 g, 2.05 mmol, 5mol%) were dissolved in *N,N*-dimethylformamide (DMF, 140 mL) under argon atmosphere. The reaction mixture was stirred and refluxed for 24 h at 165 °C. After allowing it to cool to room temperature, the reaction mixture was diluted with MeOH (500 mL) and collected by filtration then dried under vacuum at 60°C. The resulting yellow solid was dissolved in hot toluene and filtered through silica gel pad and evaporated with a rotary evaporator. The crude product was purified by column chromatography by ethyl acetate/*n*-hexane (1/3) then the product was recrystallized from methylene chloride/*n*-hexane and finally dried under vacuum to give 9-(3-(9H-carbazol-9-yl)phenyl)-3-(3,5-diphenyl-4H-1,2,4-triazol-4-yl)-9H-carbazole (**ET1**) as a yellow crystal in 13 g (50 %) yield. ^1H NMR (500 MHz, CD_2Cl_2): δ 8.23~8.26 (overlapped m, 3H), 8.17 (d, $J = 7.7$ Hz, 2H), 8.11 (d, $J = 7.7$ Hz, 1H), 7.92 (t, $J = 8.0$ Hz, 1H), 7.87 (t, $J = 2.0$ Hz, 1H), 7.75~7.79 (m, 2H), 7.55~7.64 (m, 6H), 7.42~7.54 (m, 7H), 7.29~7.40 (m, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 162.0, 155.5, 142.1, 141.2, 140.9, 140.0, 139.2, 132.1, 132.0, 131.8, 130.3, 129.8, 129.4, 129.2, 129.0, 127.6, 127.0, 126.9, 126.7, 126.5, 125.9, 124.5, 124.4, 124.1, 123.6, 121.4, 121.3, 120.9, 120.9, 118.6, 110.8, 110.7, 110.2; LCMS-IT-TOF: 628.24 [(M + H) $^+$]. Anal. Calcd. for $\text{C}_{44}\text{H}_{29}\text{N}_5$: C, 84.19; H, 4.66; N, 11.16. Found : C, 83.9; H, 4.6; N, 11.2

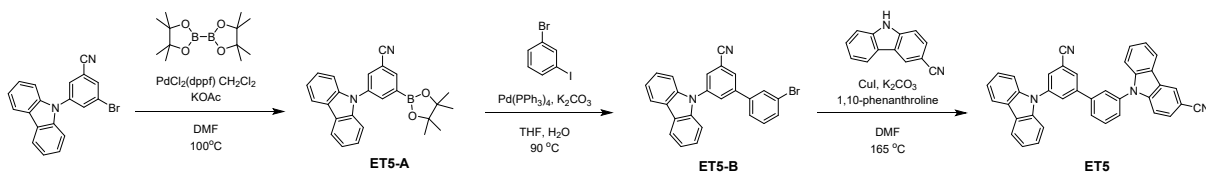


Scheme S7. Synthetic route of **ET2** host

9,9'-([1,1'-biphenyl]-3,3'-diyl)bis(9H-carbazole-3-carbonitrile) (ET2**)**

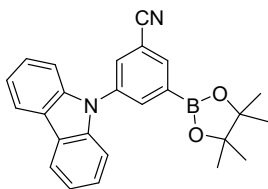


9*H*-carbazole-3-carbonitrile (27.1 g, 141 mmol), 3,3'-dibromo-1,1'-biphenyl (20.0 g, 64.1 mmol), potassium carbonate (K₂CO₃, 44.3 g, 321 mmol), 1,10-phenanthroline (5.78 g, 32.1 mmol) and Cu powder (20.4 g, 321 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (DMF, 140 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 40 h. After allowing it to cool to ambient temperature, to the reaction mixture was added methanol (2.0 L) and the precipitate was collected. The resulting solid was dissolved in hot chloroform (1.5 L) and filtered through silica gel pad and evaporated with a rotary evaporator. The product was purified by recrystallized from *N,N*-dimethylformamide /ethyl acetate was obtained. (18.0 g, 53 % yield); ¹H NMR (500 MHz, CD₂Cl₂): δ 8.48 (d, *J* = 1.5 Hz, 2H), 8.19 (d, *J* = 7.9 Hz, 2H), 7.83~7.85 (overlapped m, 2+2H), 7.76 (t, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.59 (dt, *J* = 7.6, 1.3 Hz, 2H), 7.45~7.52 (overlapped m, 6H), 7.38 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 2H); ¹³C NMR (126 MHz, CD₂Cl₂): δ 143.1, 142.7, 142.2, 137.8, 131.4, 129.8, 128.0, 127.7, 127.2, 126.3, 125.8, 124.1, 122.8, 121.8, 121.2, 120.7, 111.1, 110.9, 103.4; LCMS-IT-TOF: 535.18 [(M + H)⁺]. Anal. Calcd. for C₃₈H₂₂N₄: C, 85.37; H, 4.15; N, 10.48. Found : C, 86.1; H, 4.1; N, 10.5



Scheme S8. Synthetic route of ET5 host

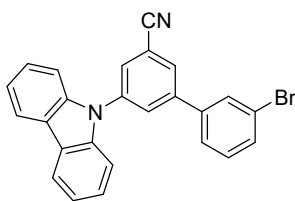
3-(9*H*-carbazol-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (ET5-A)



3-bromo-5-(9*H*-carbazol-9-yl)benzonitrile (15.0g, 43.2 mmol), bis(pinacolato)diboron (13.2 g, 51.8 mmol), potassium

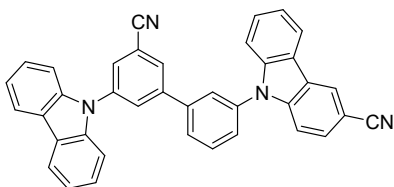
acetate (KOAc, 12.7 g, 130 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) dichloromethane complex ($\text{PdCl}_2(\text{pddf})\text{CH}_2\text{Cl}_2$, 1.76 g, 2.16 mmol, 5 mol%) were dissolved in *N,N*-dimethylformamide (DMF, 150 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 18 h. The mixture was filtered and washed with ethyl acetate. The organic layer was evaporated with a rotary evaporator. The crude product was purified by column chromatography by ethyl acetate/*n*-hexane (1/3) and the dried under vacuum to give 3-(9H-carbazol-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (**ET5-A**) (13.2 g, 77 %).

3'-bromo-5-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (**ET5-B**)

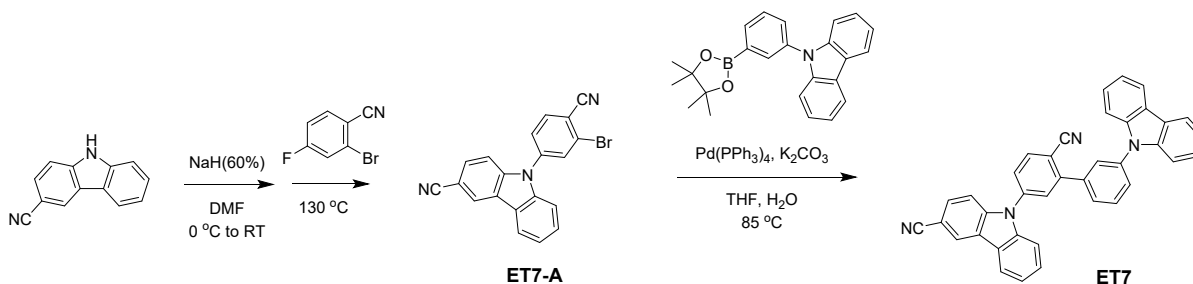


A mixture of 3-(9H-carbazol-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (**ET5-A**) (26.6 g, 67.5 mmol), 1-bromo-3-iodobenzene (12.9 mL, 28.6 mmol), potassium carbonate (K_2CO_3 , 30.0 g, 202 mmol) and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, 11.7 g, 10.1 mmol, 15 mol %) in tetrahydrofuran (THF, 220 mL) and water(110 mL) was refluxed for 18 h. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/*n*-hexane (1/3), and 25.5 g (89 %) of 3'-bromo-5-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (**ET5-B**) was obtained a white solid.

9-(3'-(9H-carbazol-9-yl)-5'-cyano-[1,1'-biphenyl]-3-yl)-9H-carbazole-3-carbonitrile (**ET5**)

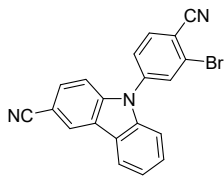


3'-bromo-5-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (**ET5-B**) (15.0 g, 35.4 mmol), 9H-carbazole-3-carbonitrile (10.2 g, 53.2 mmol), potassium carbonate (K_2CO_3 , 19.6 g, 142 mmol), 1,10-phenanthroline (2.55 g, 14.2 mmol) and copper iodide (CuI, 1.35 g, 7.09 mmol, 20 mol%) were dissolved in anhydrous *N,N*-dimethylformamide (DMF, 70 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h. After allowing it to cool to ambient temperature, to the reaction mixture was added methanol/water (800 mL/400 mL) and the precipitate was collected. The resulting solid was dissolved in hot dichloromethane (500 mL) and filtered through silica gel pad and evaporated with a rotary evaporator. The crude product was purified by column chromatography by dichloromethane/*n*-hexane (1/1) and the dried under vacuum to give **ET5** (12.2 g, 64 %). 1H NMR (500 MHz, CD_2Cl_2): δ 8.49 (d, J = 1.1 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.7 Hz, 2H), 8.14 (t, J = 1.8 Hz, 1H), 8.04 (t, J = 1.6 Hz, 1H), 7.94 (t, J = 1.7 Hz, 1H), 7.67~7.84 (overlapped m, 3H), 7.64~7.69 (overlapped m, 1+1 H), 7.43~7.54 (overlapped m, 7H), 7.40 (ddd, J = 8.9, 7.9, 1.0 Hz, 1H), 7.34 (ddd, J = 7.9, 6.8, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.8, 143.1, 142.1, 140.9, 140.9, 140.1, 138.1, 131.8, 130.6, 130.0, 129.9, 128.0, 127.7, 126.9, 126.3, 125.9, 124.3, 124.2, 122.9, 122.0, 121.4, 121.3, 121.1, 120.7, 118.3, 115.5, 111.0, 110.8, 109.9, 103.6; LCMS-IT-TOF: 535.18 [(M + H) $^+$]. Anal. Calcd. for $C_{38}H_{22}N_4$: C, 85.37; H, 4.15; N, 10.48. Found : C, 84.9; H, 4.1; N, 10.5



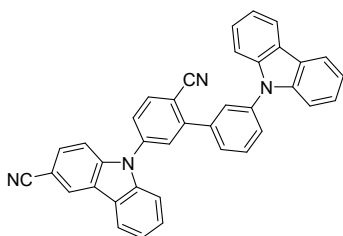
Scheme S9. Synthetic route of **ET7** host

9-(3-bromo-4-cyanophenyl)-9H-carbazole-3-carbonitrile (ET7-A)



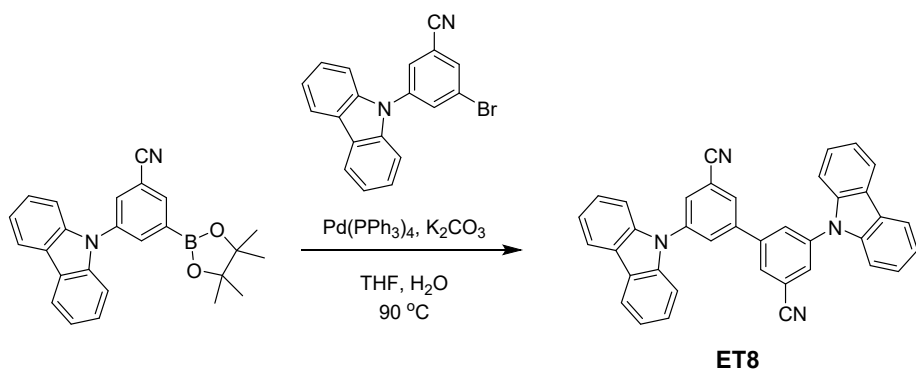
To a stirred solution of 9*H*-carbazole-3-carbonitrile (8.52 g, 44.3 mmol) in anhydrous *N,N*-dimethylformamide (DMF, 180 mL) was slowly added sodium hydride (NaH, 1.77 g, 60% dispersion in mineral oil, 44.3 mmol) at 0°C. The reaction mixture was allowed to warm up to room temperature. After stirring for 20 min at room temperature, 2-bromo-4-fluorobenzonitrile (9.75 g, 48.8 mmol) was added. The reaction mixture was stirred and refluxed for 18 h at 130 °C. The reaction mixture was quenched with ice water (100 mL) at 0 °C and collected by filtration. The resulting solid was dissolved in hot dichloromethane (700 mL) and filtered through silica gel pad and evaporated with a rotary evaporator. The product was purified by recrystallized from dichloromethane / methanol was obtained. (10.0 g, 61 % yield)

9-(3'-(9*H*-carbazole-9-yl)-6-cyano-[1,1'-biphenyl]-3-yl)-9*H*-carbazole-3-carbonitrile (ET7)



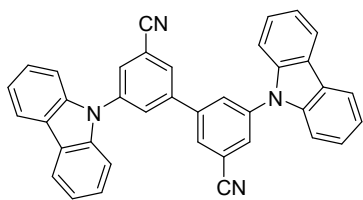
9-(3-bromo-4-cyanophenyl)-9*H*-carbazole-3-carbonitrile (**ET7-A**) (10.10 g, 27.1 mmol), 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (20.03 g, 54.3 mmol), potassium carbonate (K₂CO₃, 7.50 g, 54.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 3.13 g, 2.7 mmol, 10 mol %) in tetrahydrofuran (THF, 68 mL) and water (27 mL) was refluxed for 18 h. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/*n*-hexane (3/1), and 9.50 g (66 % yield) of 9-(3'-(9*H*-carbazole-9-yl)-6-cyano-[1,1'-biphenyl]-3-yl)-9*H*-carbazole-3-carbonitrile (**ET7**) was obtained a white solid.

^1H NMR (500 MHz, Acetone- d_6): δ 8.72 (d, J = 1.2 Hz, 1H), 8.38 (d, J = 7.7 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.23 (dt, J = 7.6, 0.9 Hz, 2H), 8.17 (d, J = 2.1 Hz, 1H), 8.05~8.06 (m, 1H), 8.00 (dd, J = 8.3, 2.2 Hz, 1H), 7.89~7.94 (overlapped m, 2H), 7.83 (dt, J = 7.2, 2.1 Hz, 1H), 7.77 (d, J = 1.2 Hz, 2H), 7.66 (d, J = 8.3 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.56 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.41~7.45 (overlapped m, 3H), 7.30 (ddd, J = 7.9, 7.0, 0.9 Hz, 2H); ^{13}C NMR (126 MHz, Acetone- d_6): δ 147.5, 142.9, 141.9, 141.8, 141.6, 140.5, 139.1, 136.9, 131.7, 130.5, 129.5, 128.8, 128.5, 127.7, 127.1, 126.4, 125.1, 124.4, 123.7, 122.9, 122.1, 121.2, 120.5, 118.9, 112.0, 111.5, 111.4, 110.9, 104.6; LCMS-IT-TOF: 535.18 [(M + H) $^+$]. Anal. Calcd. for $\text{C}_{38}\text{H}_{22}\text{N}_4$: C, 85.37; H, 4.15; N, 10.48. Found : C, 84.7; H, 4.1; N, 10.5



Scheme S10. Synthetic route of **ET8** host

5,5'-di(9H-carbazol-9-yl)-[1,1'-biphenyl]-3,3'-dicarbonitrile (**ET8**)



A mixture of 3-(9H-carbazol-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**ET5-A**) (10.0 g, 25.4 mmol), 3-bromo-5-(9H-carbazol-9-yl)benzonitrile (9.69g, 27.9 mmol), potassium carbonate (K_2CO_3 , 10.5 g, 76.1 mmol) and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, 5.86 g, 5.07 mmol, 20 mol %) in tetrahydrofuran (THF, 70 mL) and water(35 mL) was refluxed for 14 h. After allowing it to cool to ambient temperature, the resulting

solid was collected by filtration. The crude product was purified by recrystallized from *N,N*-dimethylformamide was obtained. (11.2 g, 83 % yield); ^1H NMR (500 MHz, CD_2Cl_2): δ 8.16 (overlapped d, $J = 7.8$ Hz, 4H), 8.14 (overlapped t, $J = 1.8$ Hz, 2H), 8.03 (t, $J = 1.5$ Hz, 2H), 8.00 (t, $J = 1.6$ Hz, 2H), 7.43~7.48 (overlapped m, 8H), 7.33 (ddd, $J = 7.9, 6.5, 1.7$ Hz, 4H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 141.4 (br.), 140.5 (br.), 138.1, 138.0, 136.1, 134.0, 129.1, 128.5, 128.4, 128.3, 127.2, 126.7, 125.0, 123.3, 123.0, 119.7(br.), 119.4, 118.7, 110.2, 107.9 (br.); LCMS-IT-TOF: 535.18 [(M + H) $^+$]. Anal. Calcd. for $\text{C}_{38}\text{H}_{22}\text{N}_4$: C, 85.37; H, 4.15; N, 10.48. Found : C, 85.2; H, 4.1; N, 10.5

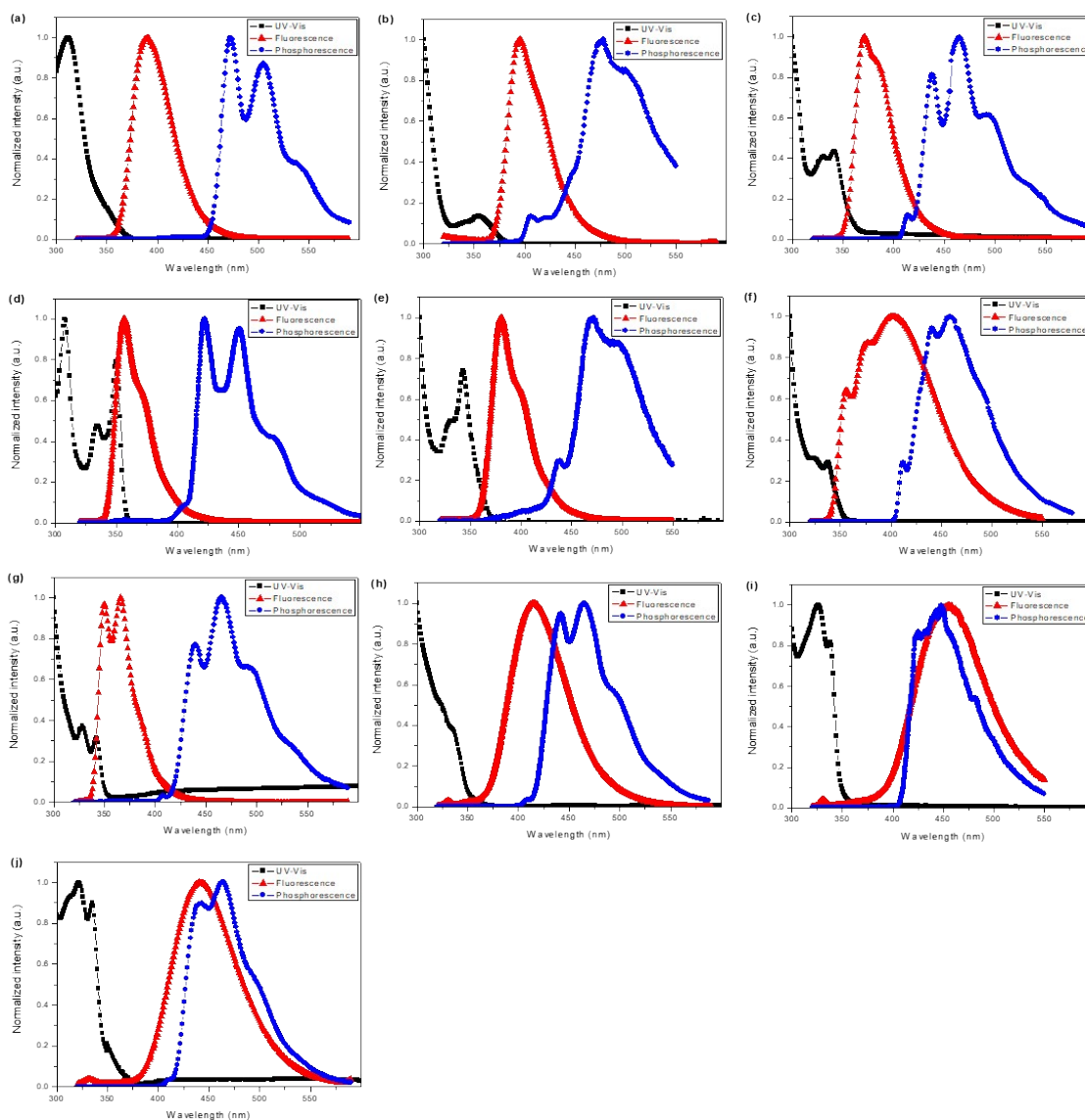


Fig. S1. The ultraviolet-visible (UV-vis), fluorescence, and phosphorescence spectra of (a) HT1, (b) HT2, (c) HT3, (d) HT5, (e) HT6, (f) ET1, (g) ET2, (h) ET5, (i) ET7 and (j) ET8.

Table S1. Summarized photophysical properties of host materials.

	S_1 (onset)	T_1 (onset)	$T_g^a)$	$T_d^b)$
	[eV]	[eV]	[°C]	[°C]
HT1	3.42	2.71	124	324
HT2	3.32	3.12	110	330
HT3	3.50	3.05	101	318
HT5	3.62	3.02	143	368
HT6	3.43	2.94	125	359
ET1	3.62	3.06	126	385
ET2	3.63	2.97	134	288
ET5	3.35	2.95	139	373
ET7	3.15	3.02	136	351
ET8	3.20	2.96	ND	353

^{a)}2nd heating scan value.

^{b)}Corresponding to 0.1% weight loss.

2. PL spectra of various exciplex-forming cohosts

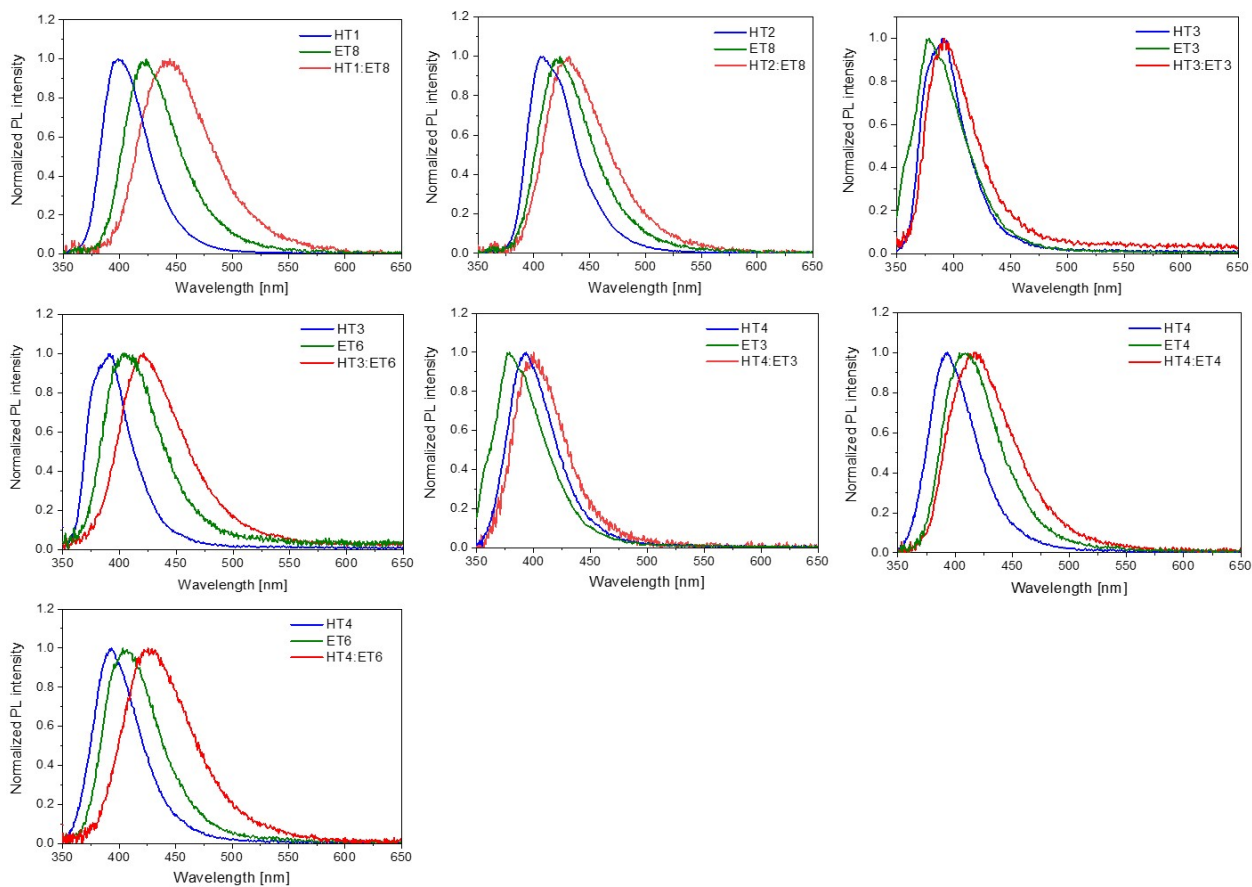


Fig. S2. PL spectra of the various cohosts and their component hosts

3. PL stability tests for the three types of cohosts

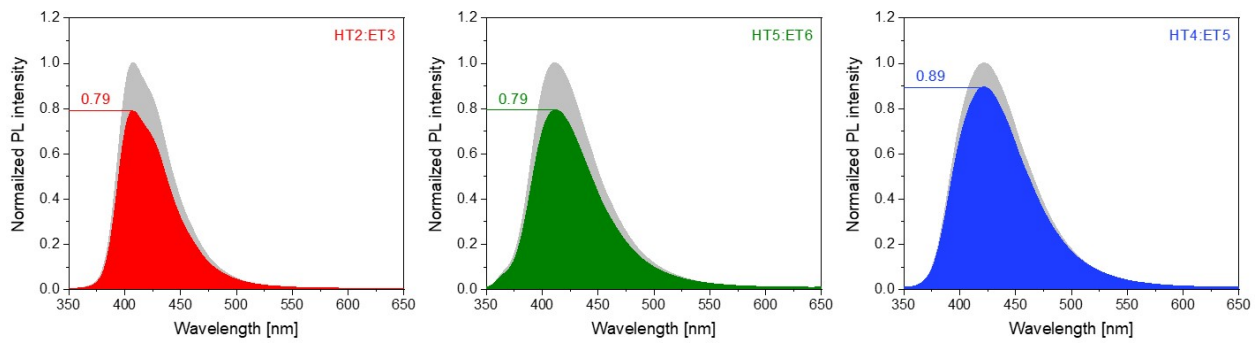


Fig. S3. Comparison of the PL spectra for the three types of cohosts, Type-I (HT2:ET3), Type-II (HT5:ET6) and Type-III (HT4:ET5), obtained from the pristine (gray color-filled) and UV-laser-exposed (325 nm) films.

4. Characteristics of various OLEDs

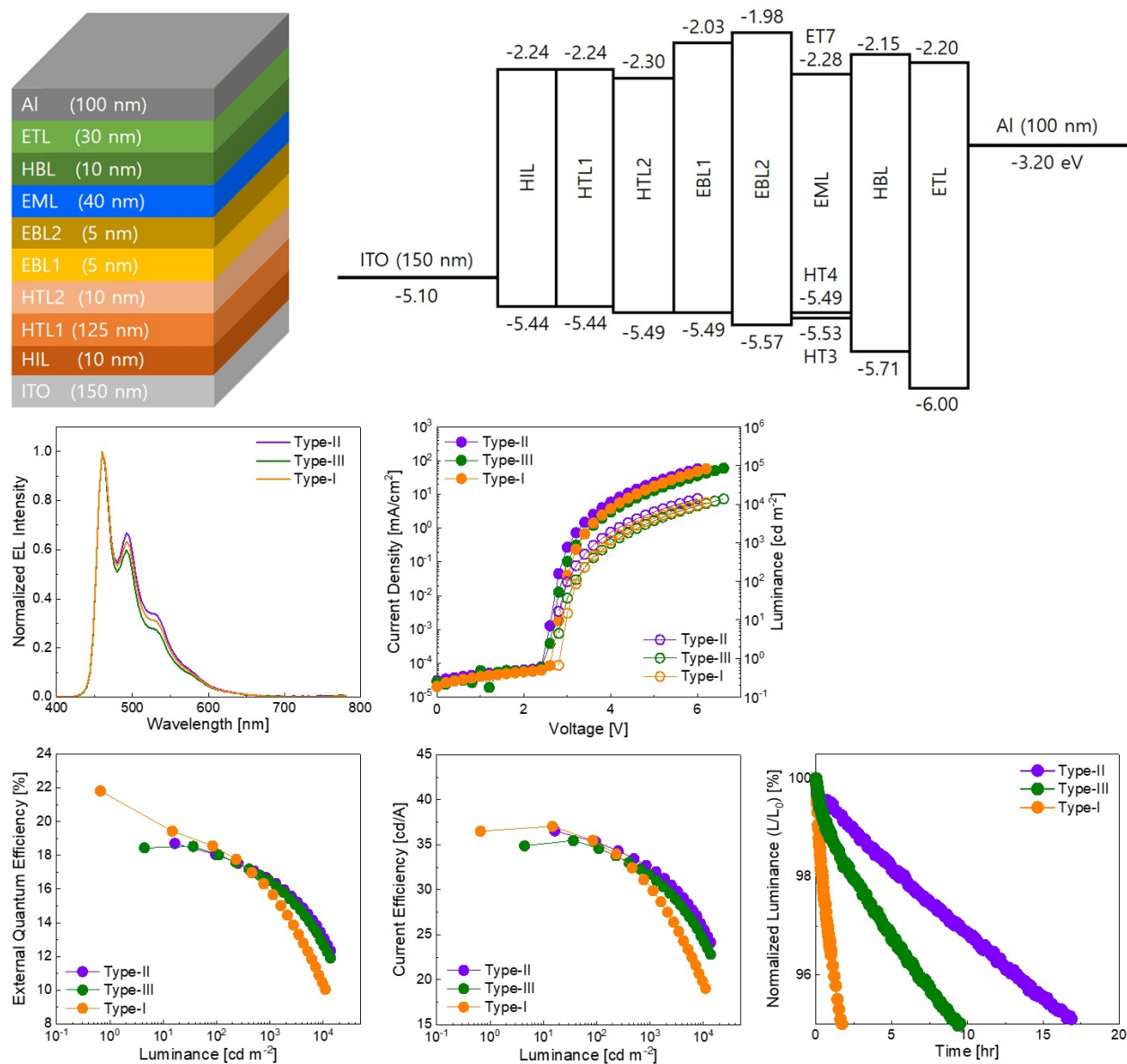


Fig. S4. Device structure and characteristics of IrE-based OLEDs employing various cohosts; HT5:ET6 (Type-II, pure exciplex), HT4:ET5 (Type-III, mixed exciplex) and HT2:ET3 (Type-I, no exciplex). The open circles with solid lines in the 3rd panel represent luminance-voltage characteristics. The values of HOMO and LUMO of the layers except for ITO and Al were obtained by using cyclic voltammetry (CV). They were measured with solution dissolved in toluene by cyclic voltammetry ($E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, $E_{\text{LUMO}} = (E_{\text{g}} + E_{\text{HOMO}})$ eV). The optical energy band gaps (E_{g}) were estimated from the absorption onset wavelengths, $E_{\text{g}} = (1240/\lambda_{\text{onset,abs}})$ eV.

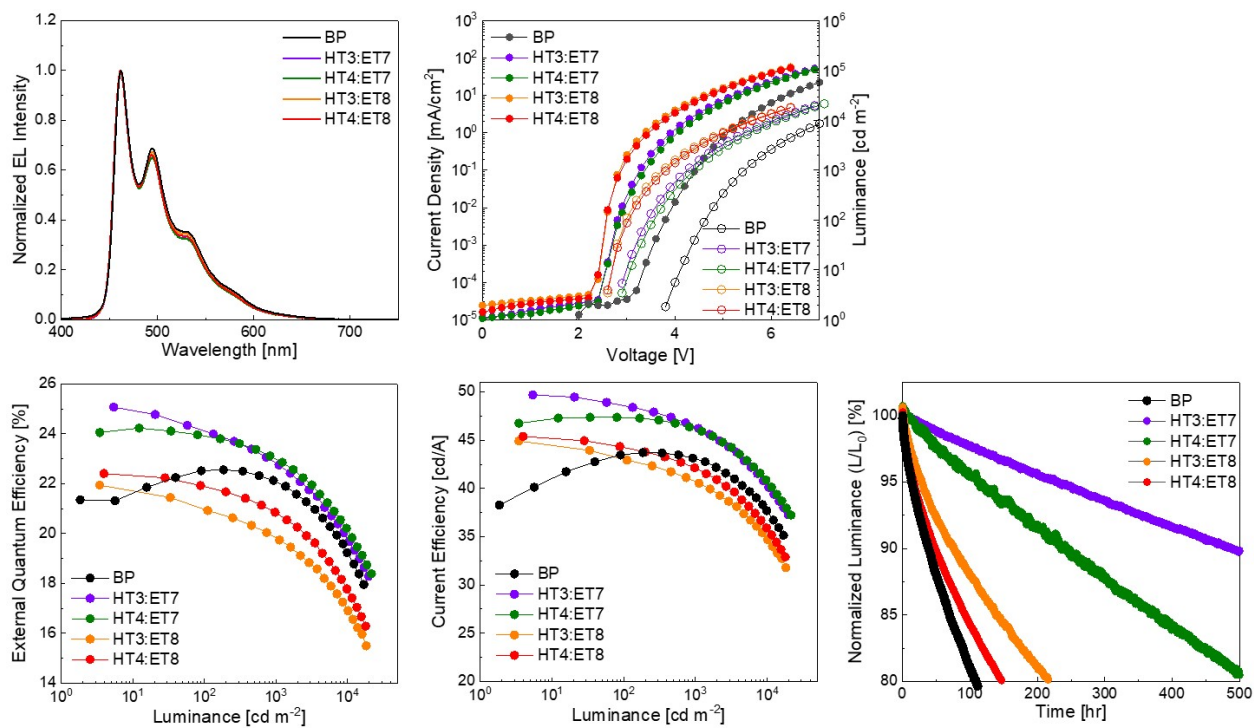


Fig. S5. Characteristics of IrE-based OLEDs employing a bipolar (BP) host and various cohosts; HT3:ET7, HT4:ET7, HT3:ET8 and HT4:ET8. The open circles with solid lines in the 2nd panel represent luminance-voltage characteristics.