Supplementary Information

Construction of Fully Conjugated Cross-linked Hole Transport Film based on Ethynyl to Enable High Mobility for Efficient Solution-Processed OLEDs

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Synthesis of N^4,N$^{4'}$-bis(4-bromophenyl)-N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine (1)

N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine (1.0 g, 2.98 mmol), 1-bromo-4-iodobenzene (3.37 g, 1.92 mmol), $Pd(OAc)_2$ (0.13 g, 0.596 mmol), sodium tert-butoxide (1.14 g, 11.92 mmol) and a solution of tri-tert-butylphosphine in toluene (2.10 mL, 1.79 mmol) were dissolved in anhydrous toluene (40 mL). The mixture was reacted at 110 °C for 10 h under argon gas atmosphere. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether/CH_2Cl_2 (15:1) to obtain compound **1** as a white solid (1.0 g, 52%). ^{1}H NMR (400 MHz, DMSO) δ 7.59 (d, J = 8.6 Hz, 4H), 7.50 – 7.44 (m, 4H), 7.35 (t, J = 7.9 Hz, 4H), 7.11 (t, J = 6.2 Hz, 2H), 7.07 (t, J = 8.0 Hz, 8H), 6.99 – 6.93 (m, 4H).

Synthesis of N^4,N$^{4'}$-diphenyl-N^4,N$^{4'}$-bis(4-((trimethylsilyl)ethynyl)phenyl)-[1,1'-biphenyl]-4,4'-diamine (2)

A mixture of compound **1** (1.29 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol), CuI (0.15 g, 0.8 mmol), PPh_3 (0.21 g, 0.8 mmol), anhydrous toluene (20 mL) and triethylamine (20 mL) was added into a two-necked round bottom flask. Under the protection of argon gas, the temperature was increased to 90 °C. Then trimethylsilyl acetylene (0.78 g, 8 mmol) was added dropwise. And after the addition, the reaction was stirred at 90°C for 24 h. After the reaction, the mixture was washed with water and extracted with CH_2Cl_2. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether/CH_2Cl_2 (10:1) to obtain compound **2** as a white yellow solid (0.97 g, 1.42 mmol, 71%). ^{1}H NMR (400 MHz, DMSO) δ 7.40 (d, J = 8.6 Hz, 4H), 7.18 – 7.11 (m, 8H), 6.93 (dd, J = 12.4, 5.0 Hz, 2H), 6.89 (dd, J = 7.9, 5.8 Hz, 8H), 6.70 – 6.66 (m, 4H), 0.01 (s, 18H).

Synthesis of N^4,N$^{4'}$-bis(4-ethynylphenyl)-N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine (E-TPD)

Compound **2** (0.682 g, 1 mmol), KOH (0.14 g, 2.4 mmol) were dissolved in dichloromethane (7.5 mL) and methanol (15 mL). The mixture was reacted at room temperature for 10 hours under an argon atmosphere. After the reaction, the mixture was washed with water and extracted with CH_2Cl_2. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether/CH_2Cl_2 (10:1) to obtain **E-TPD** as a white yellow solid (0.40 g, 0.74 mmol, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.6 Hz, 4H), 7.30 – 7.25 (m, 4H), 7.22 (t, J = 7.9 Hz, 4H), 7.06 (d, J = 8.5 Hz, 8H), 7.01 (t, J = 7.3 Hz, 2H), 6.96 – 6.92 (m, 4H), 2.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.20 (s), 147.02 (s), 146.17 (s), 135.50 (s), 133.17 (s), 129.54 (s), 127.61 (s), 125.20 (s), 124.97 (s), 123.85 (s), 122.36 (s), 115.04 (s), 83.93 (s), 76.40 (s).

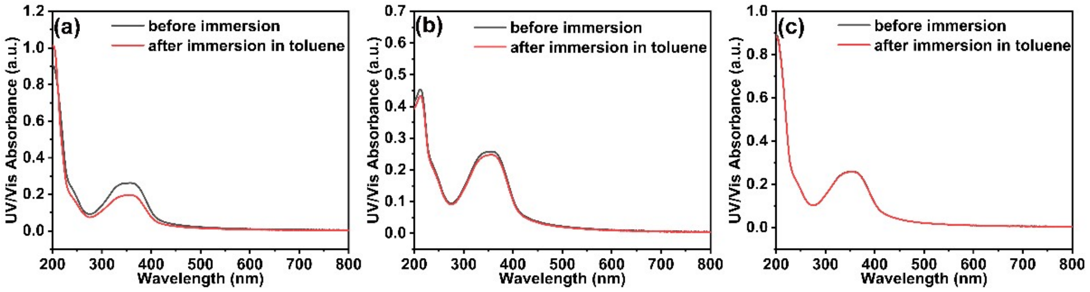

Fig. S1 UV–vis absorption spectra of cross-linked E-TPD films heated at (a) 170 °C, (b) 180 °C, (c) 190 °C before and after spin-coating toluene on films.

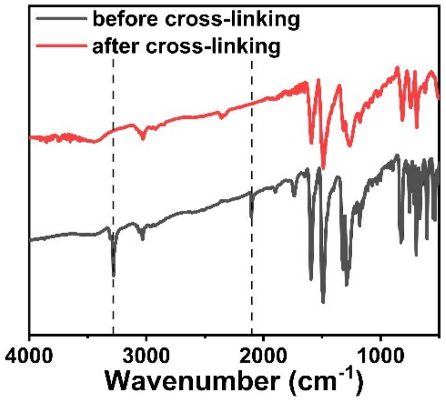

Fig. S2 FT-IR spectroscopy of E-TPD before and after cross-linking.

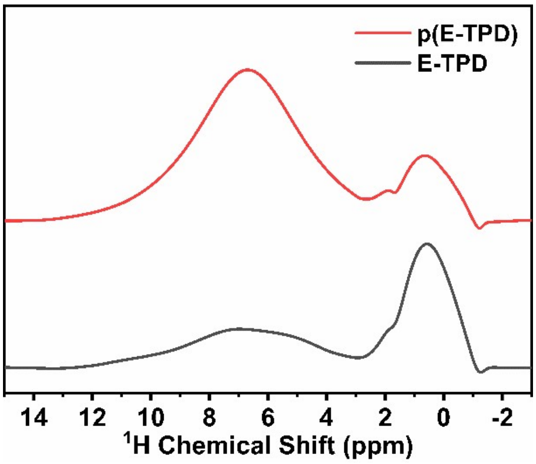

Fig. S3 Solid ^{1}H NMR spectrum of E-TPD and p(E-TPD).

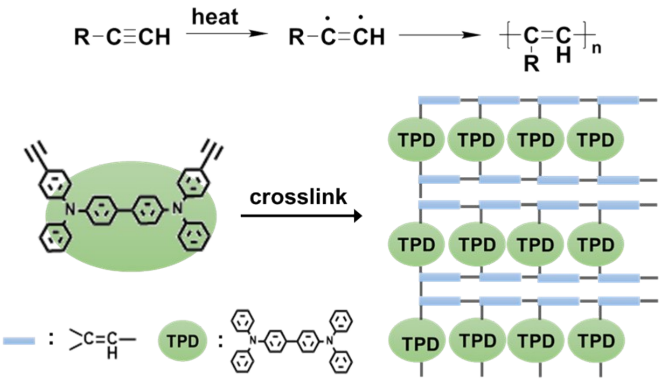

Fig. S4 The schematic diagram of the cross-linking process and the formed network structure of E-TPD.

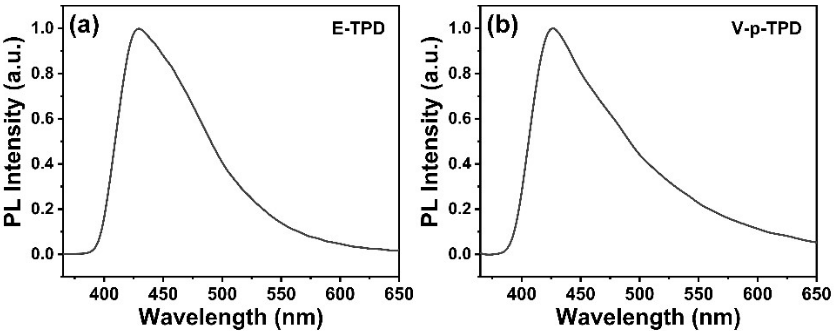

Fig. S5 PL spectra of (a) E-TPD and (b) V-p-TPD in THF (10^{-4} M).

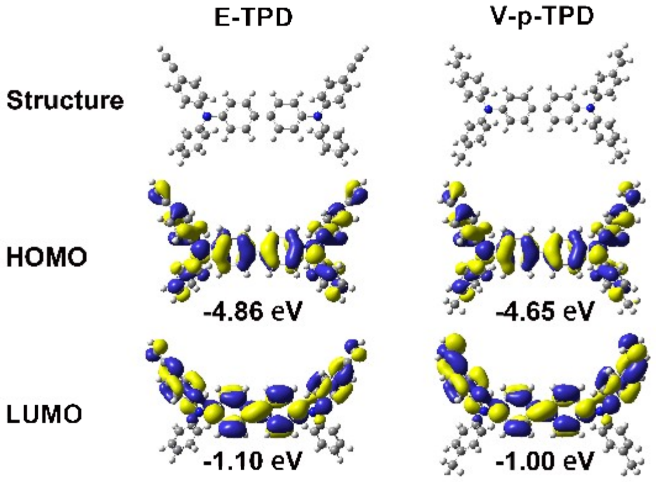

Fig. S6 Optimized structure and electron cloud distribution of E-TPD and V-p-TPD.

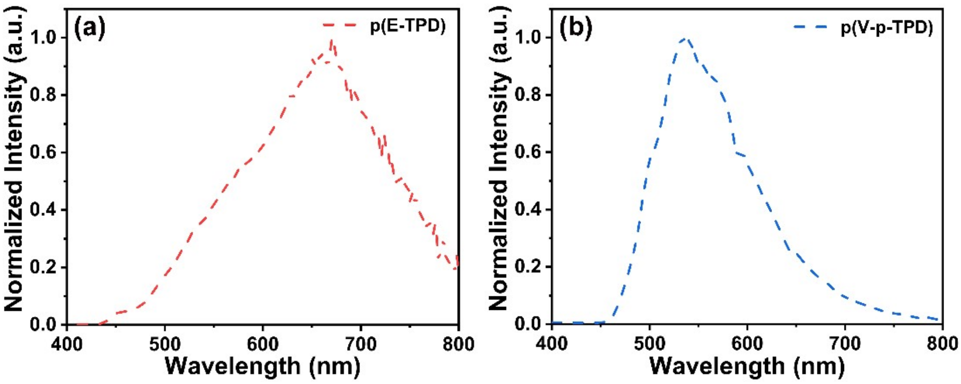

Fig. S7 Low temperature phosphorescence spectra of (a) p(E-TPD) and (b) p(V-p-TPD) films.

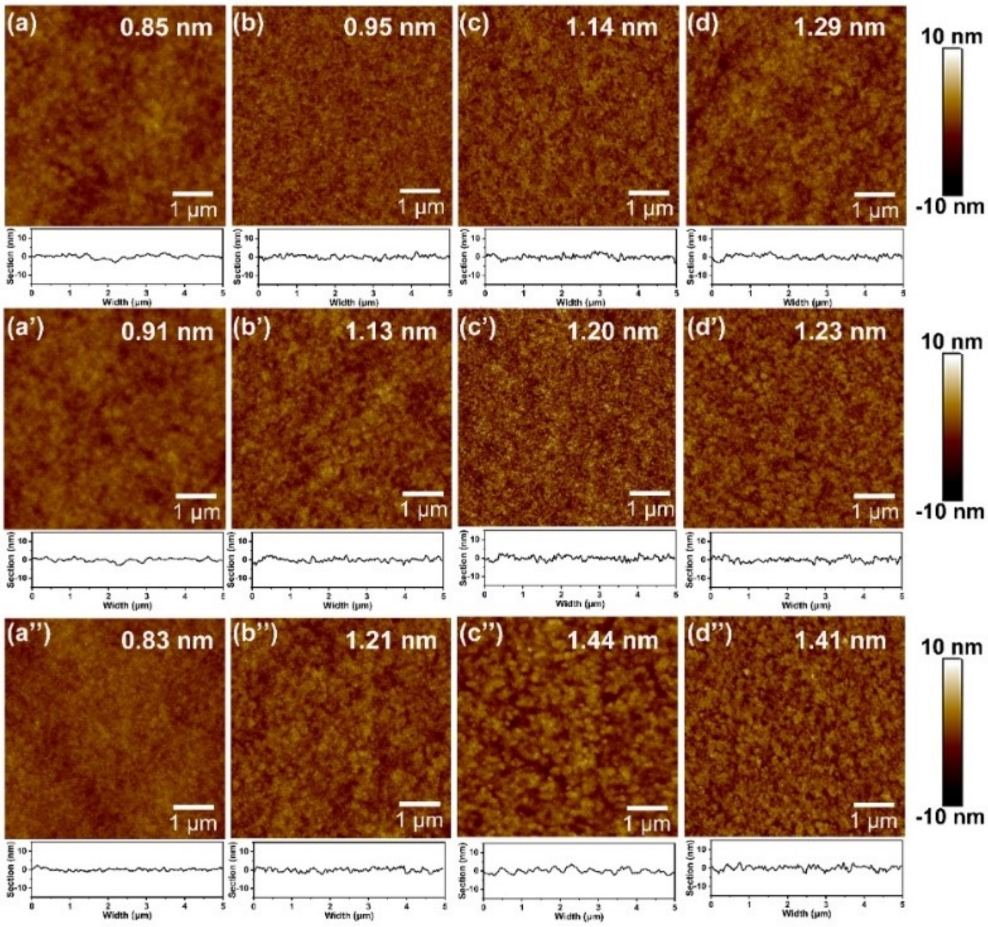

Fig. S8 AFM images of E-TPD film annealed at (a-a'') 100 °C, (b-b'')170 °C, (c-c'')180 °C and (d-d'') 190 °C.

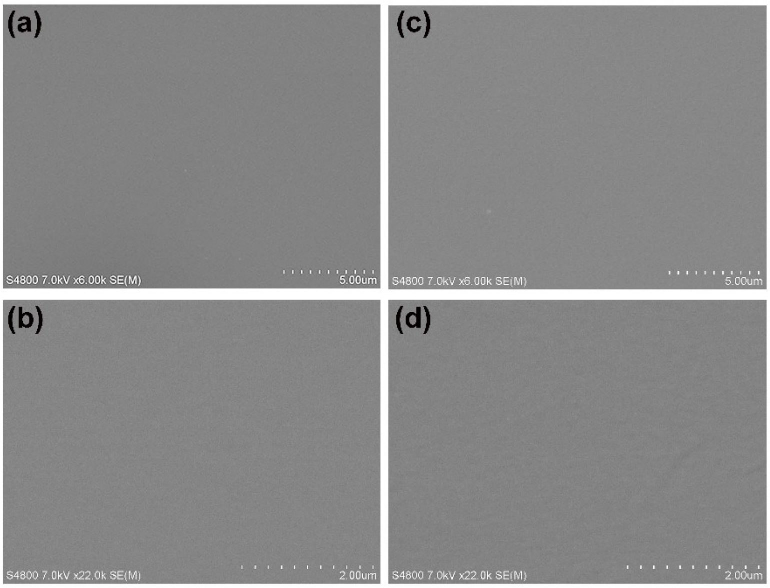

Fig. S9 SEM images of (a-b) p(E-TPD) and (c-d) p(V-p-TPD) films at different magnifications.

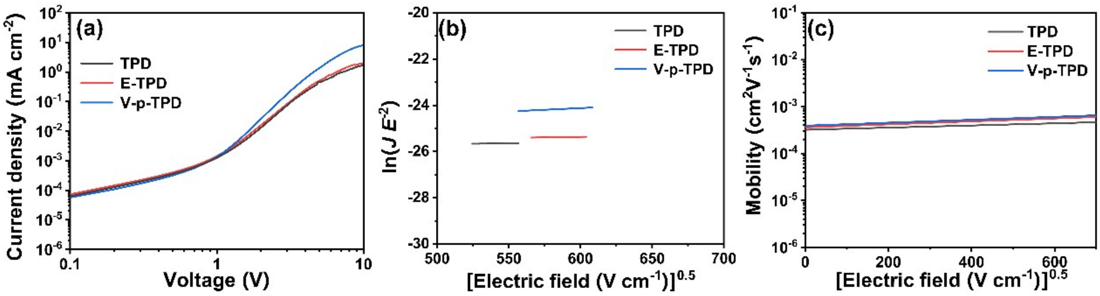

Fig. S10 (a) *J*-*V* curve, (b) the fitting curve of ln($J\ E^{-2}$) to $E^{0.5}$ and (c) the curve of μ to $E^{0.5}$ of hole-only devices of TPD, E-TPD and V-p-TPD monomer.

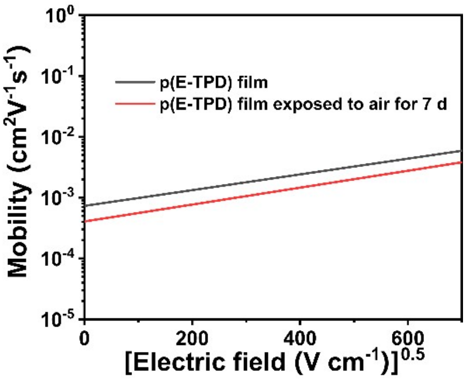

Fig. S11 Air stability of HOD based on p(E-TPD) as HTL.

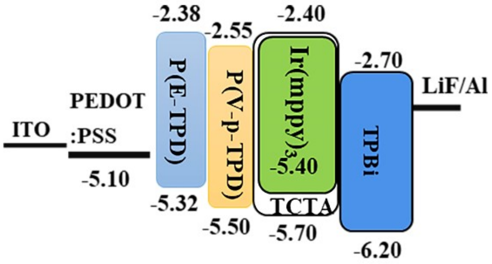

Fig. S12 Schematic diagram of the device structure.

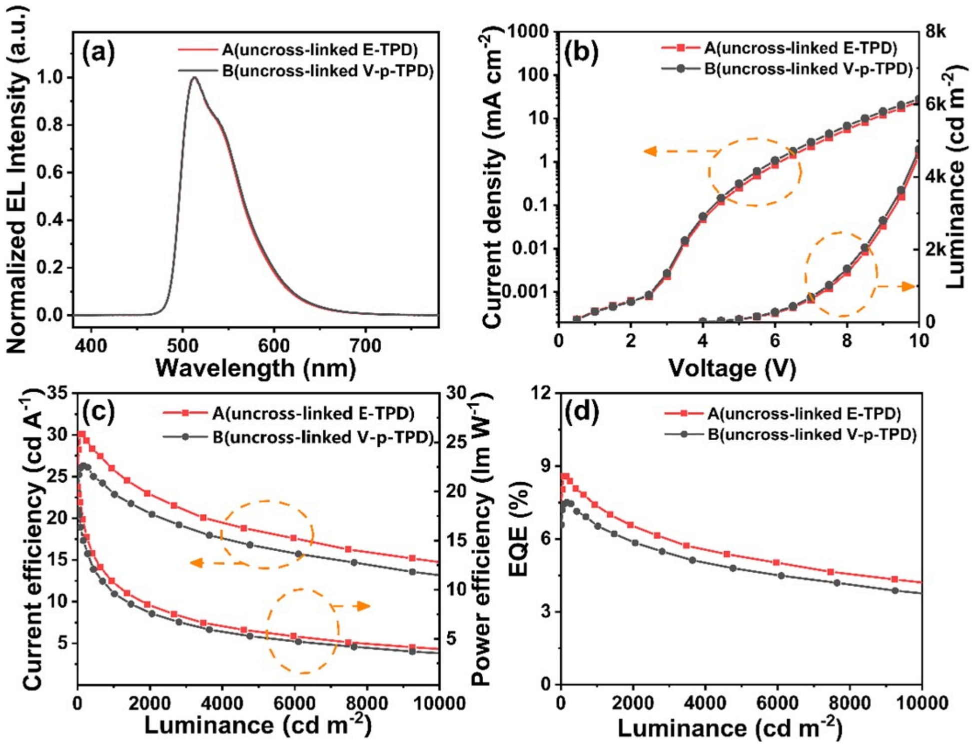

Fig. S13 (a) EL spectrum, (b) J-V-L curve, (c) CE-L-PE curve and (d) EQE-L curve of solution-processed green PHOLEDs with uncross-linked E-TPD and V-p-TPD HTL.

Table S1 Performance data of solution-processed green PHOLEDs with uncross-linked E-TPD and V-p-TPD HTL.

Device	V_{on} (V)	L_{max} (cd m^{-2})	CE_{max} (cd A^{-1})	PE_{max} (lm W^{-1})	EQE_{max} (%)	λ_{EL} (nm)	CIE (x,y) (7 V)
A(E-TPD)	3.6	22259	30.09	20.48	8.58	512	(0.29,0.63)
C(V-p-TPD)	3.6	23146	26.30	18.10	7.50	512	(0.29,0.63)

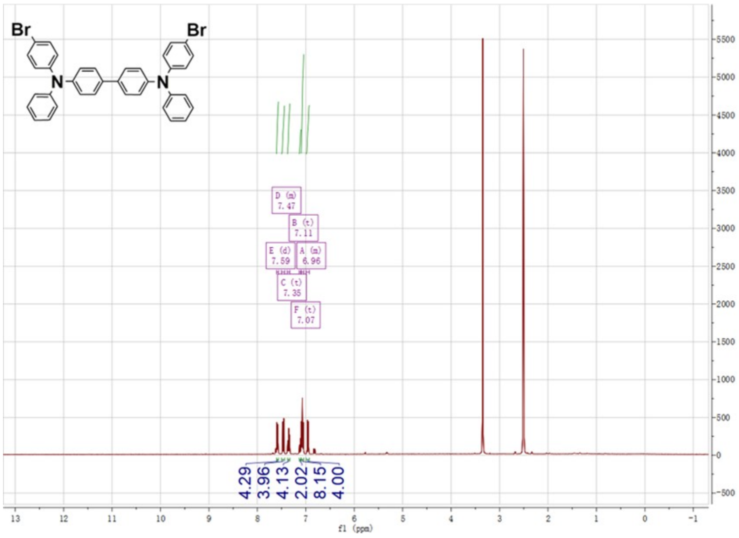

Fig. S14 ^{1}H NMR spectra of N^4,N$^{4'}$-bis(4-bromophenyl)-N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine.

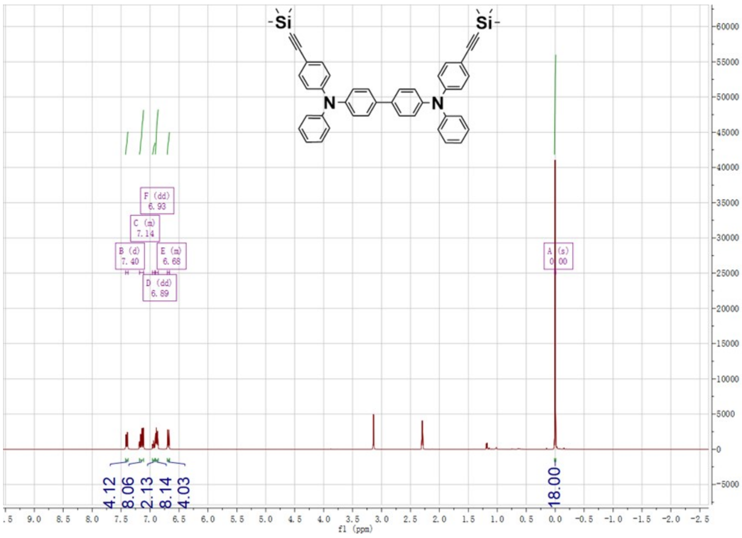

Fig. S15 ^{1}H NMR spectra of N^4,N$^{4'}$-diphenyl-N^4,N$^{4'}$-bis(4-((trimethylsilyl)ethynyl)phenyl)-[1,1'-biphenyl]-4,4'-diamine.

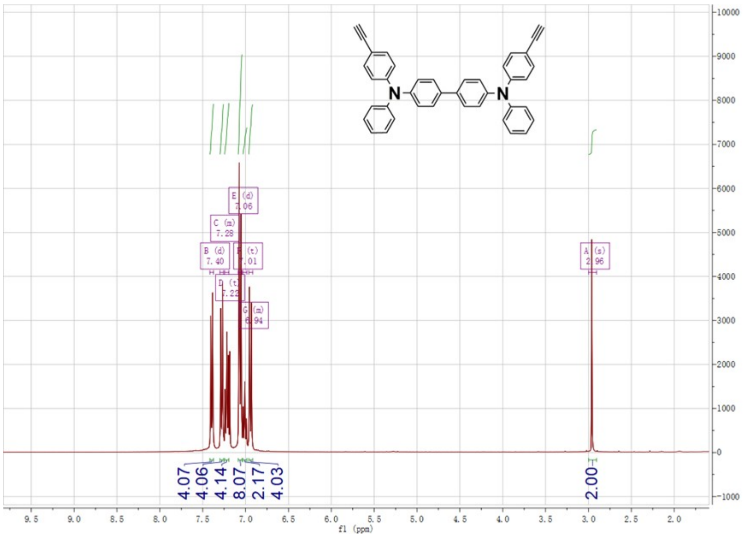

Fig. S16 ^{1}H NMR spectra of N^4,N$^{4'}$-bis(4-ethynylphenyl)-N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine.

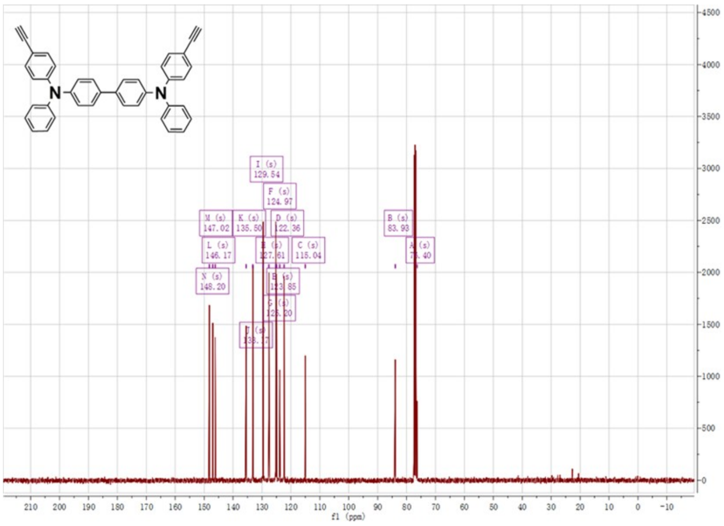

Fig. S17 ^{13}C NMR spectra of N^4,N$^{4'}$-bis(4-ethynylphenyl)-N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine.

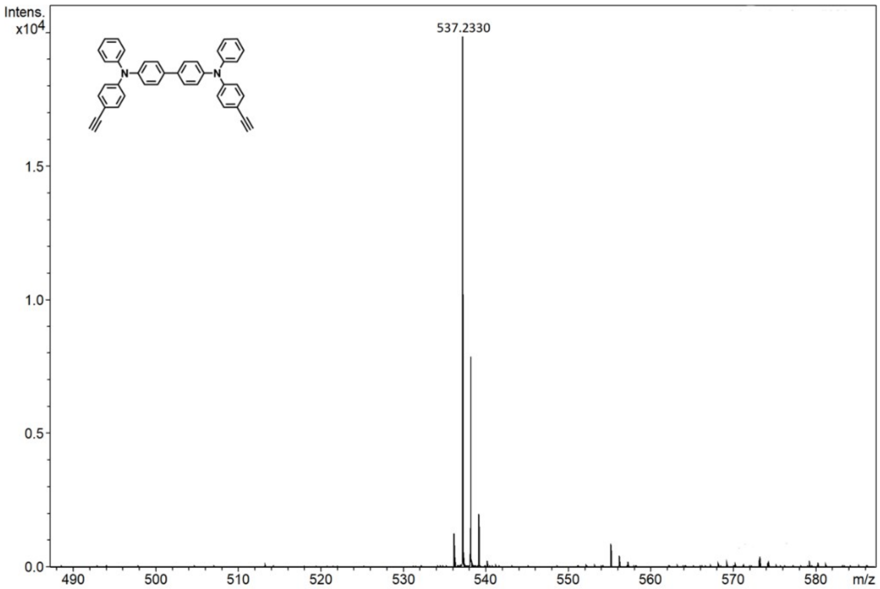

Fig. S18 HRMS spectra of N^4,N$^{4'}$-bis(4-ethynylphenyl)-N^4,N$^{4'}$-diphenyl-[1,1'-biphenyl]-4,4'-diamine.