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Electronic Supplementary Information (ESI)

Solution-Processed Thermal-Stable Amorphous Films of Small Molecular Triphenylamine-based Hole Injection/ Transport Bi-functional Materials and its Application in High Efficient OLEDs

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Experimental Details

General Information

Nuclear magnetic resonance (NMR) spectra were recorded on a INOVA 500 MHz spectrometer. Attenuated Total Reflection Fourier Transfer Infrared spectra (ATR-FTIR) were recorded using a Nicolet 760 FTIR unit equipped with an MCT detector cooled with liquid nitrogen. A total of 2000 scans were taken for each spectrum at 2 cm^{-1} resolution. Mass spectra were recorded on a FINNIGAN LCQ Advantage mass spectrometer. UV-vis spectra were collected on a Thermo Evolution 300 UV-visible spectrometer in the 10^{-5} mol L^{-1} chloroform solution. Decomposition temperature (T_d) and glass transition temperature (T_g) of the synthesized compounds were determined by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a TA Q500 thermo gravimetric analyzer and TA Q20 thermal analyzer. Cyclic Voltammetry (CV) was carried out on an IM6e electrochemistry workstation in the 10^{-3} mol L^{-1} THF solution with 0.1mol L^{-1} tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, Pt electrode as working electrode and counter electrode, saturated calomel electrode as reference electrode. The thicknesses of all spin-coated films were measured by the TencorAlfa Step-500 terrace detector. The active area of the device is 16 mm^2, determined by the cross breadth between the cathode (Al) and the anode (ITO). The scan rate was 100mV s^{-1}. The XRD images of the films were recorded on a Rigaku D/Max-2500 X-ray diffractomete. The current density-luminance-voltage (*J-L-V*) characteristics were performed with a Keithley4200 semiconductor characterization system.. All the measurements were carried out in air at room temperature without further encapsulation. The time-of-flight (TOF) measurements were conducted on TOF401 (Sumitomo Heavy Ltd., Japan).

Hole-only Devices Fabrication

Devices were prepared using a structure ITO/HTM (about 1 μm)/Al (120 nm) having an active area of 3 mm × 10 mm. Indium-tin-oxide (ITO) coated substrates (sheet resistance: 10 Ω/□) were cleaned with following sequence: in acetone, methanol, and diluted water, then annealed at 120 °C for 20 min followed by O_2 plasma treatment. The chlorobenzene solutions of $TPD(BTPA)_n$ (20 mg/mL) were spincoated on a cleaned ITO-coated glass substrate several times at a spinning rate of 2000 rpm to achieve the hole transport layers with the thickness of ~1μm, and then the films were baked at 50℃ for 25 min in nitrogen atmosphere to evaporate any residual solvent. Then, a 120nm Al were evaporated as the cathode.

OLED Fabrication

The chlorobenzene solutions of $TPD(BTPA)_n$ (20 mg/mL) were spincoated on cleaned ITO-coated glasses at 2000 rpm, then baked at 50℃ for 25 min in nitrogen atmosphere achieved the hole injection/transport layer with the thickness of ~200 nm. Then, Alq_3 layer was vacuum deposited onto the $TPD(BTPA)_n$-layer with thickness of ~70 nm at a deposition rate of 2-3 Å s^{-1} at 10^5 Torr. Finally, LiF (0.5 nm) and Al (120 nm) were evaporated as the cathode. The three-layer device using spin-coating PEDOT:PSS as hole injection layer was fabricated. The spinning rate of PEDOT:PSS solvent was 4000 rpm, then

baked at 100℃ for 20 min in nitrogen atmosphere achieved the thickness of ~100 nm.

Materials

4-[N,N-di(p-tolyl)amino]benzaldehyde and p-TPD were purchased from Tianjin Zhongmin Technology Co. LTD, and recrystallized from ethanol before use, and other reagents such as N,N-dimethylformamide phosphorus oxychloride ($POCl_3$), 1,2-dichloroethane, petroleum ether, ethyl acetate, dichloromethane, etc were purchased from Tianjin Guangfu Fine Chemical Research Institute. N,N-dimethyl formamide (DMF), $POCl_3$, THF were freshly distilled before use.

4-((4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)(phenyl)amino)benzal dehyde (1)

A suspension of TPD (2.20 g, 4.5 mmol) in DMF (80 mL) was cooled to 0 ℃ and then phosphorus oxychloride (6.90g, 45 mmol) was added dropwise under the protection of nitrogen. The mixture was stirred for 24 h at 15 ℃ and then was poured into ice water mixture (300 mL) followed by filtration to afford crude product, and then the crude product was purified by column chromatography (petroleum ether: ethyl acetate =15:1 as eluent) to afford the title compound 1 (1.20 g, 50%). Mp:164-166℃;1H NMR(500 MHz, $CDCl_3$) δ(ppm):7.025-7.055 (m, 7H), 7.095 (d, 8H, J = 8.5), 7.166 (t, 4H), 7.235 (t, 2H), 7.422 (d, 2H, J =9.0), 7.502 (d, 2H, J = 8.5), 7.668 (d, 2H, J = 8.5), 9.802 (s, 1H); ESI-MS (m/z): 544.7 [M+].

4,4'-([1,1'-biphenyl]-4,4'-diylbis(phenylazanediyl))dibenzaldehyde (2)

Compound 2 was synthesized according to the method described above. The reaction was carried out at 95℃ for 24 h after phosphorus oxychloride was added. After cooling to room temperature, the mixture was poured into ice water mixture (300 mL) and then filtered to afford crude product. The crude product was purified by column chromatography petroleum ether: ethyl acetate = 5:1 as eluent to afford the title compound 2 (2.0 g, 75%). Mp.170-172℃; ^{1}H NMR (500MHz, $CDCl_3$) δ(ppm): 7.079 (d, 4H, J=9.0), 7.209-70240 (m, 10H), 7.370 (d, 4H, J= 9.0), 7.540(d, 4H, J= 8.5), 7.702 (d, 4H, J = 8.5), 9.833 (s, 2H); ESI-MS (m/z): 545.6 [M+].

4,4',4'',4'''-([1,1'-biphenyl]-4,4'-diylbis(azanetriyl))tetrabenzaldehyde (3)

Compound 3 was synthesized according to the method described above. The reaction was carried out at 150℃ for 24 h after phosphorus oxychloride was added. After cooling to room temperature, the mixture was poured into ice water mixture (300 mL) and then filtered to afford crude product. The crude product was purified by column chromatography petroleum ether: ethyl acetate = 5:1 as eluent to afford the title compound 2 (2.1 g, 80%). Mp.181-182℃;^{1}H NMR(500 MHz,$CDCl_3$) δ(ppm): 7.080(d, 8H, J= 9.0), 7.209-7.240 (m, 12H), 7.381(d, 4H, J =9.0), 9.823 (s,4H); ESI-MS (m/z): 573.6 [M+].

4-[N,N-di-(p-tolyl)amino]styrene (4)

Methyl triphenylphosphonium bromide (17.51 g, 49 mmol) and 4-[N,N'-di(p-tolyl) amino] benzaldehyde (10.49 g, 35 mmol) were added into a round-bottom flask. The apparatus was evacuated and flushed with N_2 three times. Dry THF (100 mL) was added to the flask and the mixture was cooled to 0℃. A THF solution (20 mL) of t-BuOK (2.5 M) was injected slowly to the flask and the mixture stirred for 10 min at 0 ℃. The reaction mixture was stirred for another 4 h at room temperature, and then poured into ice water mixture followed by extraction with dichloromethane. The organic layer was dried over

$MgSO_4$. After evaporation of solvent, the crude product 4 was obtained. The crude product was purified by column chromatography petroleum ether: ethyl acetate = 10:1 as eluent to afford the title compound 4 as a pale yellow solid. Mp: 72-74 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) d (ppm): 2.32 (s, 6H), 5.13 (d, 1H, J =11.0), 5.61 (d, 1H, J =17.5), 6.68 (dd, 1H, J1 =11.0, J2 =17.5), 6.97 (d, 2H, J =8.5), 6.99 (d, 4H, J =8.5), 7.06 (d, 4H, J =8.5), 7.25 (d, 2H, J =8.5); MS:Found M + H 300.8, Calcd for $C_{22}H_{21}N$ M + 299.4.

3-(4-(N,N-di-(p-tolyl)amino)phenyl)acrylaldehyde (5)

A solution of compound 5 (1.50 g, 5 mmol) in DMF (40 mL) was cooled to 0℃and then phosphorus oxychloride (7.62 g, 50 mmol) was added dropwise to solution under nitrogen. The mixture was stirred for 6 h at 85 ℃. After cooling to room temperature, the mixture was poured into ice water mixture (300 mL) and then filtered. The crude product was purified by column chromatography (petroleum ether: ethyl acetate =9:1 as eluent) to obtain the title compound 6 (1.4 g, 86%). Mp. 130 - 132 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.63 (d, 1H, J = 8.0),7.39-7.36 (m, 3H, PhH), 7.13 (d, 4H, J= 8.5), 7.05 (d, 4H, J =8.5), 6.95 (d, 2H, J =8.5), 6.59 (dd, 1H, J = 15.5), 2.34 (s, 6H); ESI-MS (M/z): 328.4 [M+]。

3-(4-(N,N-di-(p-tolyl)amino)phenyl)propenol (6)

Compound 5 (1.97 g, 6.0 mmol) and $NaBH_4$ (0.28 g, 7.2 mmol) were heated under reflux in EtOH (10 mL) and dichloromethane (30 mL) for 1 h. The mixture was poured into ice water mixture and extracted with diethyl ether. The organic layer was dried over $MgSO_4$. After evaporation of solvent, the resulting viscous oil was allowed to solidify in methanol (20 mL) to afford the title compound 6 (1.85 g, 92%). Mp. 52-54℃;^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 2.307 (s, 6H), 4.287(d, 2H, J = 6.0), 6.517(d, 2H,J = 15.5), 6.945(d, 2H,J = 8.5), 6.975 (d, 4H,J = 8.5), 7.049 (d, 4H, J = 8.0), 7.210 (d, 2H, J = 8.5); ESI-MS (m/z): 329.2 [M+].

1-[4-(di-(p-tolyl)amino)phenyl]-3-(triphenyl) phosphoniumpropyle ne bromide (7)

To a solution of compound 6 (2.39 g, 8 mmol) in $CHCl_3$ (60 mL) was added triphenylphosphonium hydrogen bromide (2.70 g, 8 mmol). The mixture was heated under reflux for 2 h and then the solvent distilled off to dryness, then diethyl ether was added to solidifying the crude products. The title compound 7 was obtained as a light yellow solid (4.77 g, 96%). Mp. 110 - 113 ℃;1H NMR (500 MHz, $CDCl_3$) δ(ppm): 2.304 (s, 6H), 4.970 (d, 2H, J=15.0), 6.836 (d, 2H, J=8.5), 6.950-7.062 (m, 12H), 7.663-7.904 (m, 15H). ESI-MS (m/z): 573.3 [M-Br].

General Procedure for TPD(BTPA)$_1$, TPD(BTPA)$_2$ and TPD(BTPA)$_4$

Compound 7 (2.52g,4mmol) and 3 (0.30 g, 0.5 mmol) were weighed into a round-bottom flask. The apparatus was evacuated and flushed with N_2 three times. Dry THF (50 mL) was added to the flask and the mixture was cooled to 0 ℃. A THF solution (10 mL) of t-BuOK (1 M) was added dropwise to the mixture and the mixture was stirred for 10 min at 0 ℃. The reaction mixture was stirred at room temperature until compound 1 was consumed completely (monitored by thin-layer chromatography). The reaction solution was poured into ice water mixture and extracted with dichloromethane.The organic layer was dried over $MgSO_4$. The crude product was obtained after the solvents were removed under reduced pressure.

The crude product was heated under reflux for 8 h in THF with a catalytic amount of iodine, then the remaining iodine was removed by pouring into

sodium hydroxide solution (W_t =10%, 100 mL) and stirred for 2 h. After extraction with dichloromethane, the solvent was removed under reduced pressure and the residues were chromatographed on a silica gel column (petroleum ether: dichloromethane =20:1 as eluent) to give title compound as a pure E stereoisomer.

TPD(BTPA)$_1$: Yield 72%. Mp.203-2044 ℃; IR (cm^{-1}, KBr): 3025, 2919, 1597, 1500, 1331, 1280, 976, 818; ^{1}H NMR (500 MHz, Chloroform) δ = 7.83 – 7.72 (m, 4H), 7.62 – 7.50 (m, 4H), 7.44 – 7.33 (m, 4H), 7.31 – 6.94 (m, 29H), 6.71 (d, *J*=30.2, 2H), 2.32 (s, 6H); HRMS: Found: *m*/*z* 812.4313 (M+), Calcd for C60H49N3: M+H, 812.4313.

TPD(BTPA)$_2$: Yield 68%. Mp.177-178℃;IR (cm^{-1}, KBr): 2912, 1600, 1508, 1320, 969, 807; ^{1}H NMR (500 MHz, Chloroform) δ = 7.86 – 7.70 (m, 8H), 7.64 – 7.47 (m, 4H), 7.43 – 7.32 (m, 4H), 7.29 – 6.91 (m, 38H), 6.71 (d, *J*=30.2, 4H), 2.32 (s, 12H); HRMS: Found: m/z 1335.5985 (M+), Calcd for $C_{84}H_{70}N_4$:M+H,1335.5986.

TPD(BTPA)$_4$: Yield 63%; Mp. 260-262℃;IR (cm^{-1}, KBr): 2928,2853,1603, 1500, 1321,964, 823; ^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, Chloroform) δ = 7.89 (s, 16H), 7.55 (s, 8H), 7.37 (s, 8H), 7.15 (t, *J*=12.5, 48H), 6.90 (s, 8H), 2.32 (s, 24H); HRMS: Found: *m*/*z* 1782.8322 (M+), Calcd for $C_{132}H_{112}N_6$.

Synthesis and Characterizations

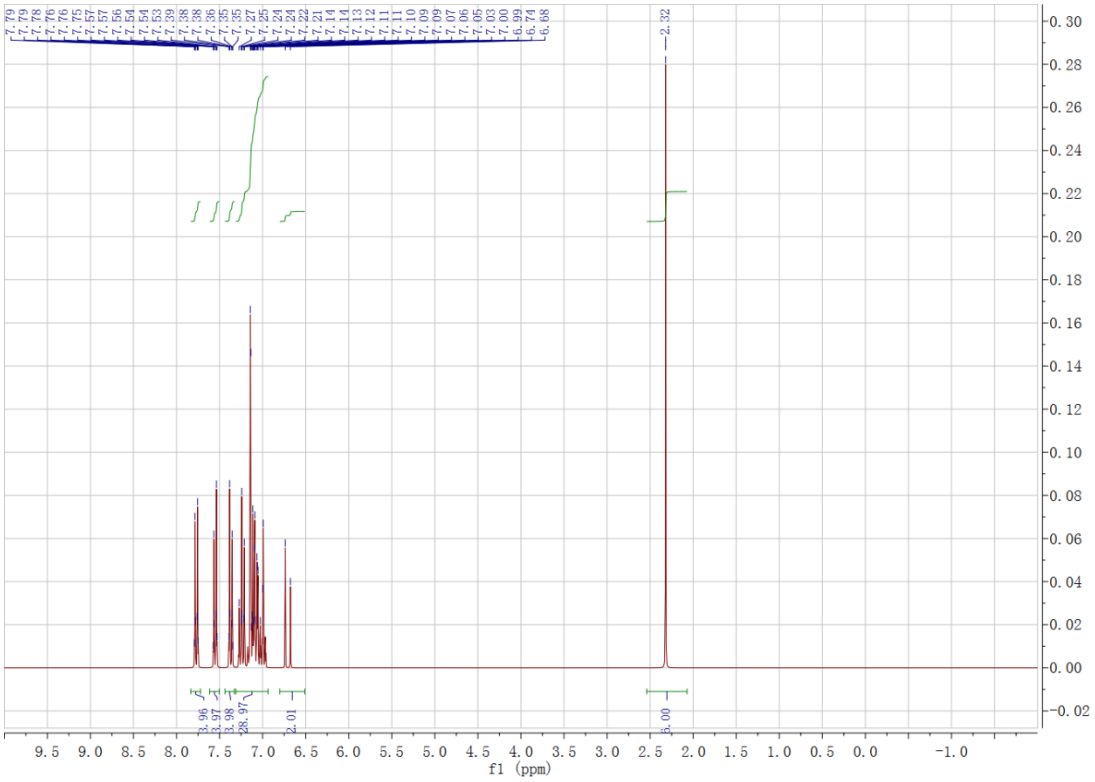


Fig. S1. ^{1}H NMR spectrum of TPD(BTPA)$_1$

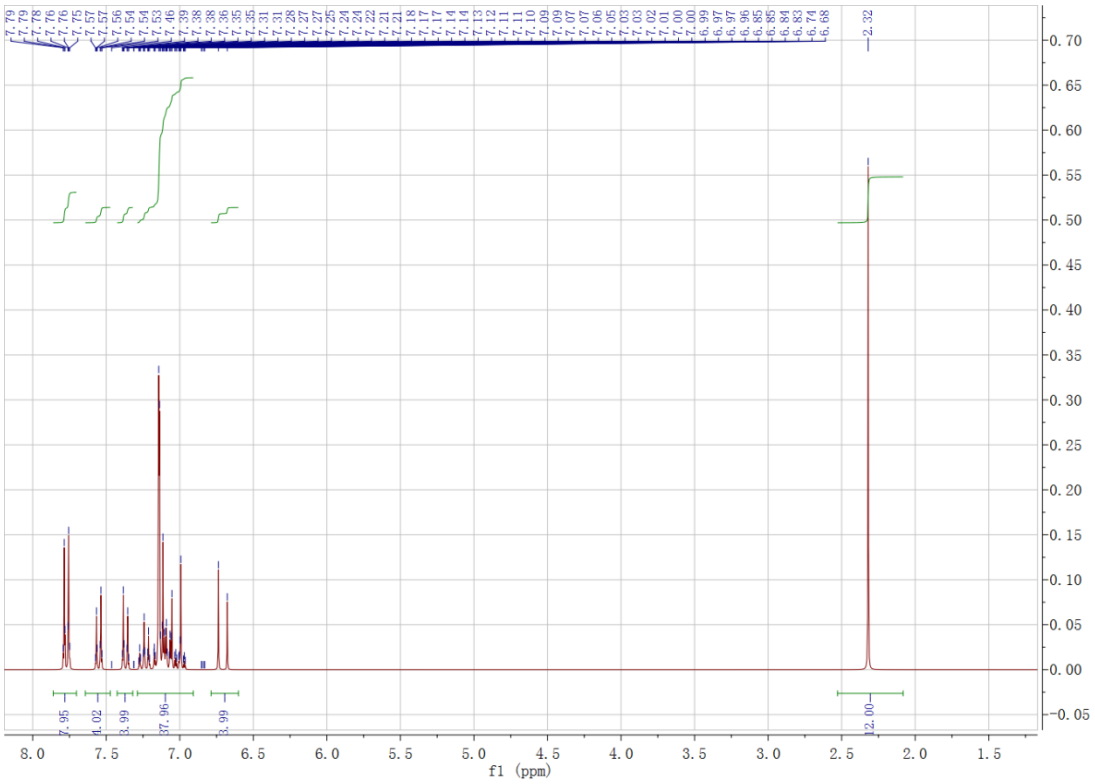


Fig. S2. ^{1}H NMR spectrum of TPD(BTPA)$_2$

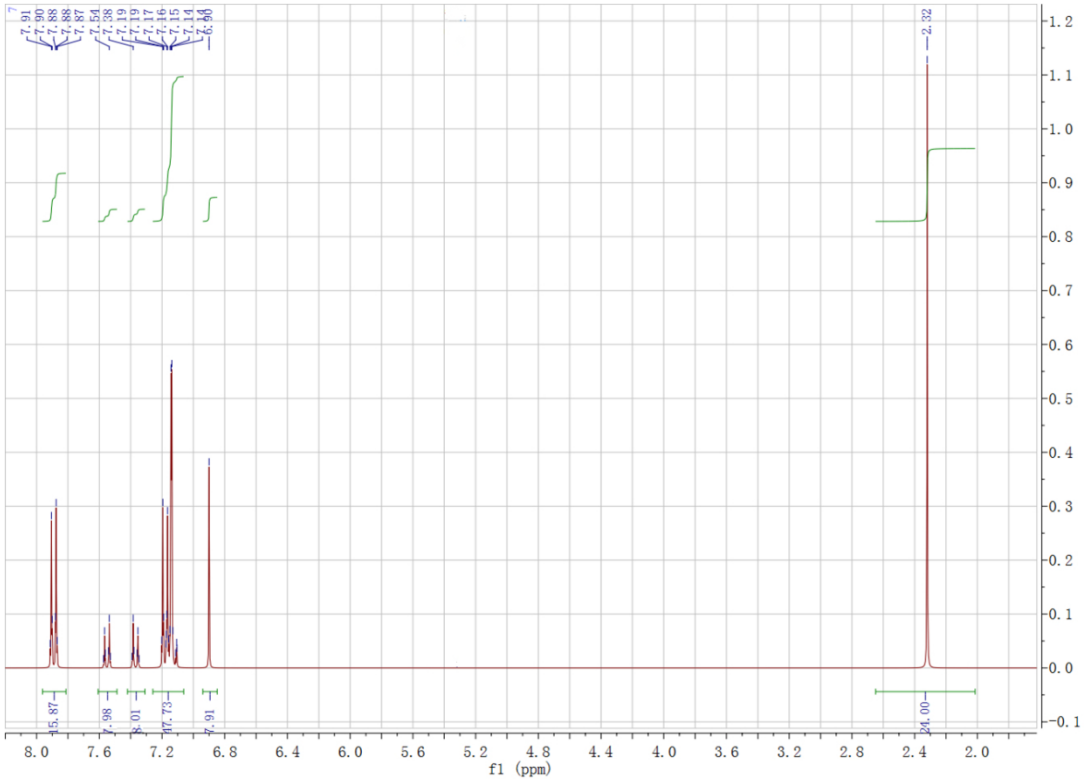


Fig. S3. ^{1}H NMR spectrum of TPD(BTPA)$_4$

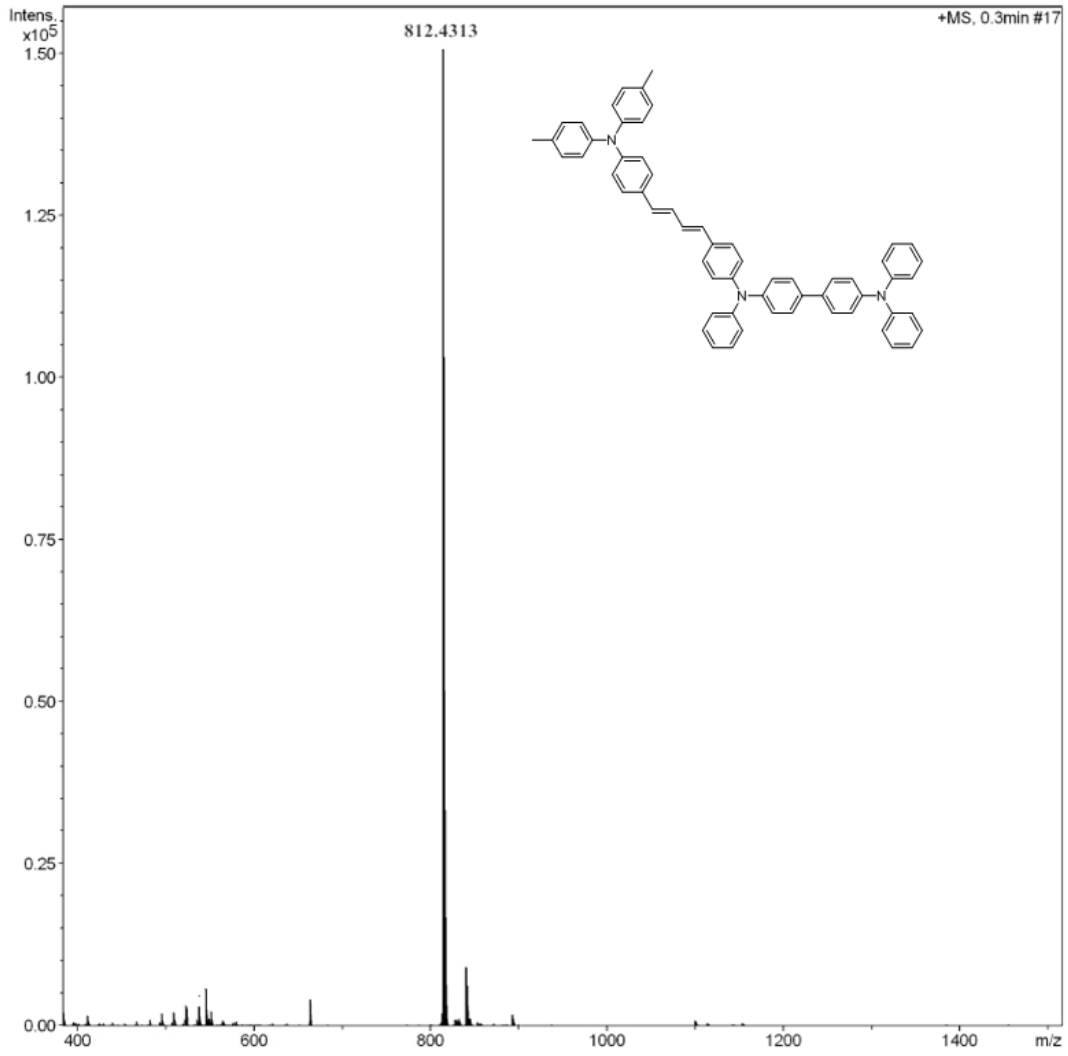


Fig. S4. RHMS spectrum of TPD(BTPA)$_1$

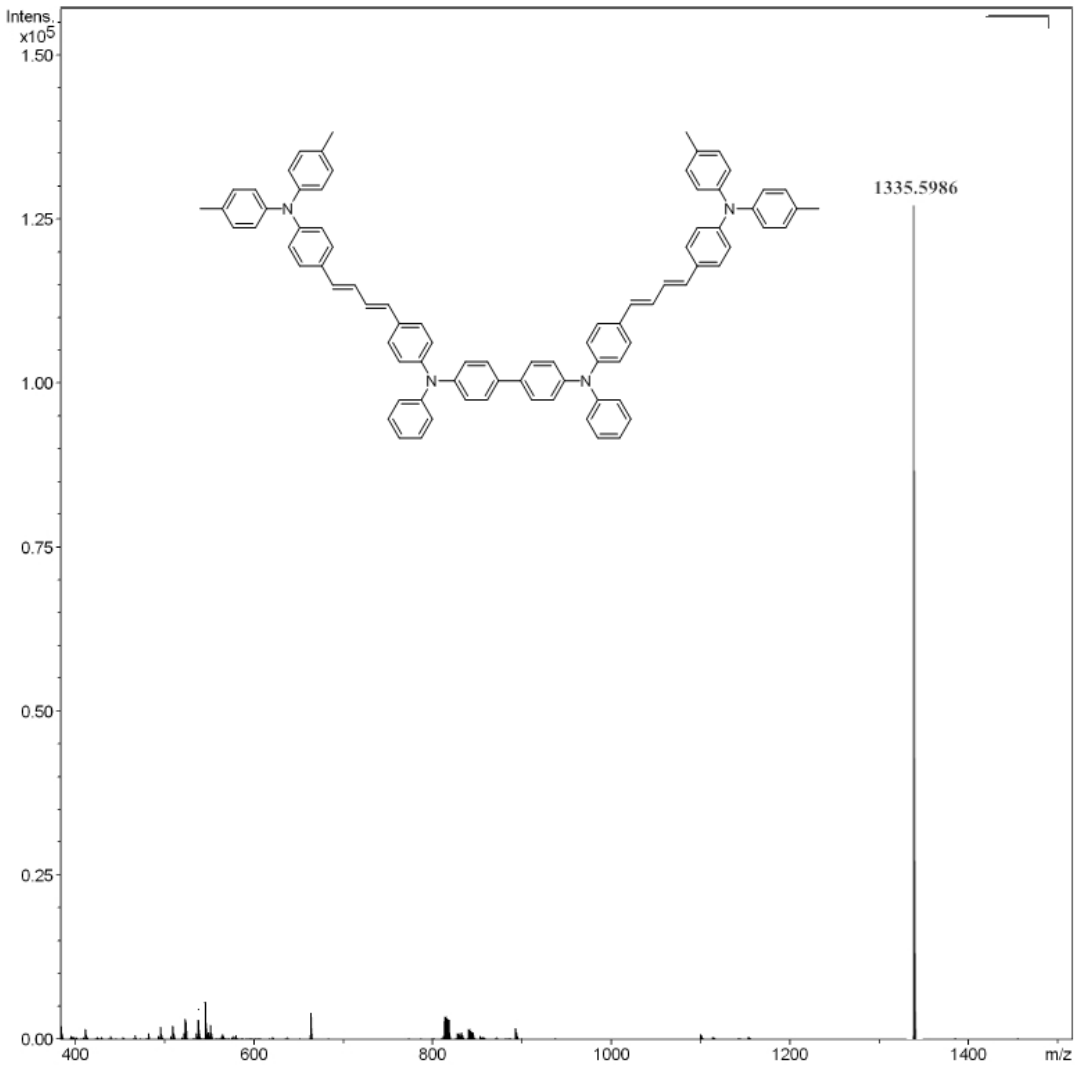


Fig. S5. RHMS spectrum of TPD(BTPA)$_2$

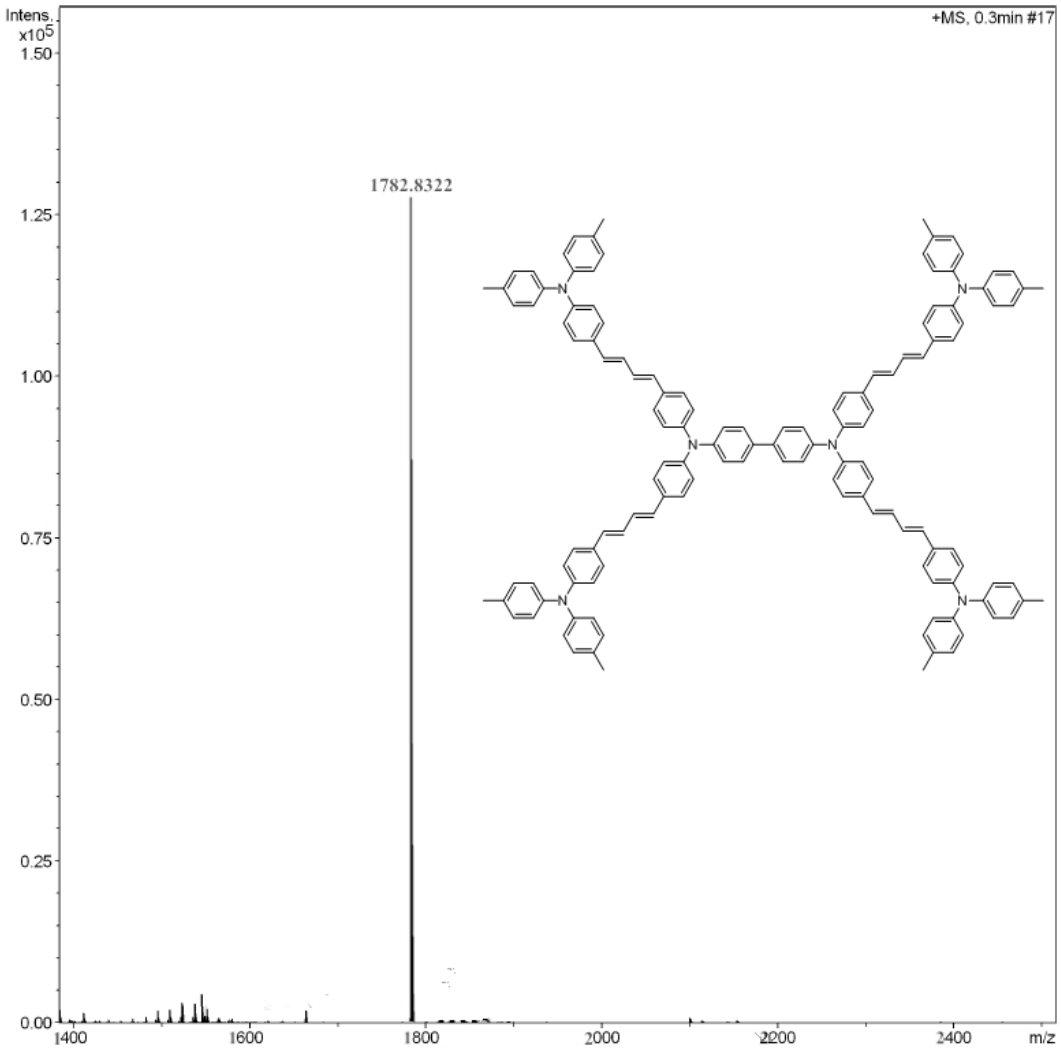


Fig. S6. RHMS spectrum of TPD(BTPA)$_4$

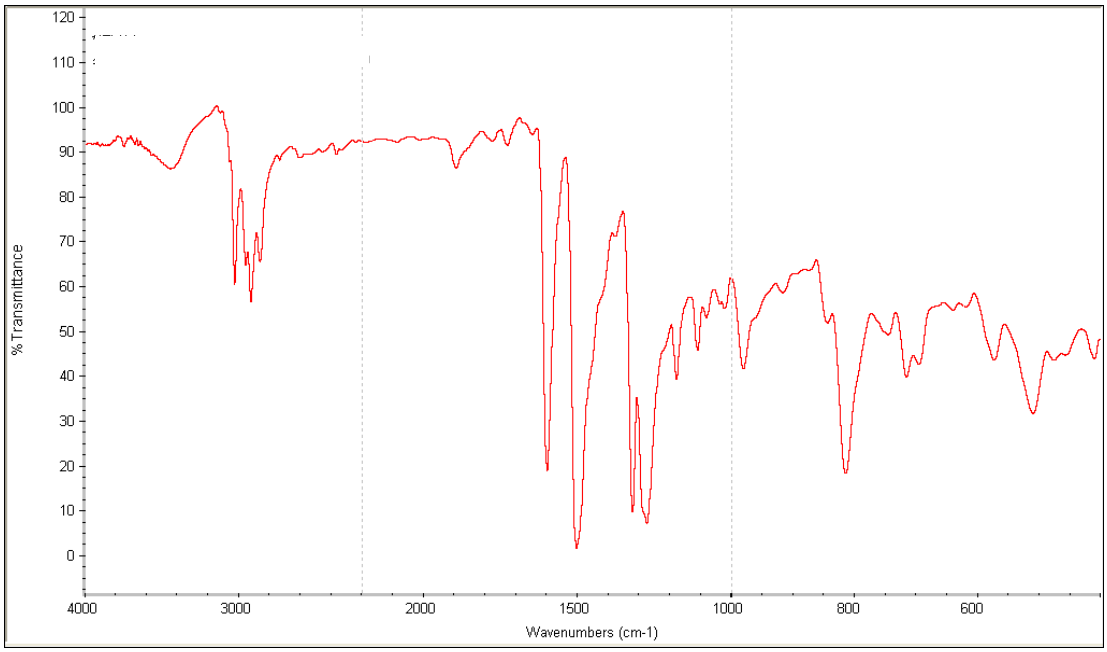


Fig. S7. IR spectrum of TPD(BTPA)$_1$

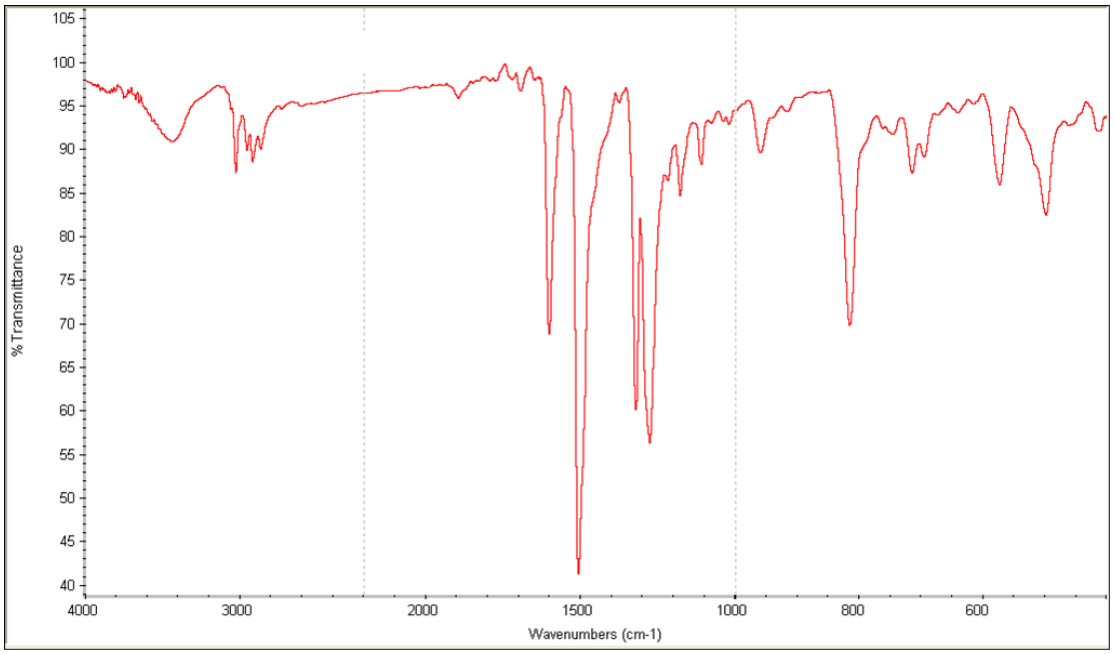


Fig. S8. IR spectrum of TPD(BTPA)$_2$

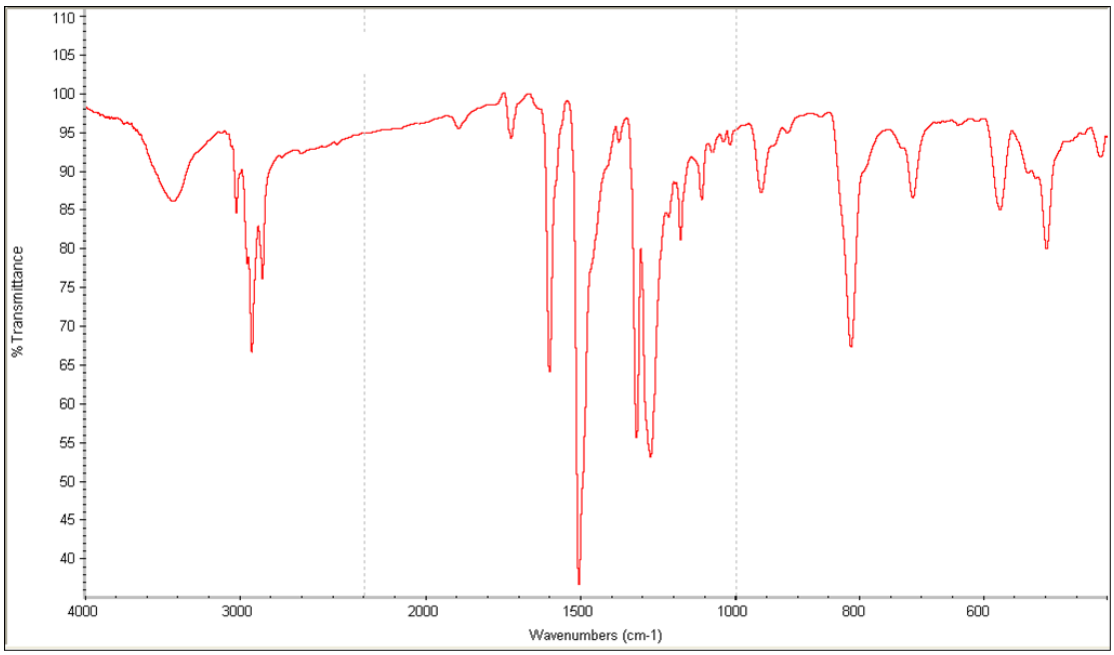


Fig. S9. IR spectrum of TPD(BTPA)$_4$

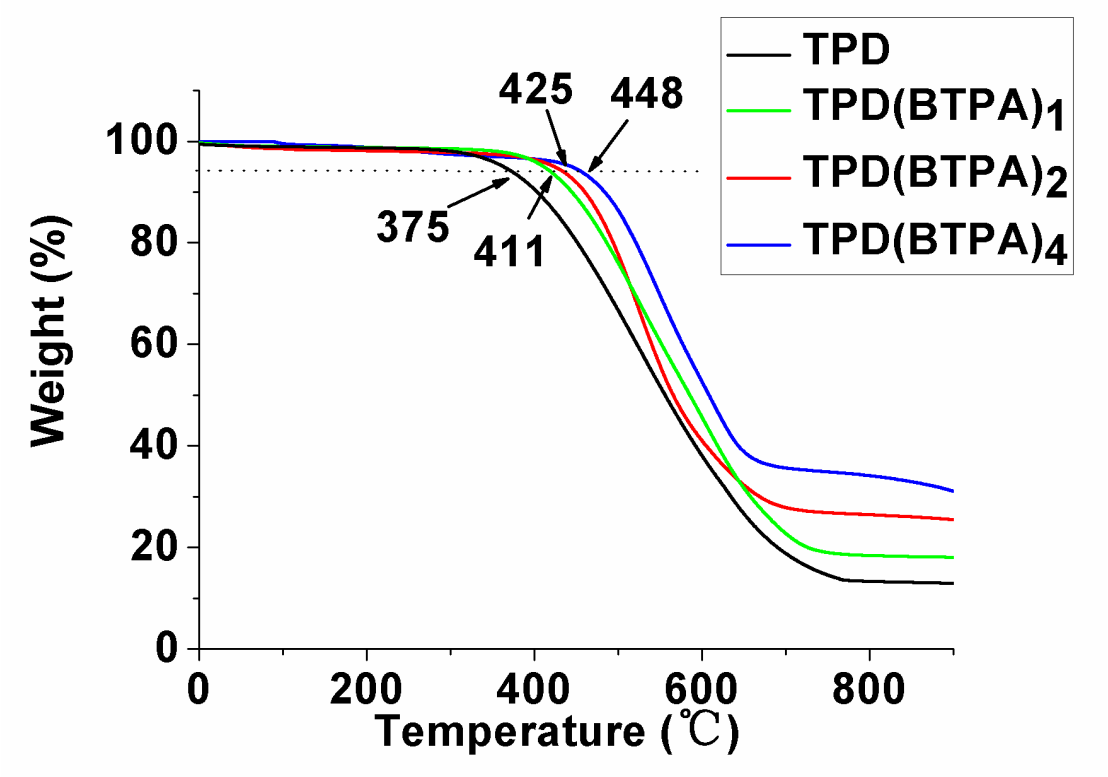


Fig. S10. TGA thermograms of TPD(BTPA)$_n$ (n=1,2,4)

Photophysical and Electrochemical Properties

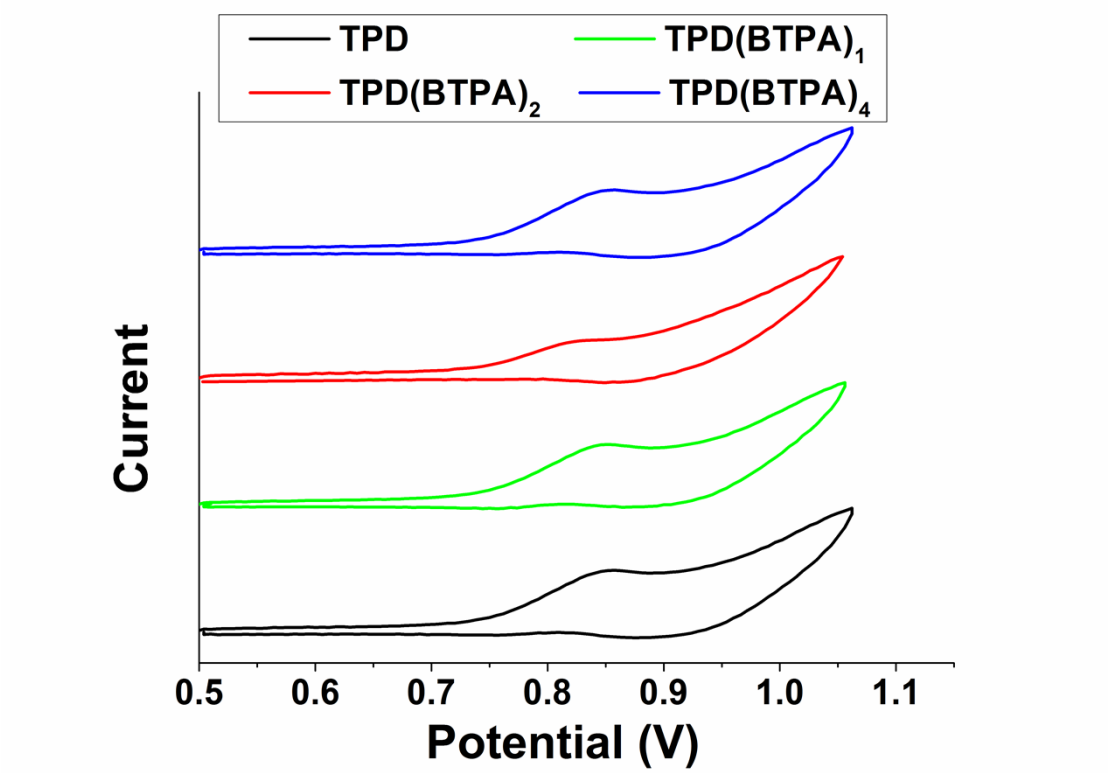


Fig. S11. Cyclic voltammograms of TPD(BTPA)$_n$ (n=0,1,2,4)

Hole Mobility Properties

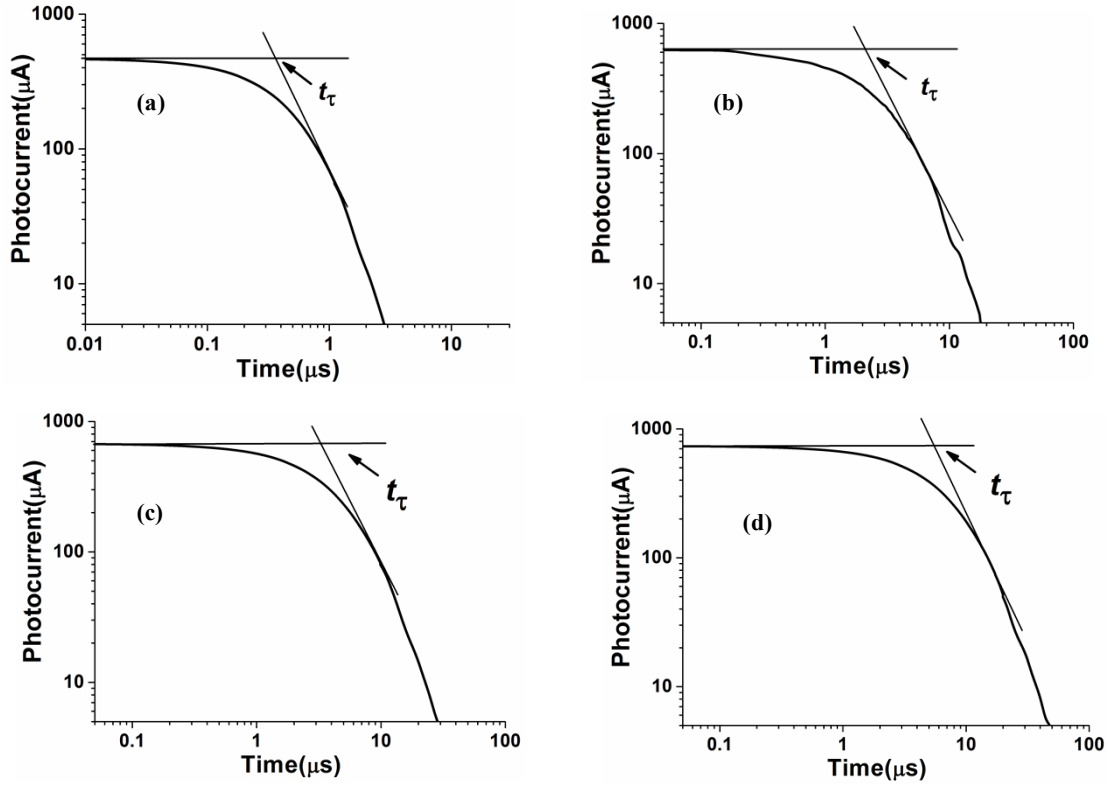


Fig. S12 TOF transients for TPD(a), TPD(BTPA)$_1$ (b), TPD(BTPA)$_2$ (c), TPD(BTPA)$_4$ (d) at room temperature.

Molecular Geometry

To get further insight into the effect of molecular structures and electron distributions of HTM, the geometries of the obtained compounds TM1wTM4 were optimized and their energies were estimated by density functional theory (DFT) calculation at the B3LYP/6-31G(d) level with Gaussian 03 program. [1]

Table S1. The optimized molecular structures and frontier molecular orbital of compounds TPD(BTPA)$_n$ (n=0,1,2,4)

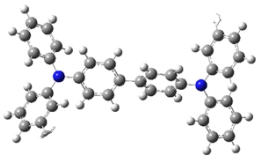
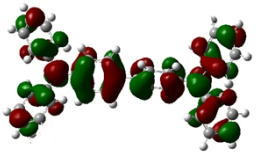
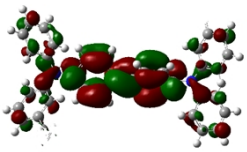
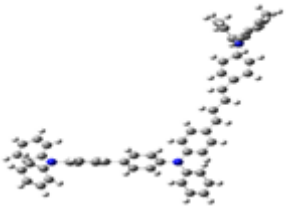
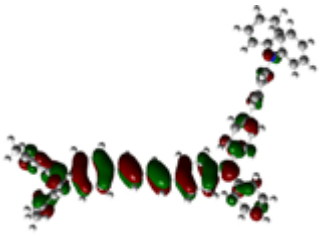
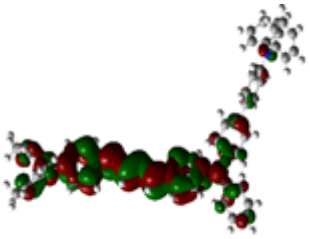
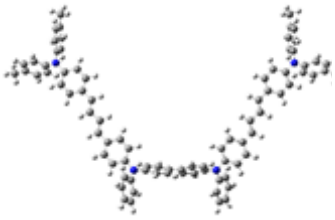
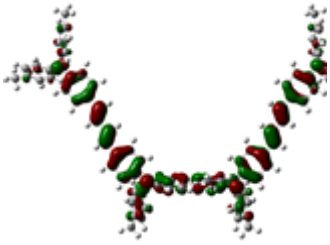
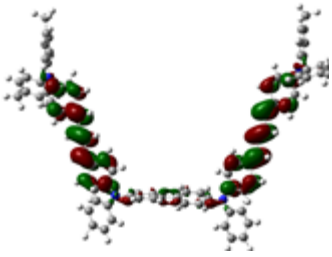
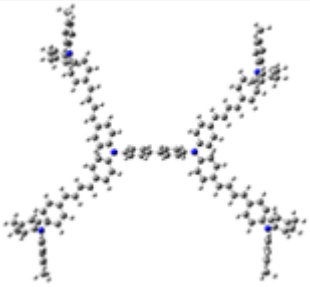
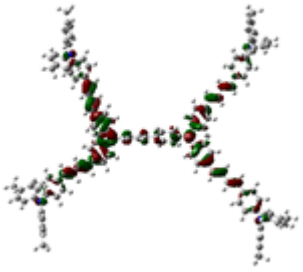
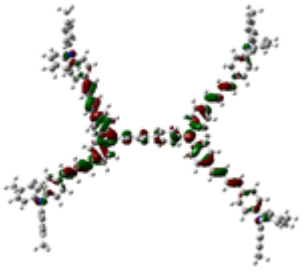
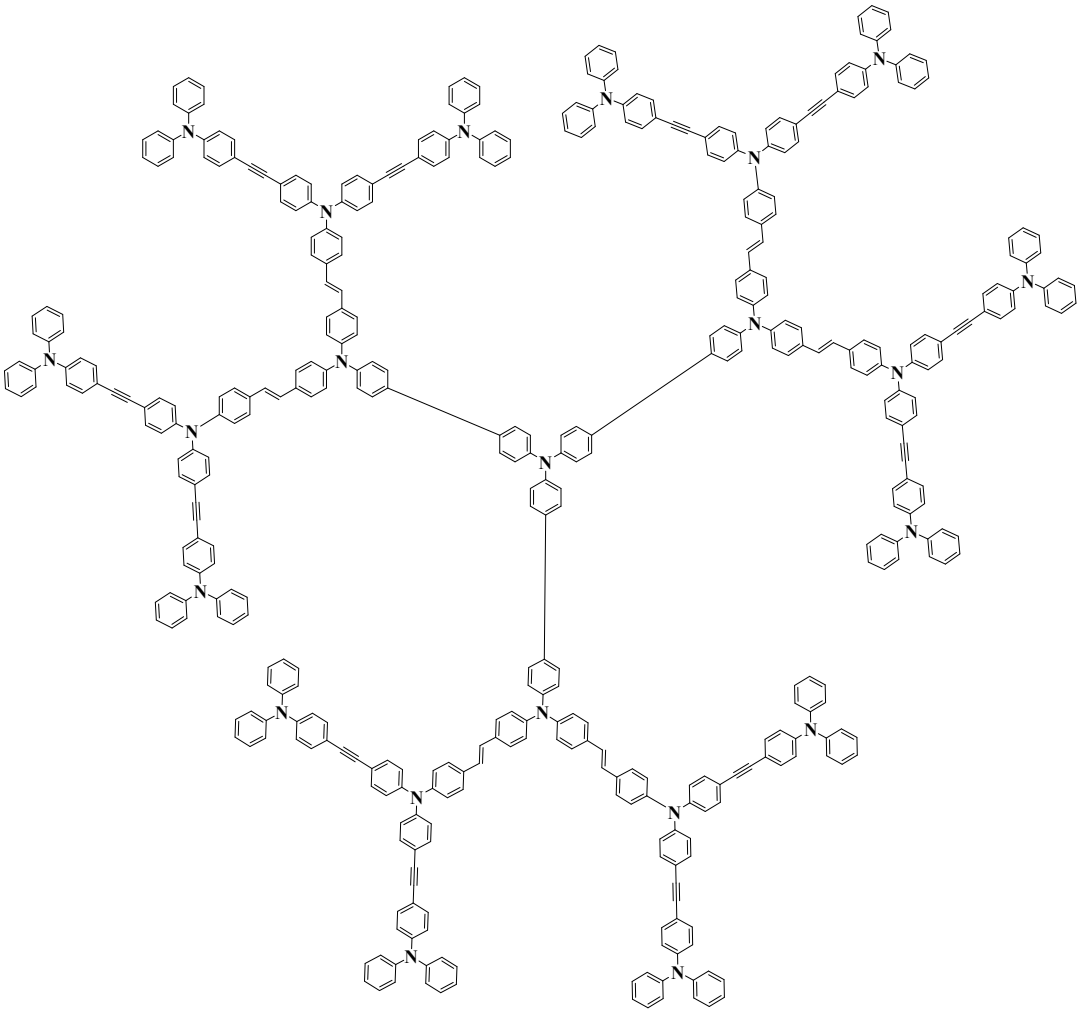
Compound	Opt Structure	HOMO	LUMO
TPD			
TPD(BTPA)$_1$			
TPD(BTPA)$_2$			
TPD(BTPA)$_4$			

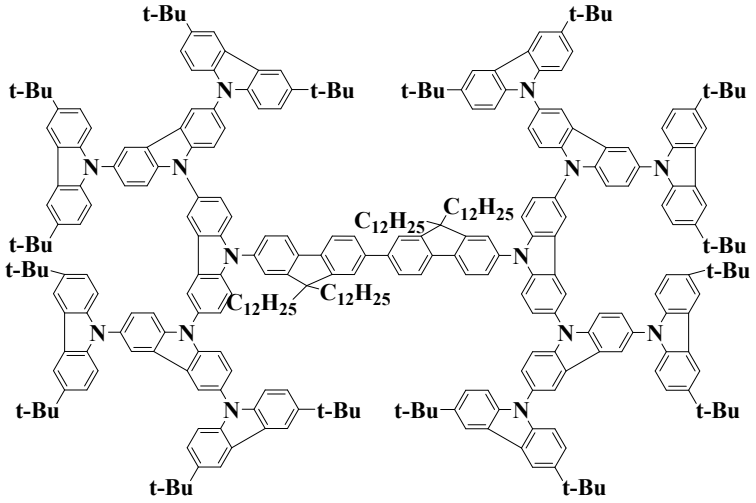
Table S2. The quantum chemistry calculational data of compounds $TPD(BTPA)_n$ (n=0,1,2,4)

Compound	HOMO(eV)	LUMO(eV)	E_g(eV)
TPD	-4.85	-1.40	3.45
$TPD(BTPA)_1$	-4.42	-1.44	2.98
$TPD(BTPA)_2$	-4.42	-1.46	2.96
$TPD(BTPA)_4$	-4.39	-1.49	2.90

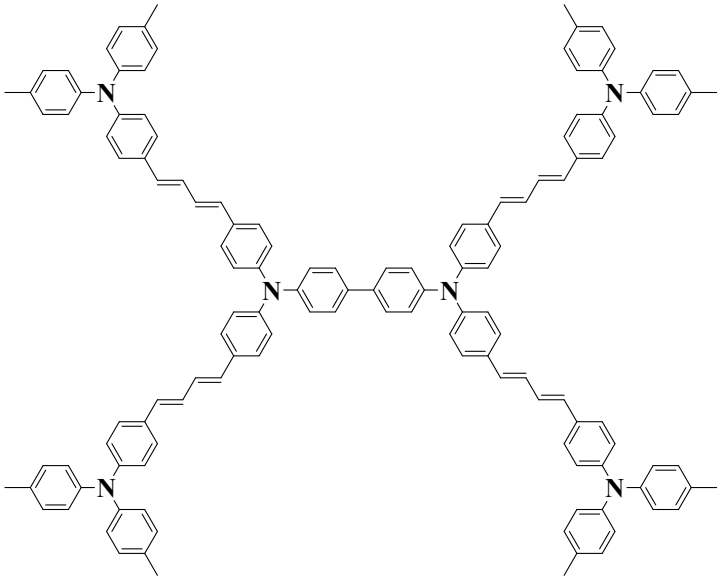
Hole Injection/Transport Properties in OLEDs



DT2[2]



G3F2[3]



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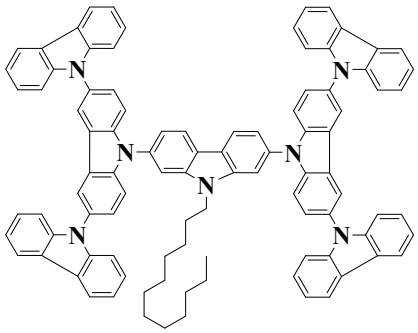

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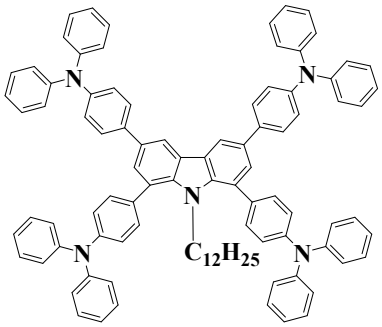

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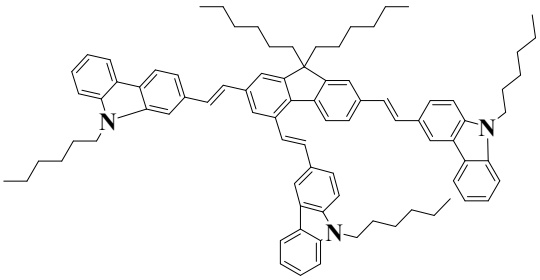
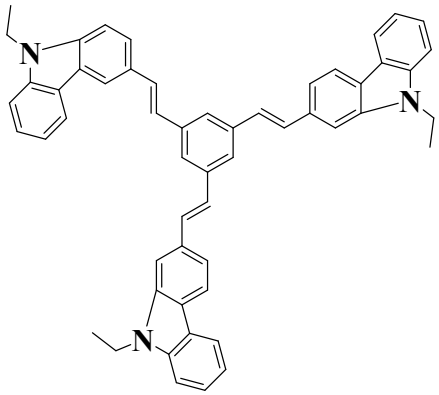


FC[6]



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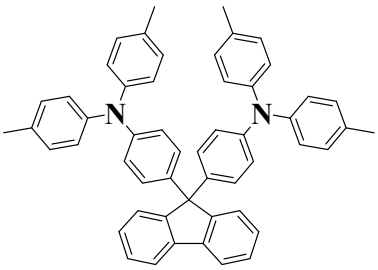

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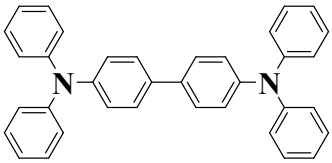

TPD[9]

Fig. S13. Molecular structure of HTMs

1. M. J. Frisch, *Chem Listy*, 2006, **100**, A9-A9.
2. Z. A. Li, T. L. Ye, S. Tang, C. Wang, D. G. Ma and Z. Li, *J Mater Chem C*, 2015, **3**, 2016-2023.
3. P. Moonsin, N. Prachumrak, S. Namuangruk, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk and V. Promarak, *J Mater Chem C*, 2014, **2**, 5540-5552.
4. N. Prachumrak, S. Pansay, S. Namuangruk, T. Kaewin, S. Jungsuttiwong, T. Sudyoadsuk and V. Promarak, *Eur J Org Chem*, 2013, **2013**, 6619-6628.
5. P. Kochapradist, N. Prachumrak, R. Tarsang, T. Keawin, S. Jungsuttiwong, T. Sudyoadsuk and V. Promarak, *Tetrahedron Lett*, 2013, **54**, 3683-3687.
6. C. S. Wu, S. W. Fang and Y. Chen, *Phys Chem Chem Phys*, 2013, **15**, 15121-15127.
7. J. Y. Li, D. Liu, Y. Q. Li, C. S. Lee, H. L. Kwong and S. T. Lee, *Chem Mater*, 2005, **17**, 1208-1212.
8. O. T. Okutsu S, Tamano M, et al, *Electron Devices*, 1997, **44**, 1302-1306.
9. S. Feng, L. Duan, L. D. Hou, J. Qiao, D. Q. Zhang, G. F. Dong, L. D. Wang and Y. Qiu, *J Phys Chem C*, 2011, **115**, 14278-14284.