Supporting Information

Synthesis of compounds

*Synthesis of 2,2'-bithiophene (**1**)*

2-bromothiophene (1) (14.5 g, 89 mmol), dichloro[1,3-bis(diphenylphosphino)propane] nickel (II) ($Ni(dppp)Cl_2$) (0.1 g) and 50 mL of freshly distilled THF were placed into a 250 mL flask under argon flux. To the reaction mixture 2-thienylmagnesium bromide [1] was dropwise added 2M solution in THF (44.5 mL, 89 mmol) at 0 °C. After addition, the solution was stirred for 2h at room temperature. Then 20 mL of 2M hydrochloric acid was added and the resulting mixture was extracted three times with 10 mL of chloroform. The combined organic layer was washed with $NaHCO_3$ and brine, and the organic layer was dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporation and pale yellow oil was distilled under reduced pressure giving 3.1 g of the pure title compound as a colorless solid at room temperature, with a 21 % yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25 (dd, 2H); 7.22 (dd, 2H); 7.07 (t, 2H) ppm.

*Synthesis of [2,2'-bithiophen]-5-yltriisopropylsilane (**2**)*

Solution of **1** (3.1 g, 18.6 mmol.) in THF (30 mL) was placed into a 100 mL three-neck round-bottom flask, which was previously evacuated/backfilled with argon three times. The flask was then cooled to -78 °C in an acetone bath, and 5.96 mL of 2M BuLi solution (14.9 mmol) in hexane was added dropwise. The reaction mixture was stirred at -60°C for 1 h. Then the solution of chlorotriisopropylsilane (3.57 g, 18.6 mmol) was added in one portion. The mixture was stirred at RT for 2 h. The solvent was removed at the rotary evaporator producing a viscous oily residue. The crude product was obtained with the yield of 52% (3.1 g) and used in the next step without purification. ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.29 (d, 1H); 7.23 (s, 1H); 7.22 (m, 1H); 7.18 (d, 1H); 7.03 (m, 1H), 1.40-1.33 (m, 3H), 1.16 (d, 18H) ppm.

*Synthesis of triisopropyl(5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)silane (**3**)*

Compound **3** was synthesized following the method described for compound **2** using [2,2'-bithiophen]-5-yltriisopropylsilane (3 g, 9.3 mmol), 5.57 mL of 2 M BuLi in hexane (13.9 mmol), and trimethylchlorostannane (3.15 g, 15.8 mmol). The target compound was obtained with the yield of 90% (4.06 g). ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.33 (d, 2H), 7.28 (d, 1H), 7.18 (d, 1H), 7.11 (d, 1H), 7.39-7.33 (m, 3H), 1.15 (d, 18H), 0.41 (s, 9H) ppm.

*Synthesis of **TPA-TT***

The solutions of tris(4-bromophenyl)amine (0.3 g, 0.62 mmol) and compound **3** (1.51 g, 3.12 mmol) in toluene were placed into the three-necked round-bottom flask. The mixture was degassed and purged with argon for 30 min. $Pd(OAc)_2$ (0.007 g, 0.031 mmol) and PPh_3 (0.032 g, 0.124 mmol) was added under argon. The mixture was heated at reflux for 24h, and then cooled to the room temperature. The solvent was removed by evaporation under reduced pressure. The residue was further purified by column chromatography on silica gel with a mixture of hexane-toluene (v/v= 8: 2) as an eluent to yield the compound **TPA-TT** as pale yellowish solid. The yield was of 85%. The purity according HPLC analysis was 98%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.54-7.53 (m, 6H); 7.31 (d, 3H); 7.19 (m, 9H); 7.18-7.16 (m, 6H); 1.42-1.33 (m, 9H); 1.16 (d, 54H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 142.62, 142.39, 136.44, 136.23, 133.70, 129.09, 129.04, 128.23, 126.52, 124.63, 124.50, 124.46, 123.15, 18.60, 11.80 ppm.

*Synthesis of **PhFF-TT***

Compound **PhFF-TT** was synthesized and purified following the method described for compound **TPA-TT** using 1,3,5-tribromo-2,4,6-trifluorobenzene (0.2 g, 0.54 mmol), compound **3** (1.32 g, 2.7 mmol), $Pd(OAc)_2$ (0.007 g, 0.031 mmol) and PPh_3 (0.032 g, 0.124 mmol). The yield of **PhFF-TT** was of 79% (0.47 g). The purity according HPLC analysis was 96.8%. ^1H NMR ($CDCl_3$, 500 MHz, δ): 7.48 (d, 2H); 7.36 (d, 2H); 7.29 (d, 2H); 7.22 (d, 2H); 1.41-1.35 (m, 9H); 1.16 (d, 54H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 141.59, 139.34, 136.49, 134.61, 130.56, 129.05, 128.24, 126.68, 125.16, 123.55, 18.59, 11.80 ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, δ): -108.17 (3F) ppm.

*Synthesis of **DPAMes-TT***

Compound **DPAMes-TT** was synthesized and purified following the method described for compound **TPA-TT** using N,N-bis(4-bromophenyl)-2,4,6-trimethylaniline (0.24 g, 0.55 mmol), compound **3** (0.8 g, 1.64 mmol), $Pd(OAc)_2$ (0.007 g, 0.031 mmol) and PPh_3 (0.032 g, 0.124 mmol). The yield of **DPAMes-TT** was of 82% (0.42 g). The purity according HPLC analysis was 97.6%. ^1H NMR ($CDCl_3$, 500 MHz, δ): 7.45 (d, 4H); 7.18 (d, 2H); 7.16 (d, 2H); 7.13 (d, 2H); 7.02-6.99 (m, 8H); 2.37 (s, 3H); 2.05 (s, 6H); 1.40-1.34 (m, 6H); 1.15 (d, 36H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 145.16, 143.12, 142.54, 139.42, 137.49, 137.22, 136.41, 135.58, 133.43, 130.06, 128.23, 129.95, 126.39, 124.59, 124.34, 122.47, 119.86, 18.60, 11.80 ppm.

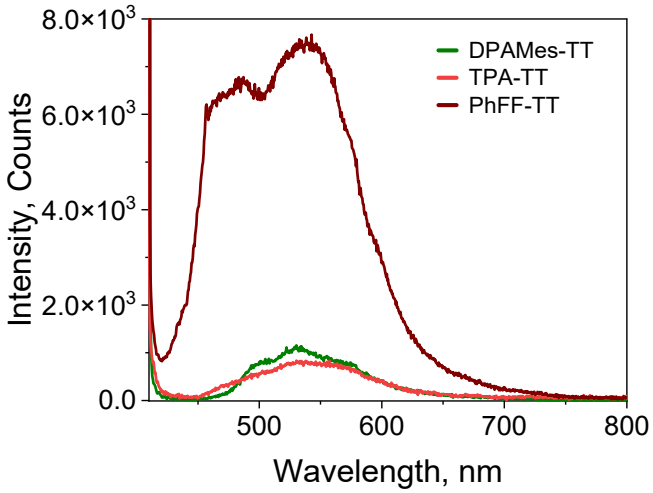

Figure S1. Photoluminescence (PL) Spectra of DPAMes-TT, TPA-TT, and PhFF-TT Thin Films

Table S1. TRPL Decay Parameters of $MAPbI_3$ and Perovskite/HTM Bilayer Films with DPAMes-TT, TPA-TT, and PhFF-TT:

HTM	A1	A2	τ1 (ns)	Δτ1 (ns)	τ2 (ns)	Δτ2 (ns)	R^2
$MAPbI_3$	0.89	0.11	25.09	0.60	109.60	3.58	0.92
DPAMes-TT	0.86	0.14	9.29	0.30	112.47	1.55	0.95
TPA-TT	0.81	0.19	11.15	0.39	102.27	1.27	0.96
PhFF-TT	0.50	0.50	18.46	1.13	91.10	0.94	0.98

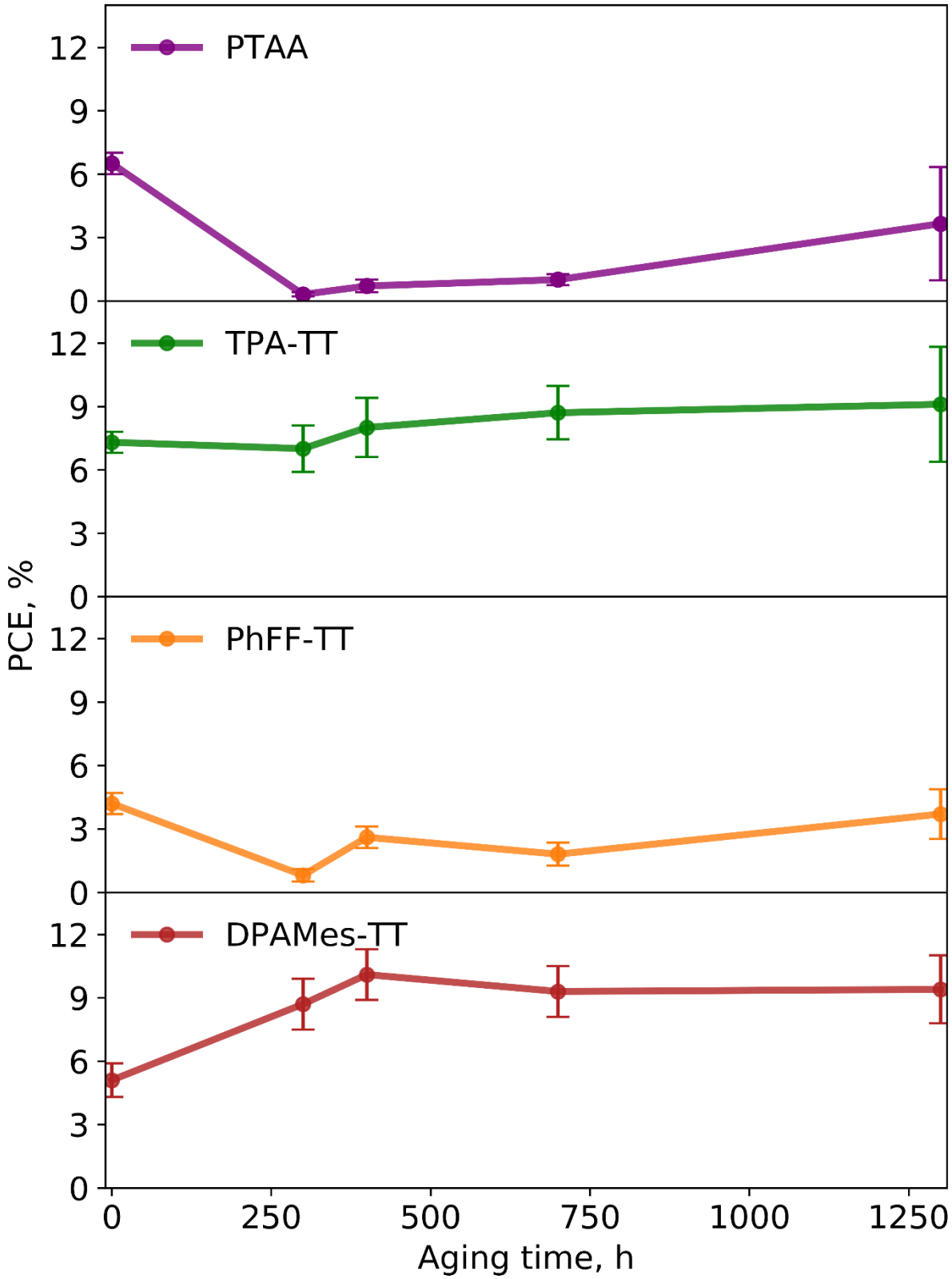

Figure S2. Long-term stability of unencapsulated devices (ITO/ZnO/MAI/PCBA/CsFAPbI3/HTM/VO_x/Al) under continuous illumination in a glovebox, comparing DPAMes-TT, TPA-TT, PhFF-TT, and PTAA as hole transport materials.

Table S2. Comparison of HTM Performance in n-i-p Perovskite Solar Cells with Relevant Literature

Device architecture	***PCE, %***	***DOI***
ITO/SnO_2/ $FA_{0.9}MA_{0.05}Cs_{0.05}Pb(I_{0.95}Br_{0.05})_3$/HTM/$MoO_3$/Ag	*18.3*	*https://doi.org/10.1002/cssc.202301489*
FTO/ TiO_2/Pero/PTAA+Li-TFSI/Au	*18.8*	*https://doi.org/10.1039/D4TA02036G*
ITO/SnO_2/$MAPbI_3$/PTAA+Li-TFSI /Au	*19.2*	*https://pubs.acs.org/doi/10.1021/jacs.1c05122*
FTO/c-TiO_2/m-TiO_2/$CH_3NH_3PbI_3$/ PTAA w/o-dopant/Au	*12.7*	*https://doi.org/10.1039/C8EE00036K*
FTO/SnO2/$Cs_{0.05}FA_{0.95}PbI_3$/ Spiro-OMeTAD w/o-dopant /Au	*16,7*	*https://doi.org/10.1002/anie.202320152*
FTO/SnO2/ $Cs_{0.05}FA_{0.95}PbI_3$/ Py-DB /Au	*24,3*	*https://doi.org/10.1002/anie.202320152*
ITO/SnO2/ $Cs_{0.05}FA_{0.95}PbI_3$/ DTTP-ThSO/MoO3/Ag	*23,3*	*https://doi.org/10.1002/anie.202403083*
ITO/SnO2/ $FA_{0.9}MA_{0.1}Pb(I_{0.95}Cl_{0.05})_3$/ BDT-DPA-F/$MoO_3$/Ag	*23.1*	*https://doi.org/10.1002/anie.202210613*
ITO/SnO_2/PCBA/$MAPbI_3$/ ***DPAMes-TT*** */MoO_x/Ag*	*19,5*	***This work***

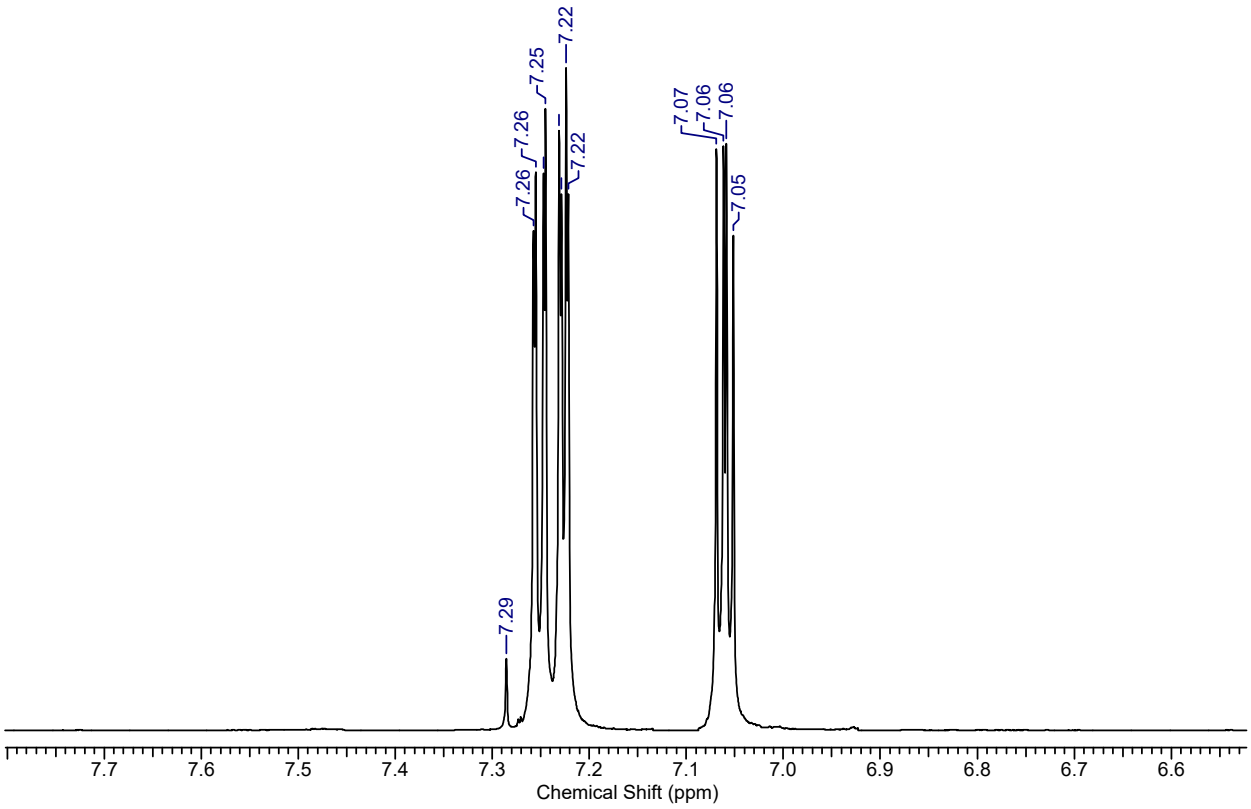

Figure S3. ^{1}H NMR spectrum of compound **1**

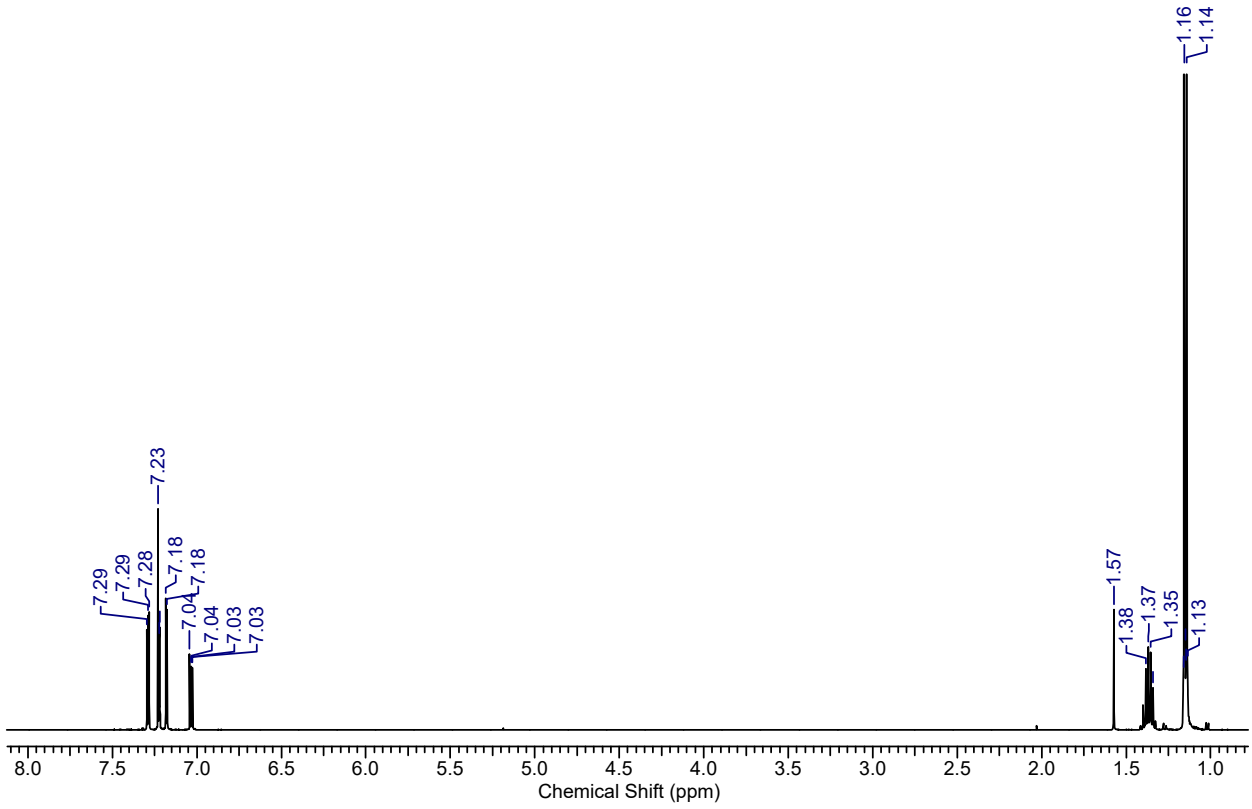

Figure S4. ^{1}H NMR spectrum of compound **2**

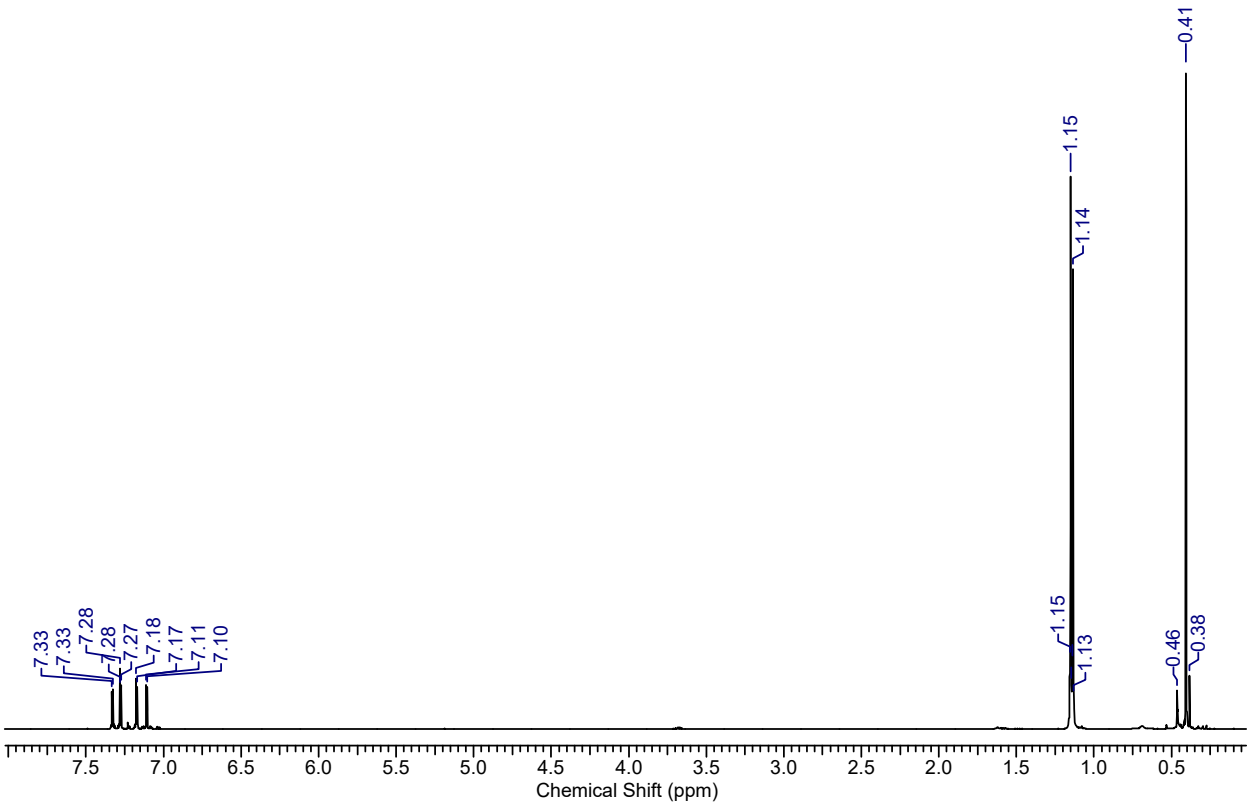

Figure S5. ^{1}H NMR spectrum of compound **3**

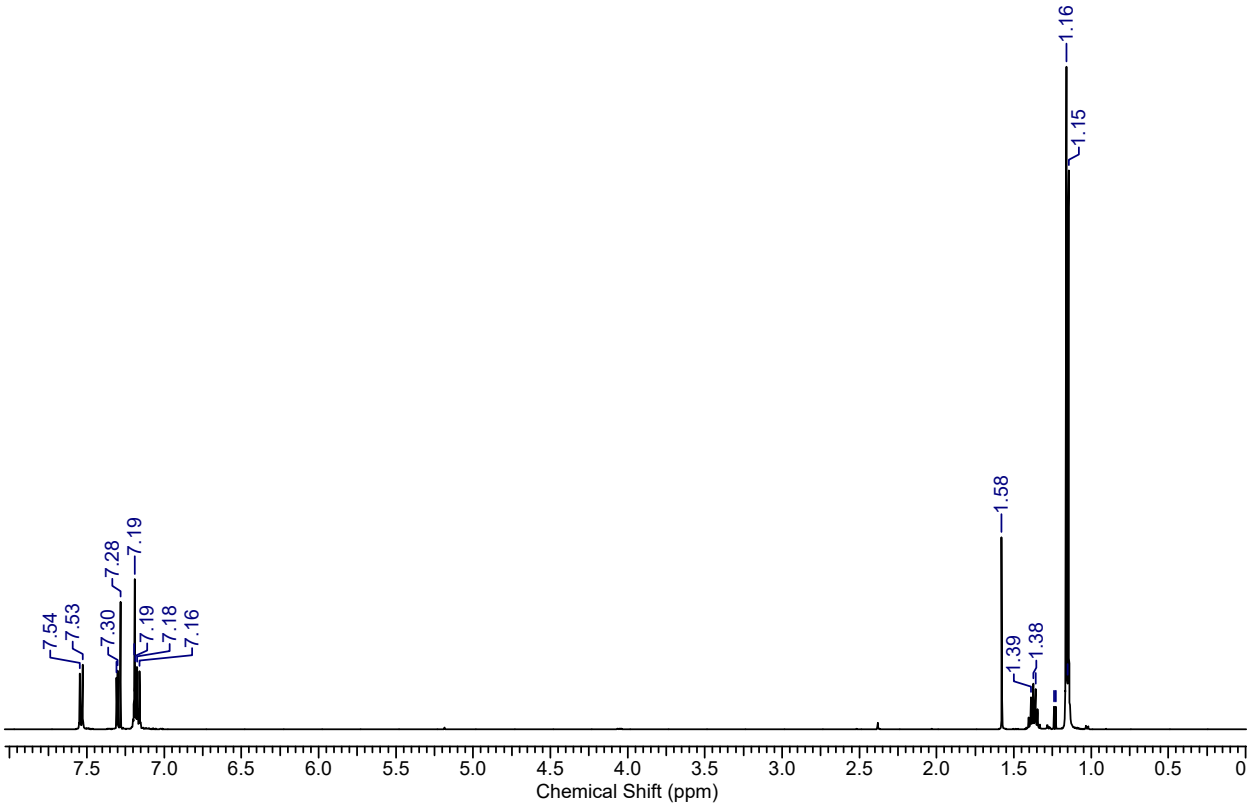

Figure S6. ^{1}H NMR spectrum of compound **TPA-TT**

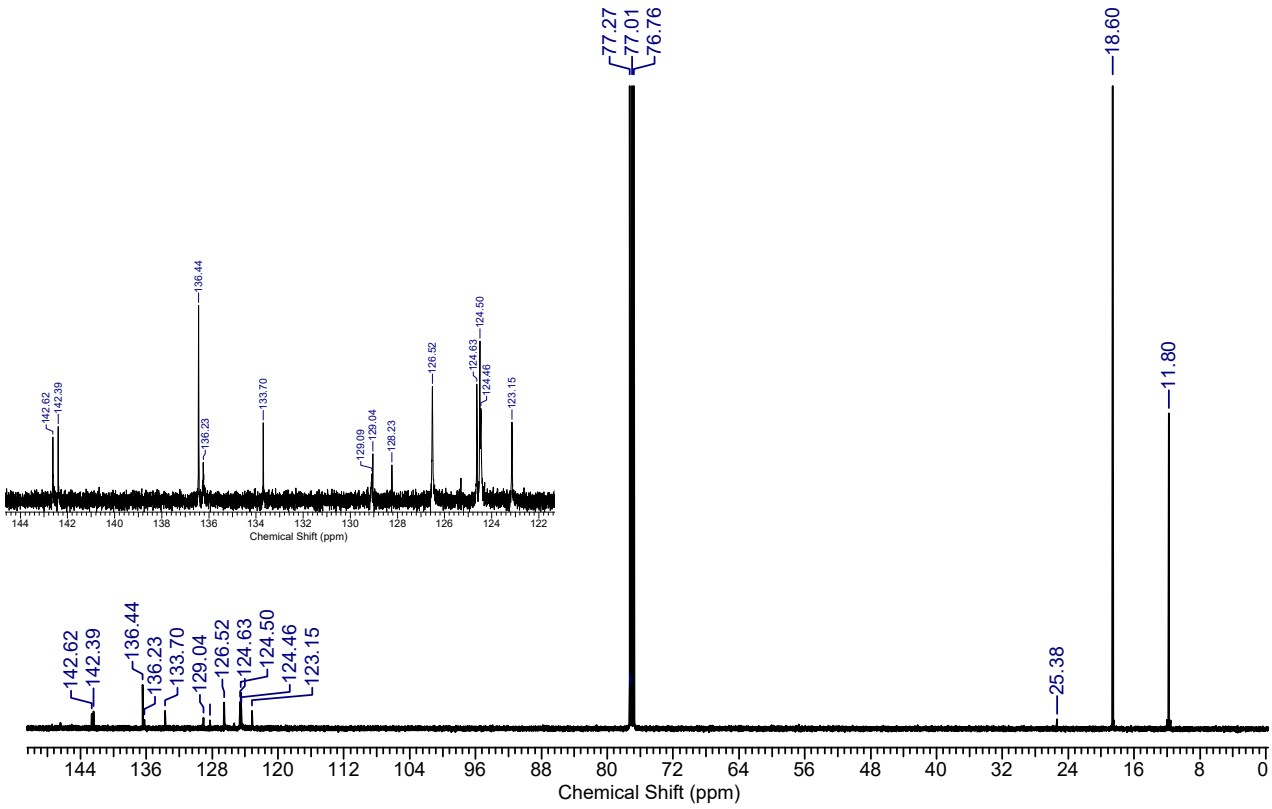

Figure S7. ^{13}C NMR spectrum of compound **TPA-TT**

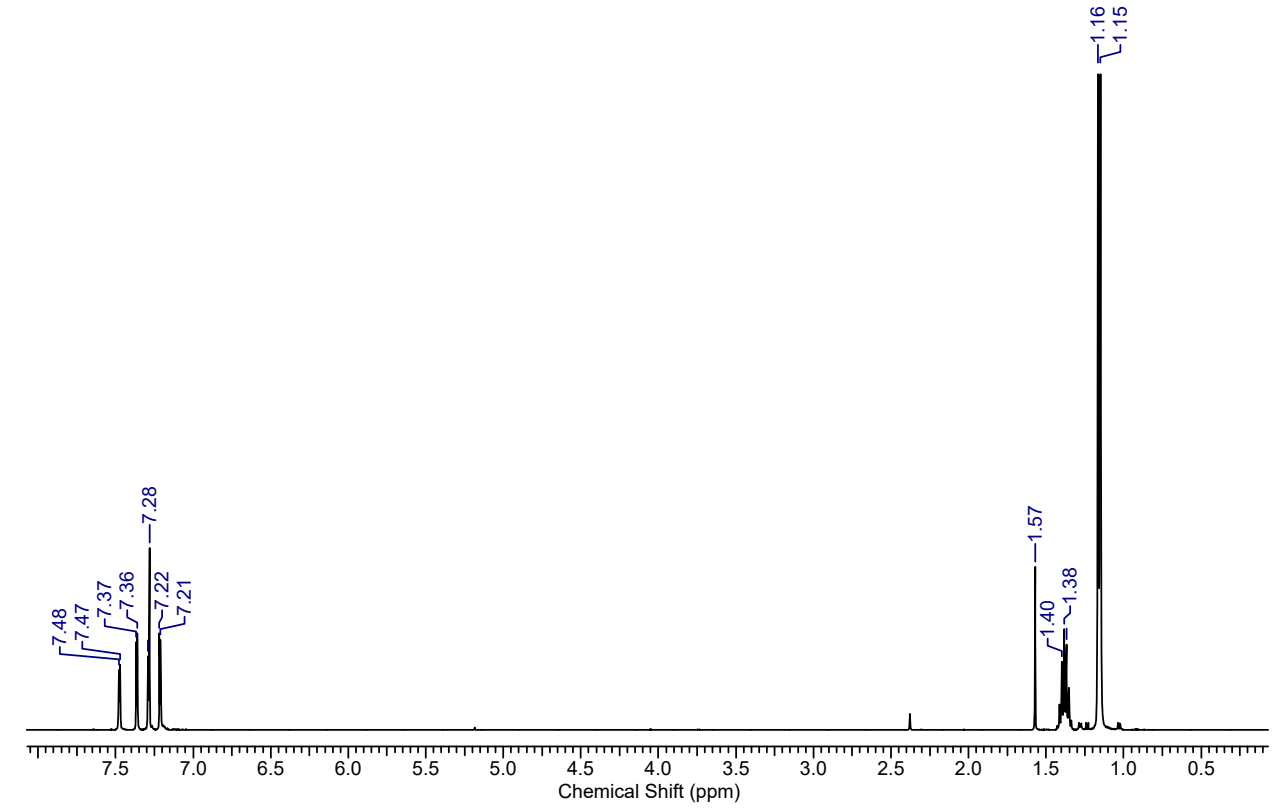

Figure S8. ^{1}H NMR spectrum of compound **PhFF-TT**

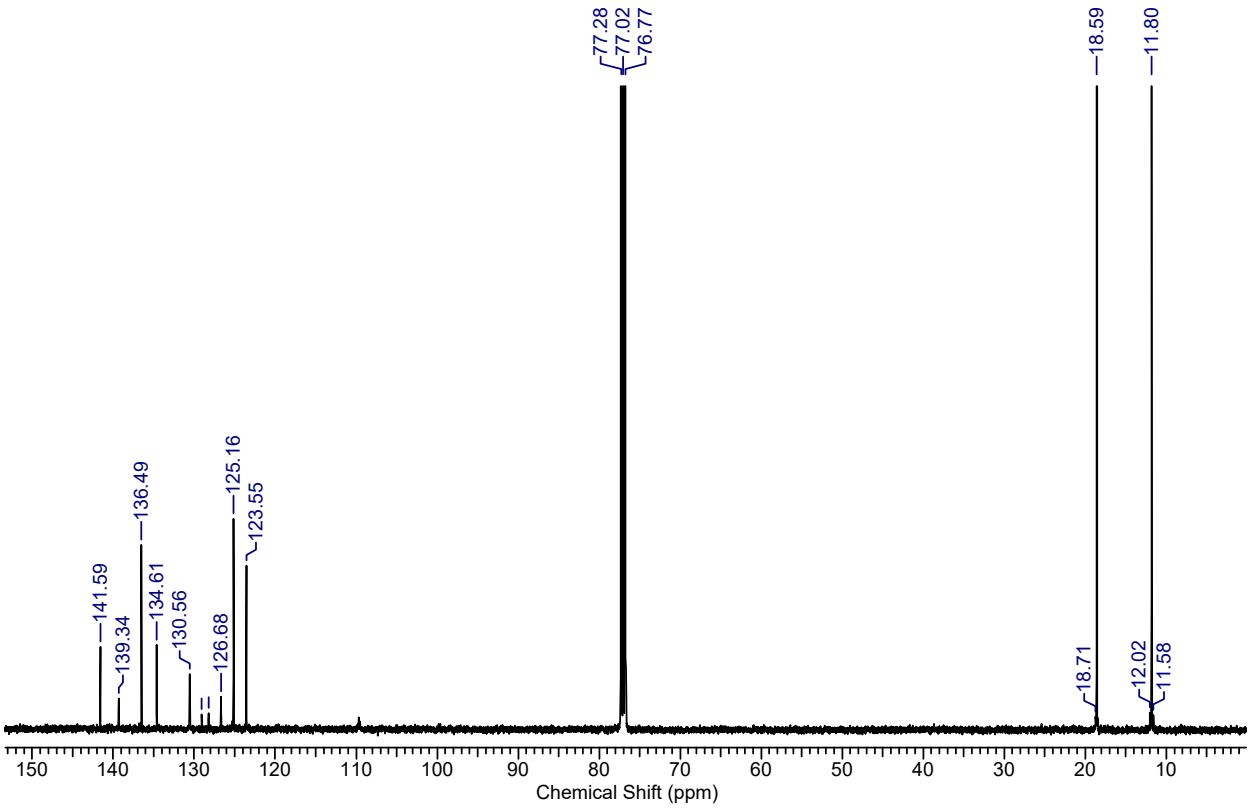

Figure S9. ^{13}C NMR spectrum of compound **PhFF-TT**

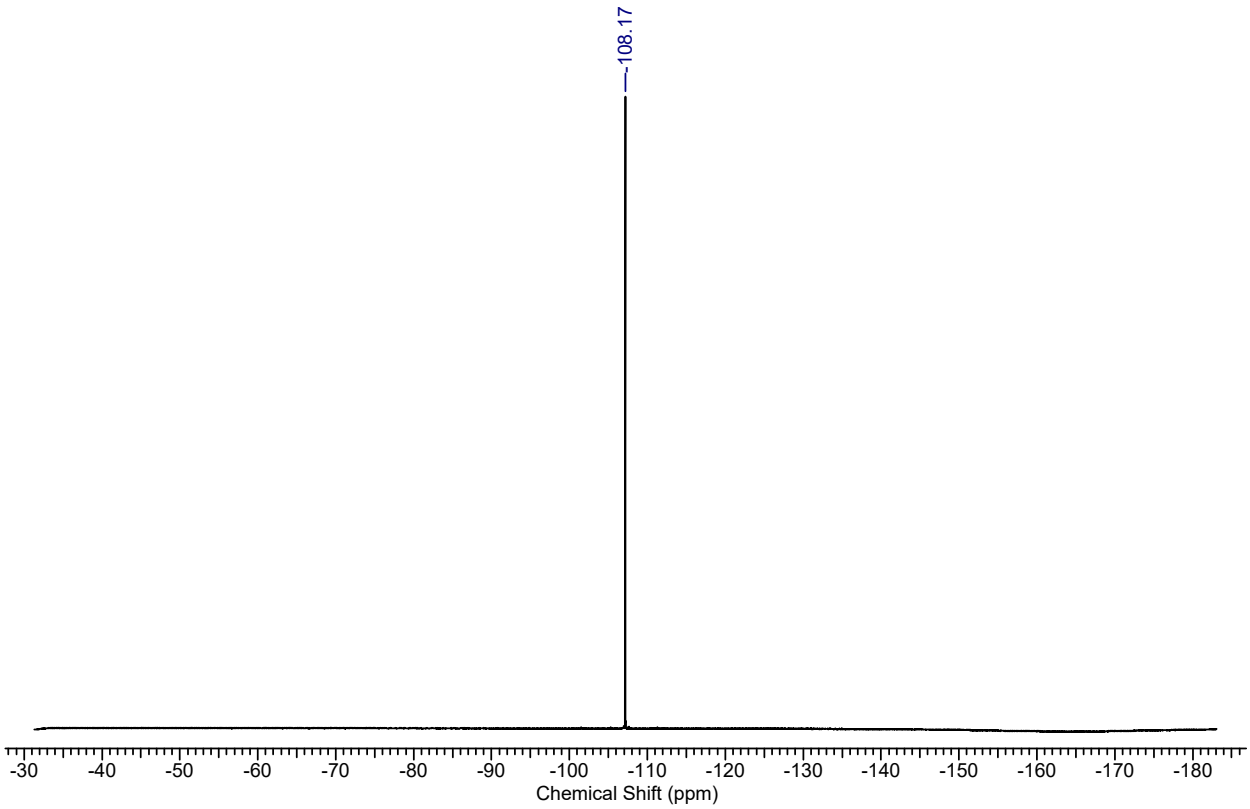

Figure S10. ^{19}F NMR spectrum of compound **PhFF-TT**

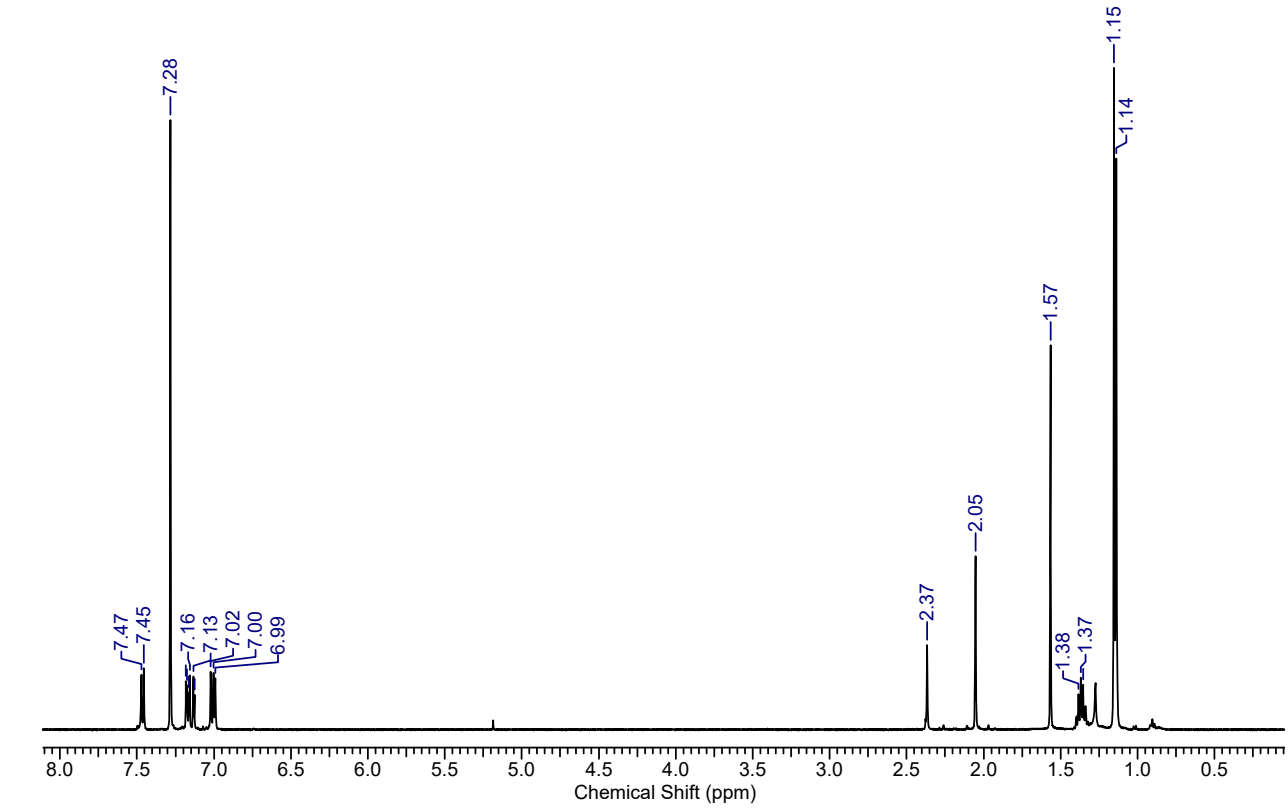

Figure S11. ^{1}H NMR spectrum of compound **DPAMes-TT**

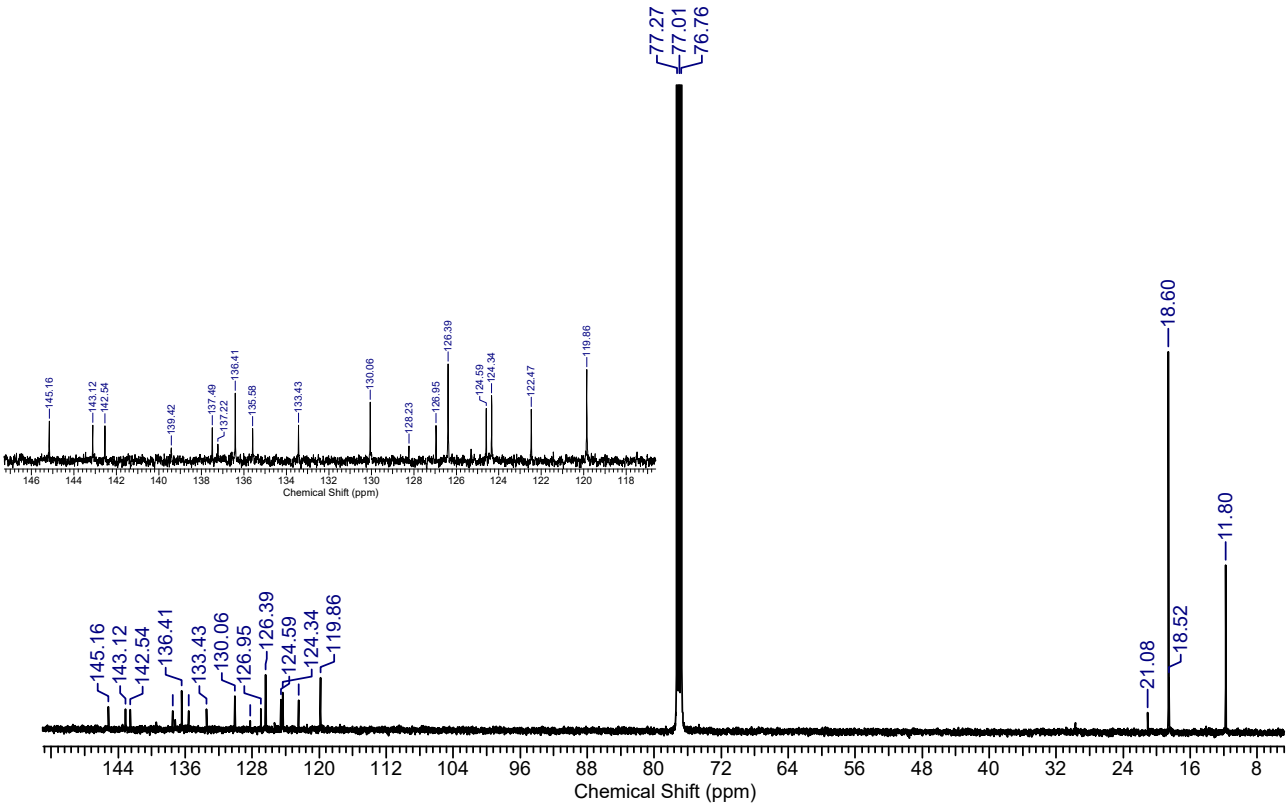

Figure S12. ^{13}C NMR spectrum of compound **DPAMes-TT**

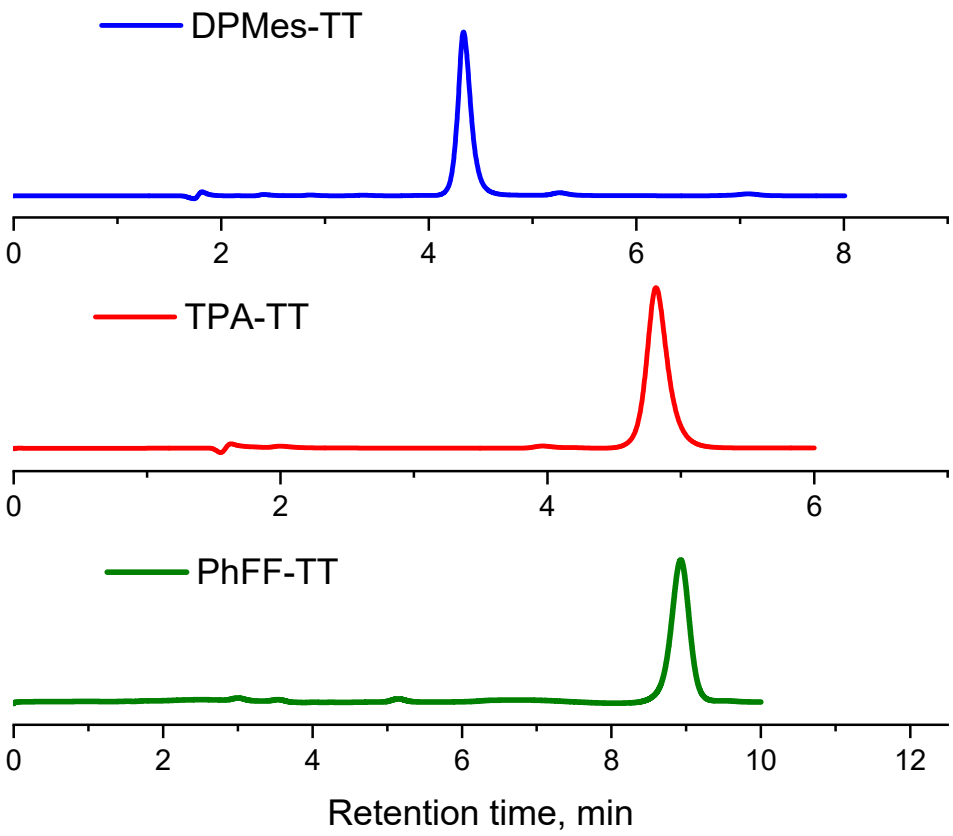

Figure S13. HPLC chromatograms of **TPA-TT**, **PhFF-TT**, and **DPAMes-TT.** Conditions: Orbit C18, 150*4.6 mm, 5um, 100A; 290 nm; 40°; acetonitrile:toluene (70:30), 1 mL/min.