Supporting Information

Conjugated Small Molecules Based on Alkylsilyl-Modified Triphenylamine: A Promising Hole Transport Materials in Perovskite Photovoltaics

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Materials and methods

All solvents and reagents were purchased from Merk, Macklin or Acros Organics and used as received or purified according to standard procedures.

The ^{1}H and ^{13}C spectra were obtained using Bruker AVANCE 500 instrument (Figure S1-S10).

FTIR-ATR spectra were recorded in the 500–4000 cm^{-1} range (48 scans, resolution 4 cm^{-1}) using a Bruker ALPHA (Figures S11-S12).

Chemical analysis was performed using Vario El Cube instrument.

Tris(4-bromophenyl)amine (compound 1)

Compound 1 was prepared according to previously reported method.[1] Triphenylamine (1.0 g, 4 mmol) was dissolved in 20 mL of *N,N*-dimethylformamide and *N*-bromosuccinimide (0.726 g, 12 mmol, 3 eq.) was added in small portions. The mixture was stirred at room temperature for 6 hours, then poured into water. The precipitated white crystals were filtered, recrystallized from toluene and dried in air. Yield =98%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.34 (d, 6H); 6.91 (d, 6H).

Tris(4-(thiophen-2-yl)phenyl)amine (compound 2)

Compound 2 was prepared according to previously reported method.[2] Solution of compound **1** (1.93 g, 4 mmol) in *N,N*-dimethylformamide (20 mL) was placed into 50 mL three-neck round-bottom flask equipped with reversed condenser. Then tributyl(thiophen-2-yl)stannane (4.48 g, 12 mmol, 3 eq.), and $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) were added. The reaction mixture was stirred at 150°C for 12h under inert atmosphere. The mixture was cooled down to room temperature and the solvent was removed at the rotary evaporator. Purification was carried out using column chromatography using hexane as eluent. The yield of pure compound was 80%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.54 (d, 3H); 7.29 (d, 3H); 7.16 (d, 6H); 7.10 (t, 3H).

Tris(4-(5-(triisopropylsilyl)thiophen-2-yl)phenyl)amine (TPA-t)

Compound TPA-t was prepared according to previously reported method.[2] Tris(4-(thiophen-2-yl)phenyl)amine (1.48 g, 3 mmol) was dissolved in 100 mL anhydrous THF in two-necked round-bottom flask under inert atmosphere. The mixture was cooled down to -78°C in acetone bath and 1.6 mL (4 mmol, 2.5 M in hexane) of n-BuLi was added dropwise through septum. After stirring at 0°C for 1h, 0.62 g (0.772 g, 4 mmol) chlorotriisopropylsilane was added slowly and the mixture stirred two hours at room temperature. The reaction was quenched with 25 mL

water and extracted with ethylacetate in the separating funnel. The organic solution was dried over $MgSO_4$, filtrated, and solvent was removed at the rotary evaporator. The crude product was purified by column chromatography, using hexane, which resulted in a pale yellow solid with a yield of 83%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.58 (d, 6H); 7.38 (d, 3H); 7.27 (d, 3H); 7.16 (d, 6H); 1.45 - 1.38 (m, 9H); 1.18 (d, 54H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 149.11; 146.45; 136.74; 133.35; 129.31; 126.86; 124.37; 123.52; 18.65; 11.84. FT-IR (KBr, ν): 2944, 2860, 1600, 1527, 1495, 1459, 1426, 1378, 1326, 1281, 1173, 1072, 992, 939, 878, 827, 790, 722, 677, 654, 573, 517 cm^{-1}.Chemical analysis (%) for $C_{57}H_{81}N_1S_3Si_3$: C, 71.26; H, 8.50; N, 1.46; S, 10.01; found C, 71.48; H, 8.62; N, 1.41; S, 10.11

3-(2-ethylhexyl)thiophene (compound 3)

Compound 3 was prepared in the similar way reported previously for 3-decylthiophene.[3] 3-bromothiophene (1) (56.2 g, 345 mmol), dichloro[1,3-bis(diphenylphosphino)propane] nickel (II) (Ni(dppp)Cl_2) (1.9 g, 0.01 eq.) and 100 mL of freshly distilled THF were placed into a 500 mL flask under argon flux. To the reaction mixture 2M (2-ethylhexyl)magnesium bromide solution in THF (172.5 mL 345 mmol) was added dropwise at 0 °C. The brown 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 50 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 (1 mm Hg) giving 41 g of the pure title compound as a colorless oil. The yield was of 62 %. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.16 (d, 1H), 6.75 (d, 1H), 2.48 (d, 2H), 1.57 (m, 1H), 1.40-1.15 (m, 8H), 0.85 (t, 6H).

2-bromo-3-(2-ethylhexyl)thiophene (compound 4)

Compound 4 was prepared in the similar way reported previously for 2-bromo-decylthiophene .[3] *N*-bromosuccinimide (NBS) (121 mmol, 21.5 g) was added portionwise to a solution of 3-(2-ethylhexyl)thiophene (127 mmol, 25 g) in 100 mL mixture of chloroform and acetic acid (1:1 (v/v)), at 5 °C. The mixture was stirred at room temperature for 60 min. Then, 200 mL of H_2O was added, the chloroform layer was separated and washed with saturated solution of $NaHCO_3$ and distilled water. Organic solution was dried over Na_2SO_4, filtered and the solvent was removed by rotary evaporation to afford 33 g of product as a colorless oil. The yield of compound **4** was 94%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.21 (d, 1H); 6.80 (d, 1H); 2.54 (d, 2H); 1.67 - 1.62 (m, 1H); 1.35 - 1.22 (m, 8H); 0.94 (t, 6H).

(3-(2-ethylhexyl)thiophen-2-yl)triisopropylsilane (compound 5)

Compound 5 was prepared in the similar way reported previously.[4] Solution of **4** (5 g, 18 mmol) in THF (70 mL) was placed into a 250 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 2.5 M BuLi (18 mmol, 7.26 mL) was added dropwise. The reaction mixture was stirred at -60°C for 2 h. Then the solution of chlorotriisopropylsilane (3.82 g, 19.8 mmol) was added in one portion. The mixture was stirred at room temperature for 2 h. Then the solvent was removed using a rotary evaporator, producing a viscous oil, which was then distilled under reduced pressure (1 mm Hg) to give 4.82 g of the pure title compound as a colorless liquid with a yield of 76%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.50 (d, 1H); 7.08 (d, 1H); 2.61 (d, 2H); 1.75 - 1.72 (m, 1H); 1.45 - 1.38 (m, 3H); 1.35 - 1.22 (m, 8H); 1.12 (d, 18H); 0.87 (t, 6H).

(3-(2-ethylhexyl)-5-(trimethylstannyl)thiophen-2-yl)triisopropylsilane (compound 6)

Compound 6 was prepared according to the procedure reported previously.[4] (3-(2-ethylhexyl)thiophen-2-yl)triisopropylsilane (3.52 g, 10 mmol) in THF (50 mL) was placed into a 100 mL two-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 2.5 M BuLi (10 mmol, 4 mL) was added dropwise. The reaction mixture was stirred at 0°C for 2 h. Then the solution of chlorotrimethylstannane (2.19 g, 11 mmol) in THF (5 mL) was added in one portion. The mixture was stirred at room temperature for 2 h. The solvent was removed at the rotary evaporator producing a viscous oily residue. The crude product was used in the next step without further purification. The yield of **6** was 90%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm) 7.18 (s, 1H); 2.70 (d, br, 2H); 1.65(m, 1H); 1.25-1.45 m (8H); 1.12 (m, 21H); 0.91 (m, 6H); 0.37 (s, 9H)

Tris(4-(4-(2-ethylhexyl)-5-(triisopropylsilyl)thiophen-2-yl)phenyl)amine (TPA-t EH)

Solution of compound **1** (0.48 g, 1 mmol, 1 eq.) in *N,N*-dimethylformamide (20 mL) was placed into 50 mL three-neck round-bottom flask equipped with reversed condenser and thermometer. Then compound **6** (1.55 g, 3 mmol, 3 eq.), and $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) were added. The reaction mixture was stirred at 150°C for 12h under inert atmosphere. The mixture was cooled down to room temperature and the solvent was removed at the rotary evaporator. The crude product was dissolved in 10 mL of toluene and filtered through a syringe filter (PTFE, 0.45

μm). The solution was processed further using a preparative Phenogel GPC column (21.2 mm × 300 mm) and acetonitrile as eluent. The yield of TPA-t EH was 69%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.49 (d, br, 6H); 7.22 (s, 3H); 7.08 (s, br, 6H); 2.58 (d, 6H); 1.77 - 1.75 (m, 3H); 1.45 - 1.38 (m, 9H); 1.35 - 1.22 (m, 24H); 1.12 (d, 54H); 0.87 (m, 18H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 150.94; 147.47; 146.35; 129.39; 128.35; 126.58; 125.49; 124.29; 40.16; 36.72; 32.94; 29.12; 26.13; 23.08; 19.06; 14.15; 13.10; 11.18. FT-IR (KBr, ν): 2960, 2924, 2867, 1600, 1495, 1454, 1410, 1374, 1322, 1285, 1265, 1180, 1032, 943, 878, 823, 669, 645, 570, 517 cm^{-1}.Chemical analysis (%) for $C_{81}H_{129}N_1S_3Si_3$: C, 74.99; H, 10.02; N, 1.08; S, 7.41; found C, 75.07; H, 10.14; N, 1.00; S, 7.52

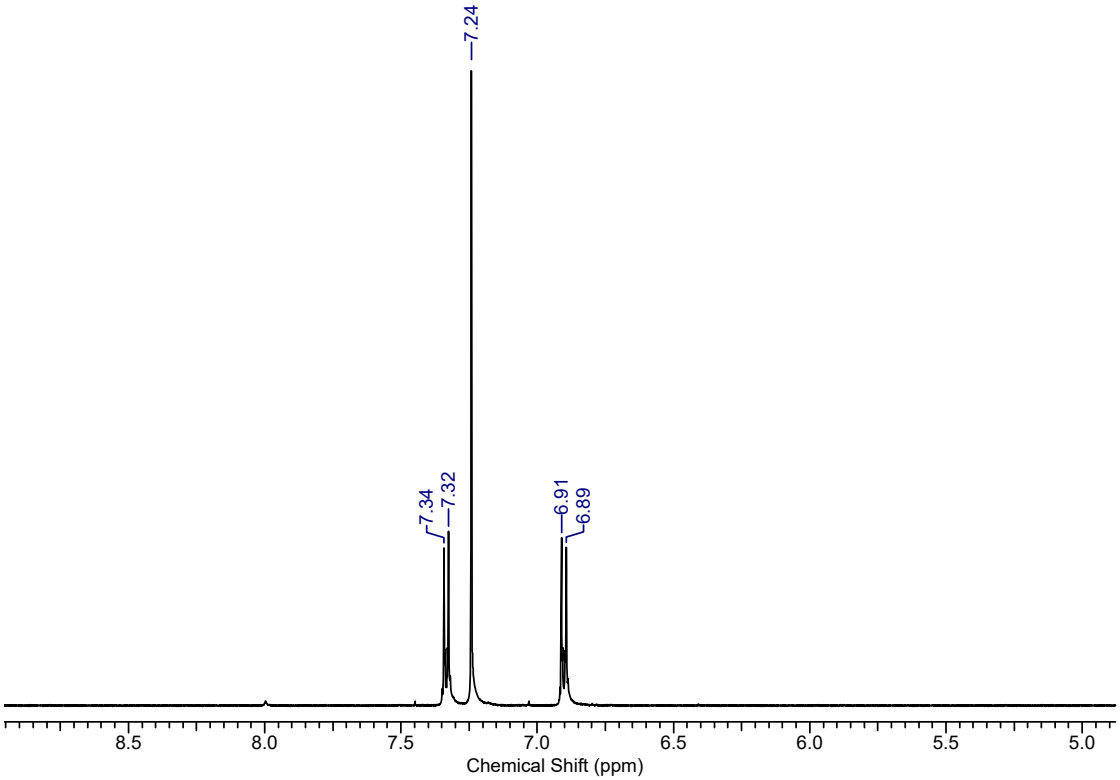

Figure S1. ^{1}H NMR spectrum of tris(4-bromophenyl)amine

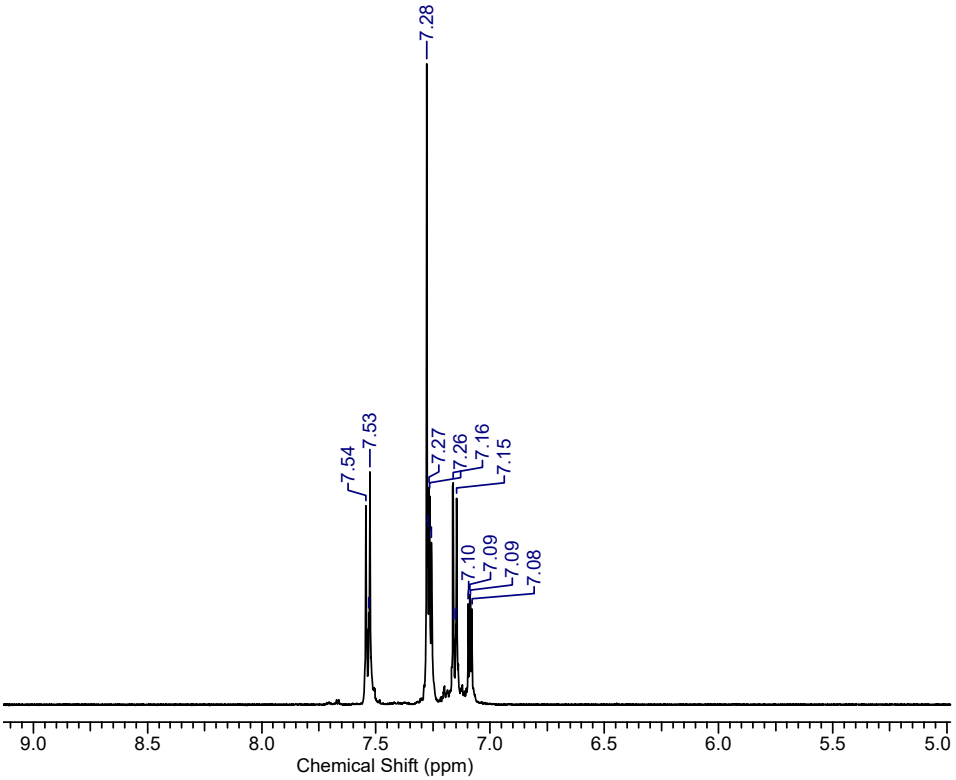

Figure S2. ^{1}H NMR spectrum of tris(4-(thiophen-2-yl)phenyl)amine

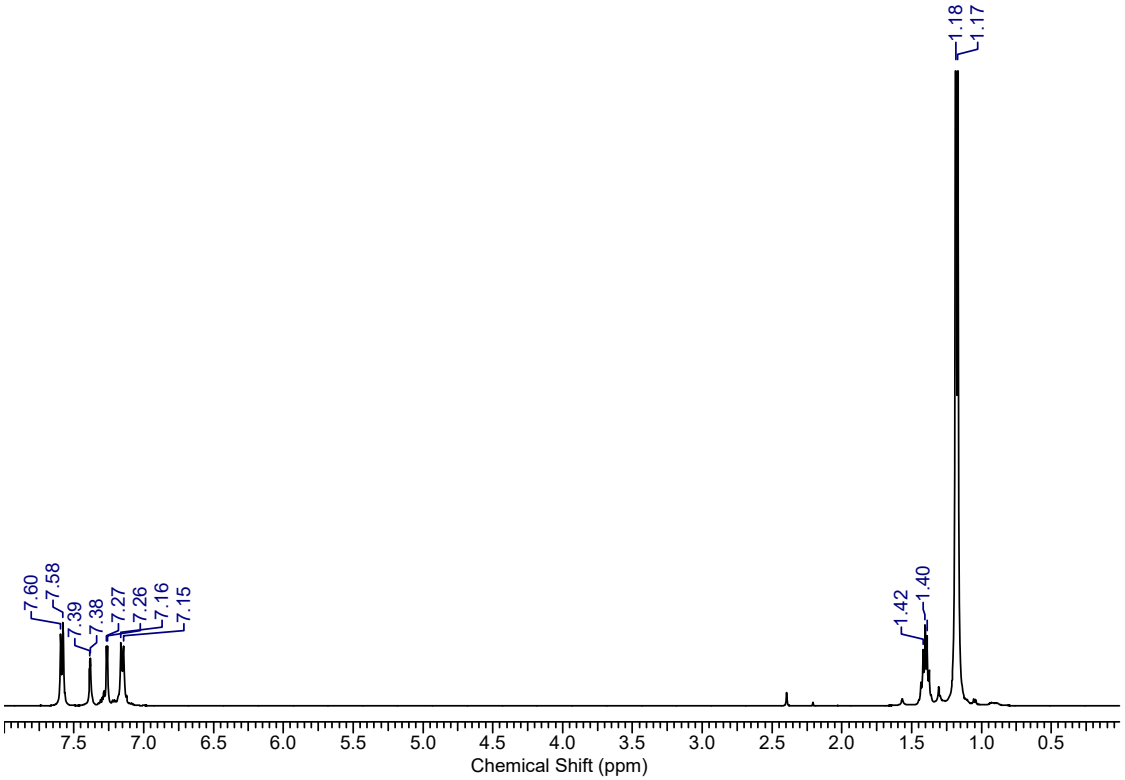

Figure S3. ^{1}H NMR spectrum of tris(4-(5-(triisopropylsilyl)thiophen-2-yl)phenyl)amine

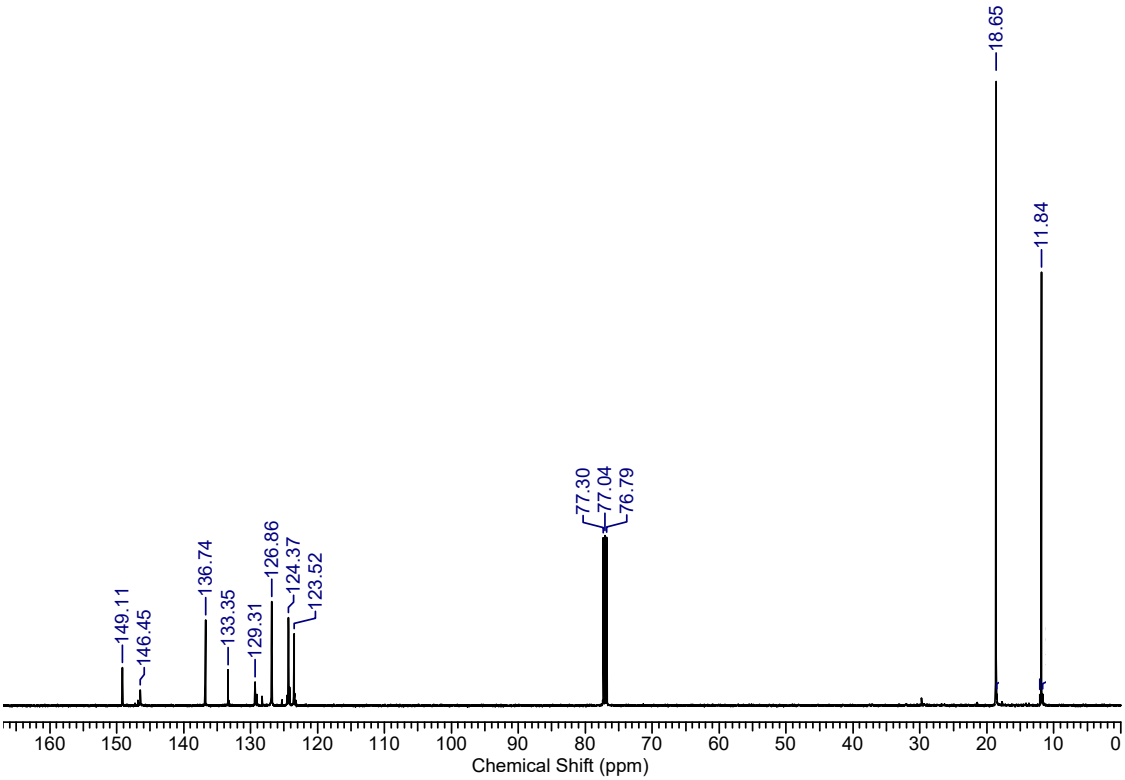

Figure S4. ^{13}C NMR spectrum of tris(4-(5-(triisopropylsilyl)thiophen-2-yl)phenyl)amine

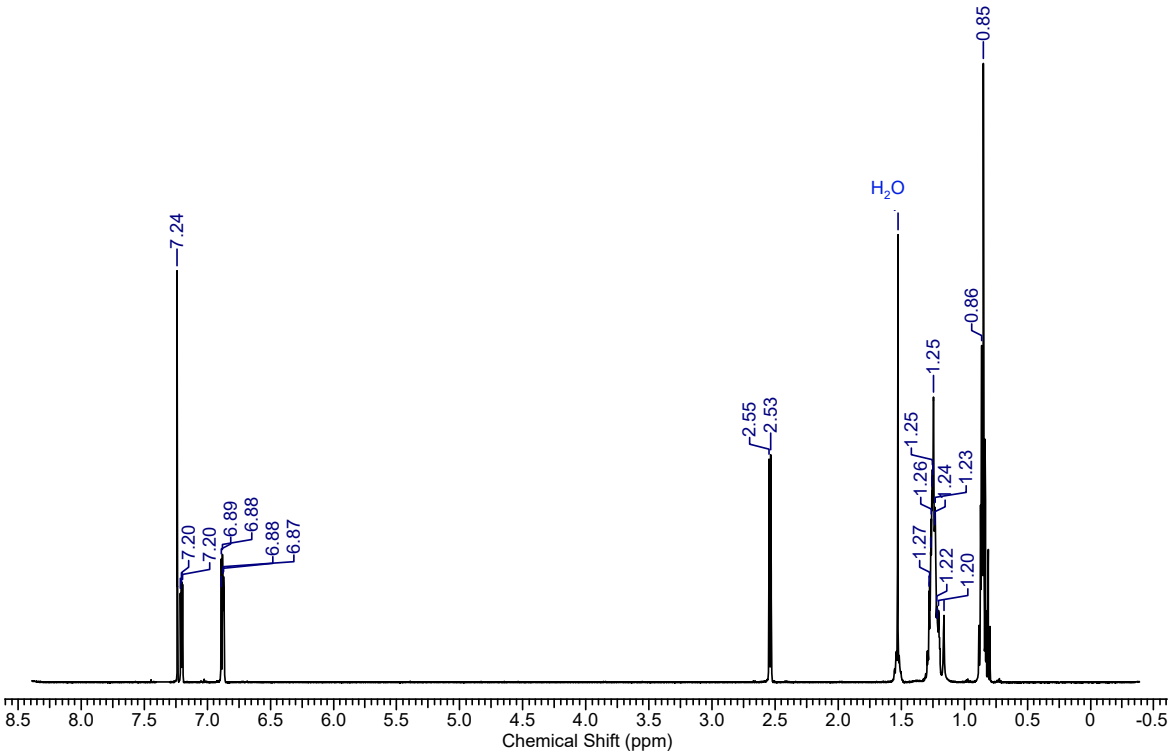

Figure S5. ^{1}H NMR spectrum of 3-(2-ethylhexyl)thiophene

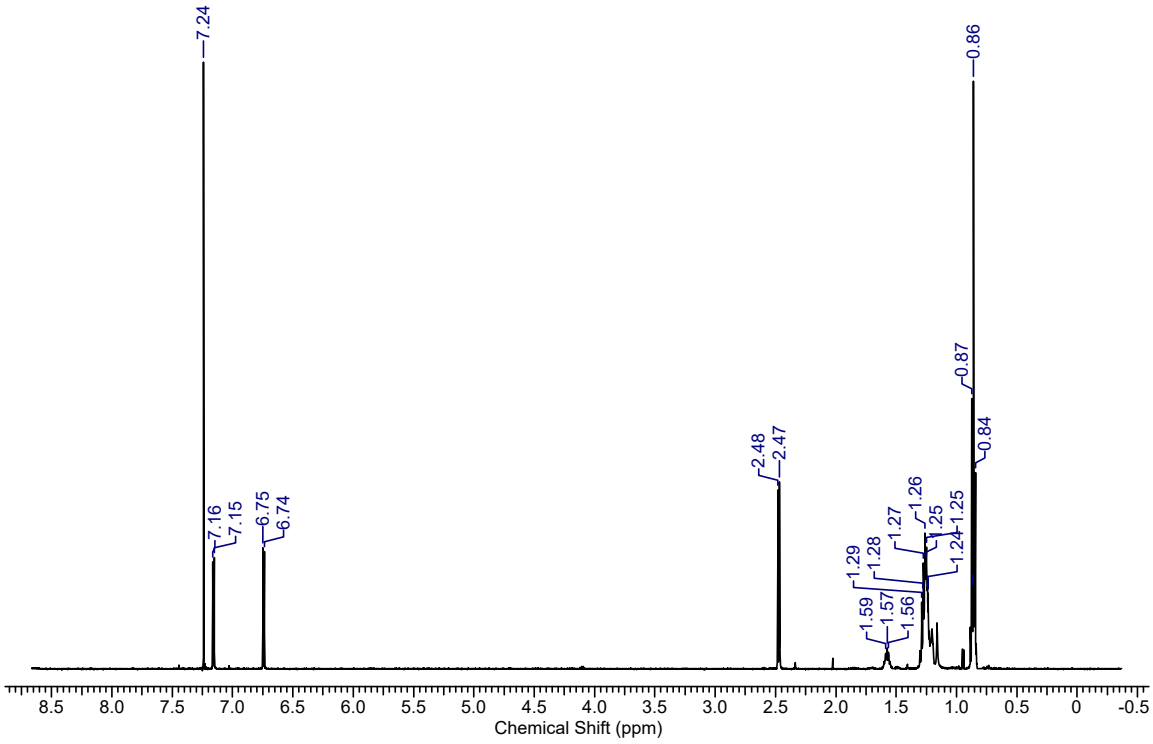

Figure S6. ^{1}H NMR spectrum of 2-bromo-3-(2-ethylhexyl)thiophene

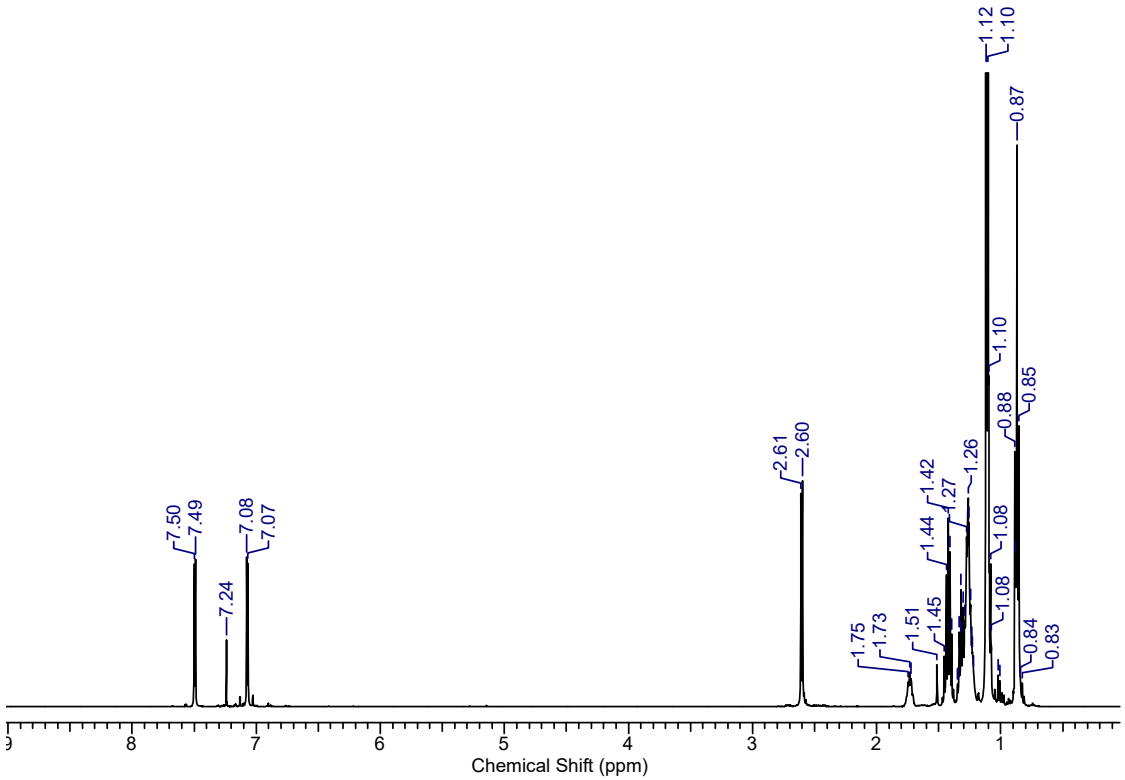

Figure S7. ^{1}H NMR spectrum of (3-(2-ethylhexyl)thiophen-2-yl)triisopropylsilane

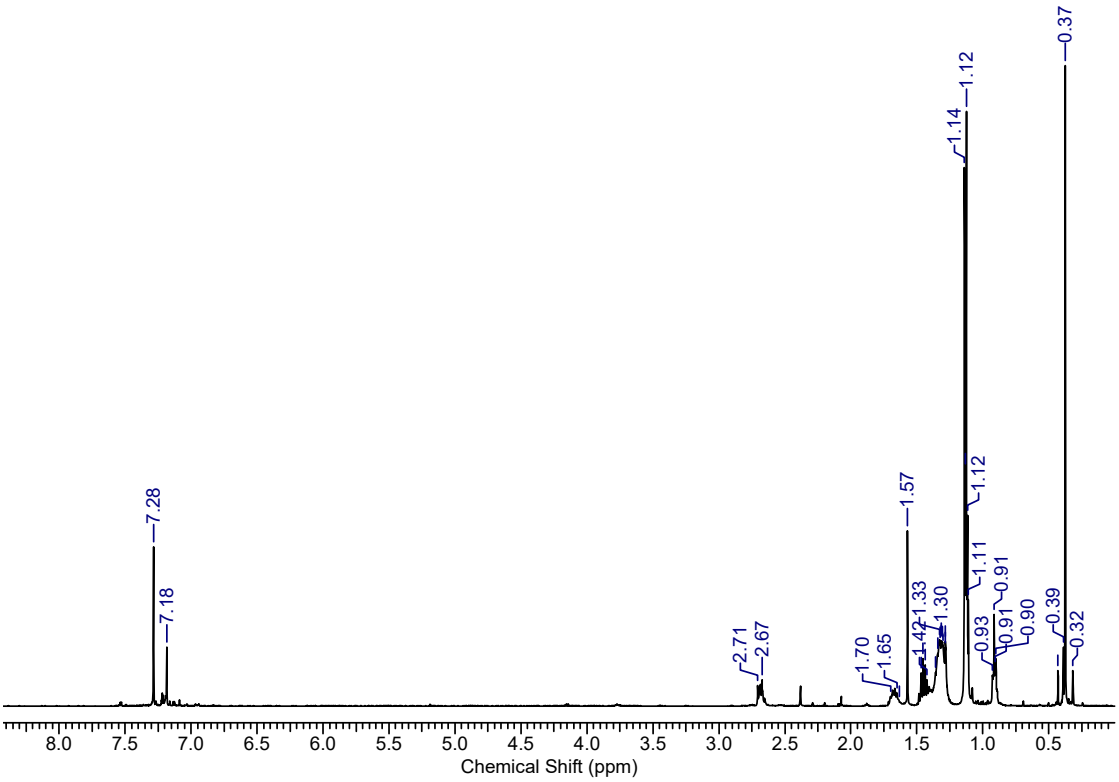

Figure S8. ^{1}H NMR spectrum of (3-(2-ethylhexyl)-5-(trimethylstannyl)thiophen-2-yl)triisopropylsilane

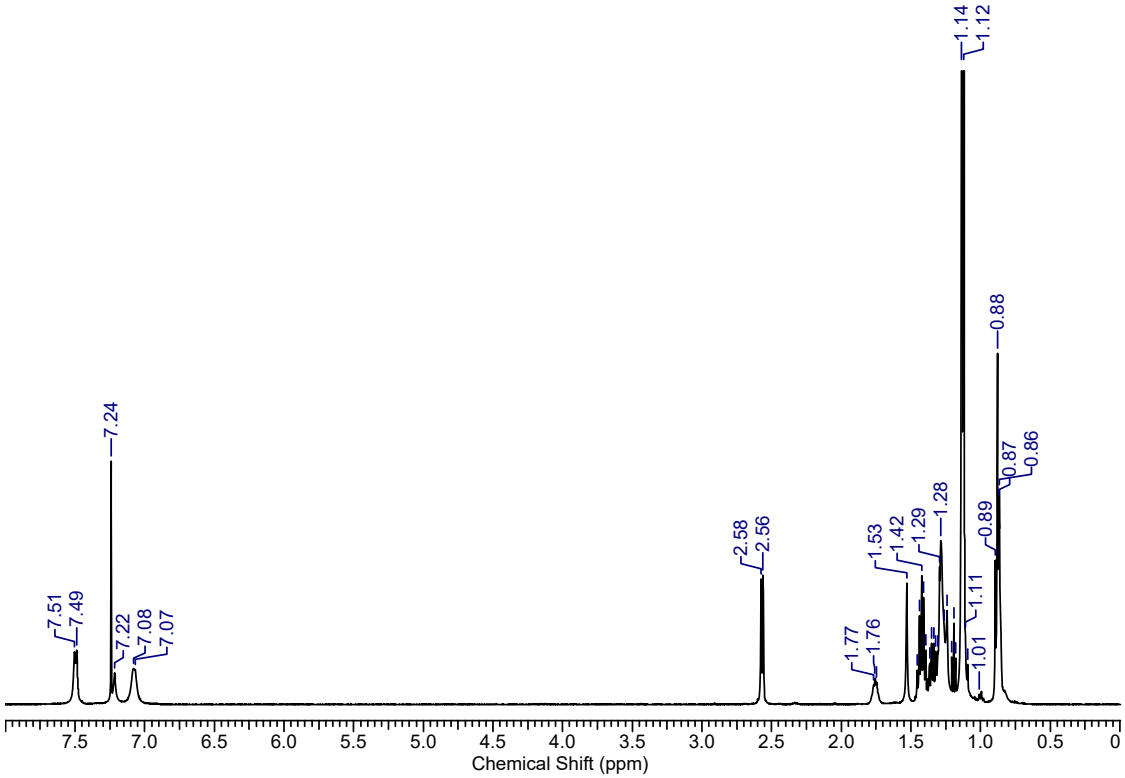

Figure S9. ^{1}H NMR spectrum of tris(4-(4-(2-ethylhexyl)-5-(triisopropylsilyl)thiophen-2-yl)phenyl)amine

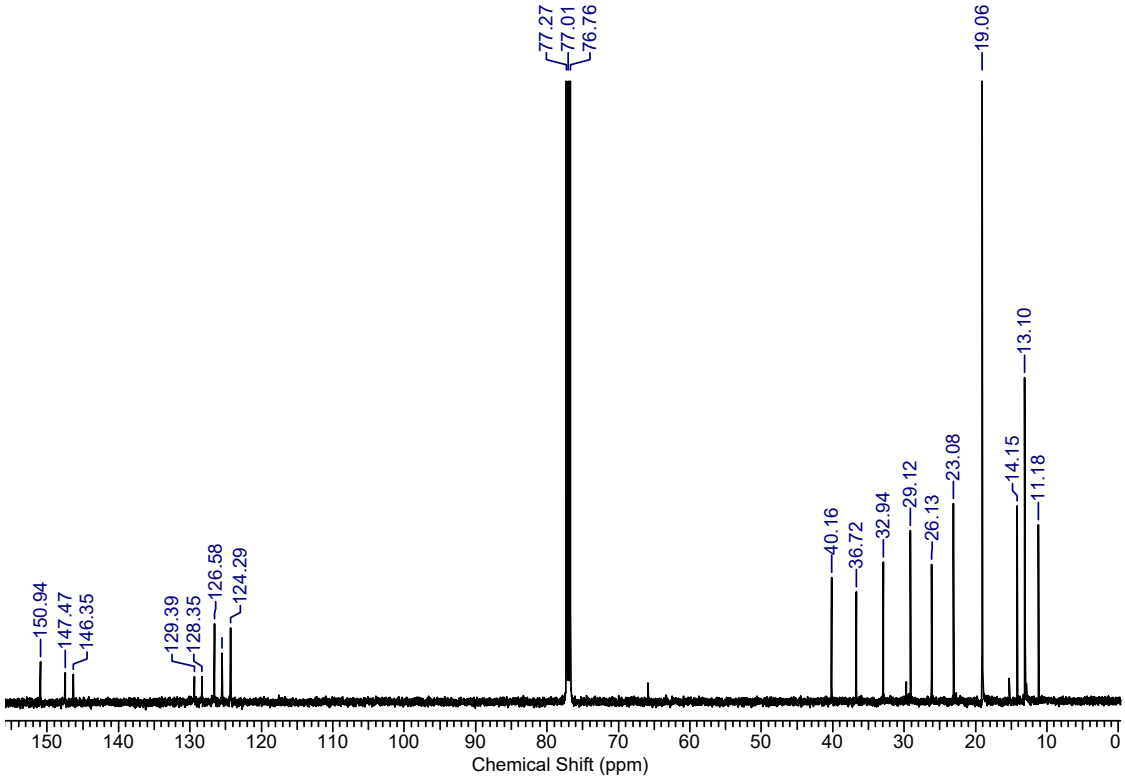

Figure S10. ^{13}C NMR spectrum of tris(4-(4-(2-ethylhexyl)-5-(triisopropylsilyl)thiophen-2-yl)phenyl)amine

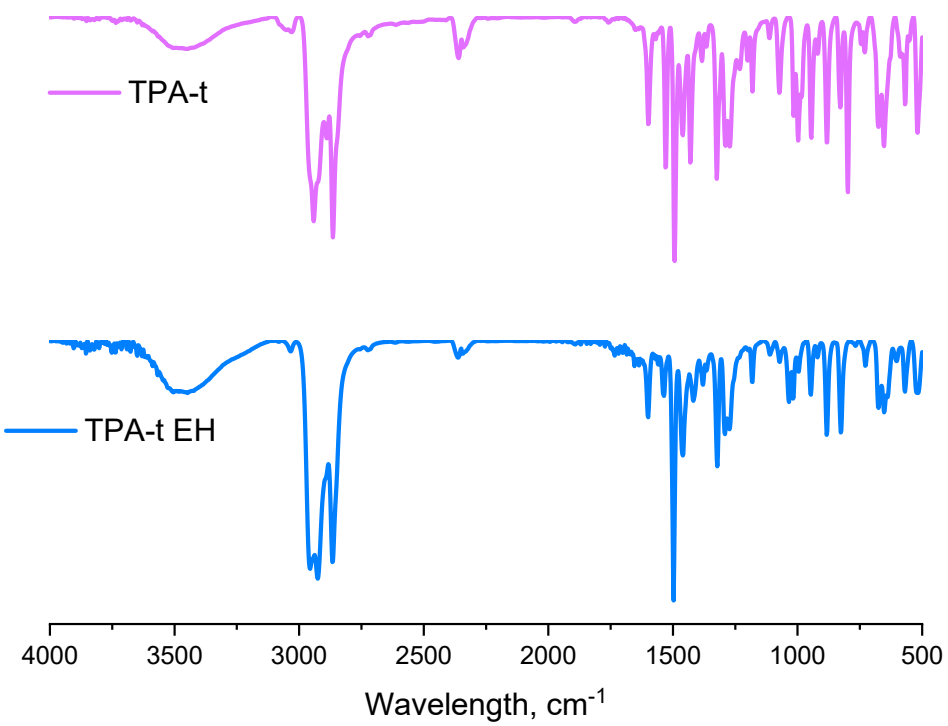

Figure S11. FT-IR spectrum of TPA-t and TPA-t EH

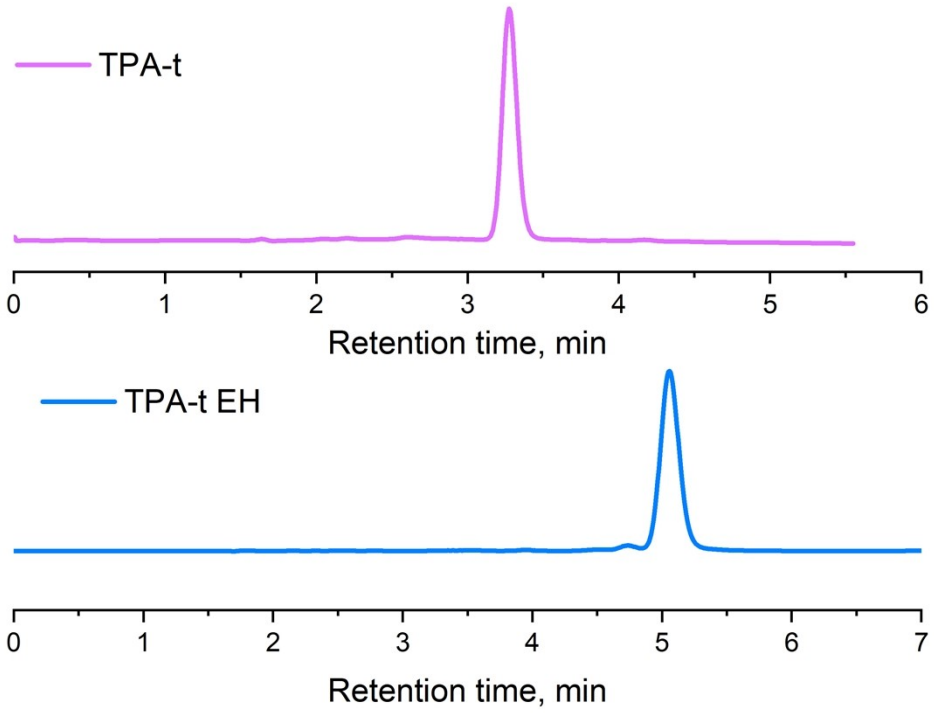

Figure S12. HPLC chromatograms for TPA-t and TPA-t EH compounds. Conditions: eluent - acetonitrile:toluene (7:3); flow rate 1 mL/min; temperature 40°C; column - Phenomenex Luna C18, 5µm (4.6 × 150 mm), detector wavelength 290 nm.

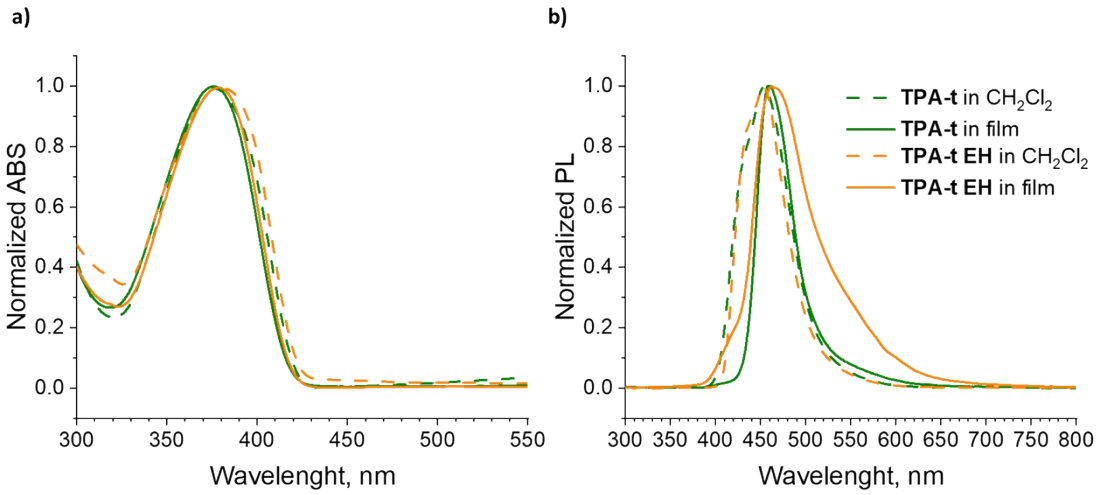

Figure. S13 Absorbance and Photoluminescence spectra in solution and thin films of **TPA-t** and **TPA-t EH.**

Table. S1 Parameters of bi-exponential model fitting of TRPL.

HTL	$\mathbf{A_1}$	$\boldsymbol{\tau_1}$	$\mathbf{A_2}$	$\boldsymbol{\tau_2}$	$\boldsymbol{\tau_{average}}$
$MAPbI_3$	0.5	20	0.4	115	98.1
TPA-t	0.3	7	0.6	36	33.4
TPA-t EH	0.4	19	0.5	125	113.5

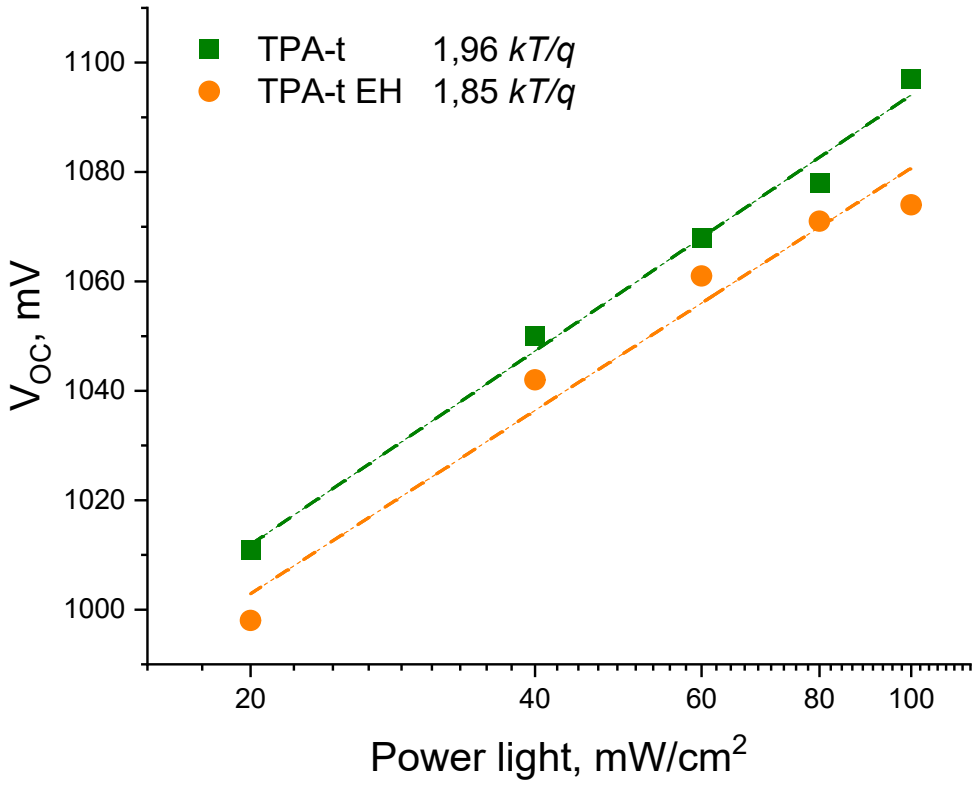

Figure S14. The open-circuit voltage is dependent on the light power for devices based on TPA-t and TPA-t EH. The corresponding light ideality factors are provided in the legends.

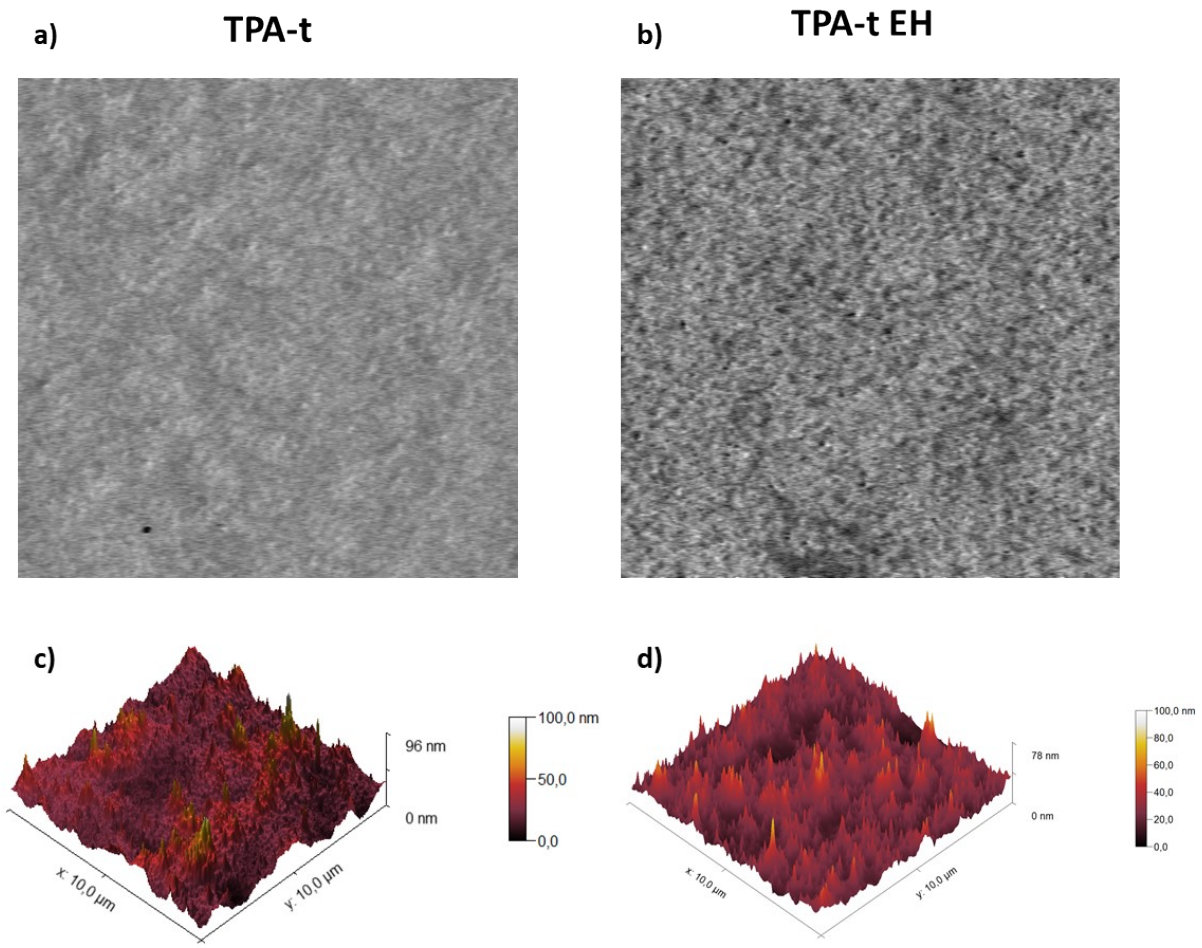

Figure S15. AFM image bilayer thin films TPA- t and TPA-t EH, glass/perovskite/HTM phase mode (a,b) and 3D topology (c,d).

References

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