Supporting Information

Structure-property relationships of Diketopyrrolopyrrole and Thienoacene based A-D-A type hole transport materials for efficient perovskite solar cells

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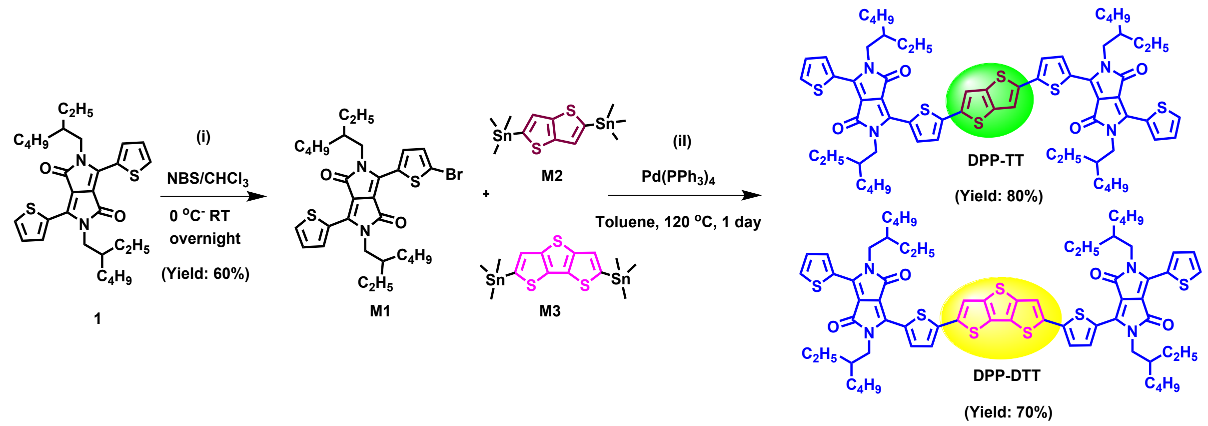
1. Experimental section

1.1 General Information

Nuclear magnetic resonance (NMR) spectra were analyzed on a Bruker ARX 400 spectrometer instrument operating at 400 MHz for ^{1}H NMR and operating at 100 MHz for ^{13}C NMR. UV-Vis absorption measurements were carried out with HP Agilent 8453 UV-Vis spectrophotometer with wavelength range 300-900 nm. All solution UV-Vis experiments were measured using chloroform (CF) as solvent and films were prepared by spin-coating solutions of material and CF onto quartz substrates. Cyclic voltammograms (CV) were determined by using a Zahner IM6eX electrochemical work station and at a scan rate of 50 mVs^{-1} at 25 °C under argon using 0.1 M tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as the electrolyte. During measurement of CV, Pt wire was used as the counter electrode, Ag/AgCl electrode [Ag in 0.1 M KCl] was used as the reference electrode and polymer was drop casted on a carbon electrode used as the working electrode. The electrochemical potential was calibrated against ferrocene/ferrocenium (Fc/Fc^+) system. The highest occupied molecular orbital (HOMO) levels of the polymers were determined using the oxidation onset value. Whereas LUMO levels were calculated from equation LUMO = E_g^{opt} – HOMO (where, E_g^{opt} is optical bandgap of polymer from the thin film state). Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH TG 209 F3 thermogravimetric analyzer, where samples were run under N_2 and heated from room temperature to 400 °C at a rate of 10 °C/min. 2D-grazing incidence wide-angle X-ray scattering (GIWAXS) were measured at PLS- 3C, 9A SAXS and U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. Space-charge-limited-current (SCLC) hole mobility was studied by making hole carrier devices (glass/ITO/PEDOT:PSS/HTM/Au). SCLC mobilities were extracted from dark J-V characteristics using the Mott-Gurney square law, $J = (9/8)\varepsilon_0\varepsilon_r\mu_0 exp(0.89\gamma (V/L)^{1/2}) (V^2 / L^3)$, where J is the dark current density, ε_0 is vacuum permittivity, ε_r is the dielectric constant of HTMs, μ_0 is the zero-field mobility, γ is the disorder parameter, V is the effective voltage and L is the film thickness.

1.2 Materials and Methods

All chemicals and solvents were purchased from Aldrich, Alfa Aesar and TCI Chemical Co. and used as received. The intermediate 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione(**M1**)[1] and monomers 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (**M2**)[2] and 2,6bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]thiophene (**M3**)[2] were prepared according to our previous reported methods.



Scheme 1: The synthetic routes of monomers and small molecules: 1) N-Bromosuccinimide, chloroform, 0°C to RT 16h (yield: 60%) and ii) Tetrakis(triphenylphosphine)palladium(0), toluene, reflux 24 h (yield: 70-80%).

1.3 Synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M1)

Compound **1** (0.53 g, 1.0 mmol) was dissolved in 40 mL of chloroform and a solution of NBS (0.19 g, 1.05mmol) in 30 mL chloroform was added dropwise to the solution at 0 – 5 °C. Then the mixture was warmed to room temperature and stirred overnight. Then reaction mixture was quenched with sodium bicarbonate solution (50ml) and product was extracted with dichloromethane, followed by washing with brine. The organic phase was dried ($MgSO_4$), the solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatograph eluting with n-hexane/chloroform (2:1 to 1:2, v : v) to afford a purple solid M1 (Yield: 60%) **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.89 (d, J = 3.9 Hz, 2H), 8.61 (d, J = 4.3 Hz, 7.62 (d, J = 5.0 Hz, 2H), 7.27 (d, J = 5.0 Hz, 2H), 4.05 (m, 2H), 4.00 (m, 2H), 1.91 (br s, 2H), 1.41-1.21 (m, 16H), 1.02-0.89 (m, 12H).

1.4 The general process for the synthesis of hole transporting materials

A solution of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**) (0.22 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (**M2**) or 2,6 bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**M3**) (0.1 mmol) and $Pd(PPh_3)_4$ (5 mol%) was charged in 50 mL reaction flask, cycled with argon and dissolved in a degassed solvent mixture of 15 mL ofanhydroustoluene. The reactionmixture was stirred for 24 h at 110 °C. The resulting mixture was cooled and precipitated into methanol (200 mL) and stirred for 5 h. The precipitate was then filtered through Whatman filter paper. The solid obtained was dissolved in a minimum volume of chloroform and reprecipitated in methanol (200 mL) and the precipitate were filtered and dried. The dried solid was subjected to flash column purification using hexane:chloroform as eluent. The desired products obtained as 70 – 80% of yield.

1.5 Synthesis of DPP-TT

Brown shining solid (95 mg, 80%), **^{1}HNMR** (400 MHz, $CDCl_3$) δ (ppm): 8.93 (t, *J* = 4.2 Hz, 2H), 8.90 (d, *J* = 3.8Hz, 2H), 7.61 (d, *J* = 4.9 Hz, 2H), 7.42 (s, 2H), 7.34 (d, *J* = 4.2 Hz, 2H), 7.28 (m, 2H), 4.04–4.00 (m, 8H), 1.93–1.84 (m, 4H), 1.42–1.23 (m, 32H), 0.94-0.83 (m, 24H).

^{13}C NMR (100 MHz, CDCl3): 161.7, 142.3, 140.1, 140.0, 139.4, 138.7, 136.6, 135.3, 130.5, 129.8, 128.6, 128.4, 125.0, 116.9, 108.4, 108.1, 45.9, 39.3, 39.1, 30.3, 29.70, 28.5, 28.3, 23.7, 23.1, 23.0, 14.1, 10.6.

1.6 Synthesis of DPP-DTT

Brown shining solid (87 mg, 70%), **^{1}HNMR** (400 MHz, $CDCl_3$) δ (ppm): 8.88 (t, *J* = 4.2 Hz, 2H), 8.84 (d, *J* = 3.9 Hz, 2H), 7.55 (m, 2H), 7.41 (s, 2H), 7.36 (d, *J* = 4.2 Hz, 2H), 7.28 (d, *J* = 4.2 Hz, 1H), 7.20 (m, 2H), 3.97 (m, 8H), 1.84–1.81 (m, 4H), 1.34–1.17 (m, 32H), 0.86-0.73 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): 161.6, 142.8, 140.0, 137.5, 136.7, 135.8, 135.5, 130.6, 128.4, 124.9, 118.1, 108.1, 45.9, 39.3, 39.1, 30.3, 30.2, 29.7, 28.5, 28.3, 23.7, 23.5, 23.14, 23.1, 14.1, 10.5.

2. Device Fabrication

For the PSC device fabrication, first, pre-etched indium-doped tin oxide (ITO) coated glass substrates were cleaned rigorously using soapy water, deionized water (DI), ethanol and isopropanol (IPA) for 20 min each under sonication. After cleaning, the substrates were N_2 blow-dried to remove the residual solvents from the substrates and then thermally treated in a convection oven at 70 °C for 30 min. Cleaned substrates were further treated in a UV-ozone plasma for 20 min prior to deposition of a electron transport layer (ETL) of compact SnO_2 (c-SnO_2) via spin coating at 3000 rpm and annealing at 150 °C for 30 min. The spin coating solution was prepared by dissolving $SnCl_2{\cdot}2H_2O$ (0.2 g) in ethanol (8 ml) and stirring for 24 h at 70 °C before use. For the perovskite absorber layer, a perovskite precursor solution was prepared with an equimolar precursor ratio of the methylammonium iodide (MAI) and lead iodide (PbI_2) (MAI:PbI_2 = 1.5:1.5) in a fixed solvent formulation of N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (DMF:DMSO = 4:1); the solution was stirred at 65 °C overnight. The perovskite films were then deposited by spin coating the precursor solution on top of the c-SnO_2 layer via a spin coating program comprising of 10 s at 1000 rpm, with a subsequent ramp to 5000 rpm for 20 s. An amount of 0.1 mL of toluene, used as the anti-solvent, was dripped dynamically onto the underlying spinning substrate, for the last 10 s of the second stage of spin coating. The film was then thermally treated at 125 °C for 20 min. For the hole transport layer (HTL), the spiro-OMeTAD (80 mg mL^{-1} in chlorobenzene) was doped with three solutions, all used in conjunction, consisting of 34 μL of 4-tert-butylpyridine (TBP), 20 μL of bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) and 11 μL of tris[2-(1H-pyrazol-1-yl)-4-tert-butylpyridine] cobalt(II) tris[bis(trifluoromethylsulfonyl)imide] (FK209). For the latter two solutions, i.e., Li-TFSI, a mother solution of 531 mg/mL in acetonitrile was used, while the FK209 required a mother solution of 300 mg/mL in acetonitrile. This spiro-OMeTAD solution was spin coated onto the underlying perovskite layer at 3000 rpm for 10 s to form the HTL. Similarly, for the DPP-TT and DPP-DTT HTLs, the precursor solutions were prepared via dissolving 8 mg of DPP-TT and 8 mg of DPP-DTT in 1 mL of chlorobenzene with addition of Li-TFSI (0 μL, 0.5 μL, 1 μL, 1.5 μL, and 2 μL) into each of the precursor solutions. These DPP-TT and DPP-DTT solutions were spin coated onto the underlying perovskite layer at 2000 rpm for 10 s to form the HTL. Finally, an ~90 nm thick Au top electrode was thermally deposited at a pressure of ~10^{-6} Torr through a shadow mask to create devices with 0.16cm^2 active area.

3. Synthesis cost estimation of 1 gram DPP-TT and DPP-DTT

We roughly estimated the synthesis cost of 1 gram DPP-TT and DPP-DTT according to the model proposed by Osedach et al.[3] Such a model has been recently applied by many other groups to estimate the cost of many other hole-transporting materials.[4-6] For every synthetic step, the actual amounts of reactants, catalysts, reagents, solvents, and materials for workup and purification required to obtain 1 gram of intermediates and final products were given in the below tables. The price per kg of the commercially available chemicals and synthesized intermediates were multiplied by the quantities required for the synthesis. Since these tables do not take into account several important parameters (e.g., energy consumption, waste treatment, and labor), it was multiplied by a factor of 1.5[5] to get a more realistic estimation of lab synthesis costs of 391.64 \$/g (260.7 x 1.5 = 391.64 \$/g) and 447 \$/g (298 x 1.5 = 447\$/g) for DPP-TT and DPP-DTT, respectively. Thus, both newly synthesized HTMs were found to be much cheaper than that of spiro-OMeTAD (~533.00 \$/g, Sigma Aldrich, India).[7]

2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1)

Chemical	Reagent mass (g)	Solvent Vol. (ml)	Reagent cost (\$/g)	Solvent cost (\$/ml)	Reagent + solvent cost (\$)	Product cost (\$/g)
3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione	3g		9.6		28.8	
K_2CO_3	7g		0.029		0.203	
DMF		100		0.065	6.5	
2-ethyl hexyl bromide	5.21		0.64		3.33	
$CHCl_3$		2000		0.0041	8.2	
magnesium sulphate	10g		0.003		0.03	
Silica gel	500g		0.0135		6.75	
Total					53.81	
Product step 1 (Yield = 76%, 4g)						**13.45**

Synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M1)

Chemical	Reagent mass (g)	Solvent Vol. (ml)	Reagent cost ($/g)	Solvent cost ($/ml)	Reagent + solvent cost ($)	Product cost ($/g)
2,5-dioctyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione	0.53		13.45		7.12	
N-Bromosuccinimide	0.19g		0.245		0.056	
Anhy. $CHCl_3$		70		0.066	3.96	
magnesium sulphate	2g		0.003		0.006	
n-hexane		1500		0.0018	2.7	
$CHCl_3$		1500		0.040	6.15	
Silica gel	500g		0.0135		6.75	
Total					26.74	
Product step 2 (Yield = 60%, 0.36g)						**74.27**

Synthesis of DPP-TT

Chemical	Reagent mass (g)	Solvent Vol. (ml)	Reagent cost ($/g)	Solvent cost ($/ml)	Reagent + solvent cost ($)	Product cost ($/g)
bis(trimethylstannyl)thieno[3,2-b]thiophene (**M2**)	47mg		57.50		2.70	
3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**)	0.132g		74.27		9.80	
Pd catalyst*	7mg		30.32		0.21	
Toluene		30ml		0.026	0.78	
magnesium sulphate	2g		0.003		0.006	
methanol	200			0.0025	0.5	
n-hexane		1000		0.0018	1.88	
$CHCl_3$		1500		0.0041	6.15	
Silica gel	400g		0.0135		4.05	
Total					26.07	
Product step 3 (Yield = 80%, 0.1g)						**260.7**

Synthesis of **DPP-DTT**

Chemical	Reagent mass (g)	Solvent Vol. (ml)	Reagent cost ($/g)	Solvent cost ($/ml)	Reagent + solvent cost ($)	Product cost ($/g)
2,6 bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**M3**)	52mg		95		4.94	
3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**)	0.132g		64.94		9.80	
Pd catalyst*	7mg		30.32		0.21	
Toluene		30ml		0.026	0.78	
magnesium sulphate	2g		0.003		0.006	
methanol	200			0.0025	0.5	
n-hexane		1000		0.0018	1.88	
$CHCl_3$		1500		0.0041	6.15	
Silica gel	400g		0.0135		4.05	
Total					28.31	
Product step 3 (Yield = 73%, 95mg)						**298.0**

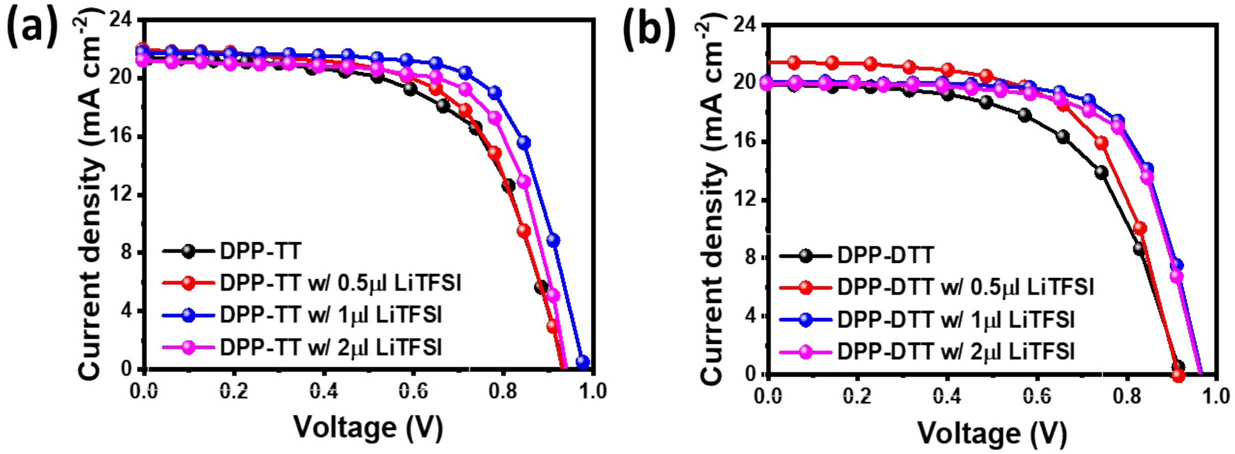


Figure S1. *J-V* characteristics of the PVSCs fabricated using (a) DPP-TT and (b) DPP-DTT HTMs with different concentration of Li-TFSI. (The concentration of the Li-TFSI added from mother solution of Li-TFSI (530mg/ml in chlorobenzene) in μl (0.5μl, 1μl, and 2μl) to the 1ml solutions of the DPP-TT and DPP-DTT).

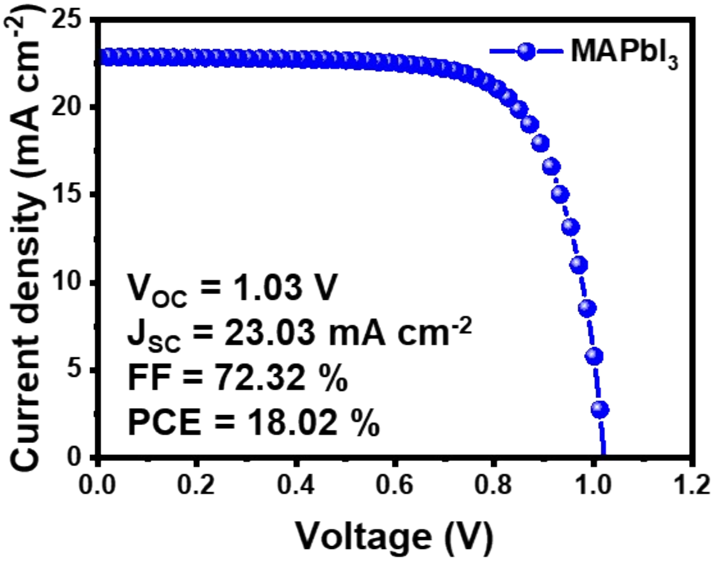


Figure S2. Current density-voltage (J-V) characteristics of the reference $MAPbI_3$ based PVSC with spiro-OMeTAD under 0.96 sun conditions. PVSC has device structure glass/ITO/SnO_2/$MAPbI_3$/Spiro-OMeTAD/Au.

Table S1. Photovoltaic (PV) performances of the PVSCs fabricated with different HTMs (DPP-TT, DPP-DTT, DPP-TT w/ Li-TFSI, and DPP-DTT w/ Li-TFSI) under standard AM 1.5G illumination. The concentration of the Li-TFSI added from mother solution of Li-TFSI (530mg/ml in chlorobenzene) in µl (0.5µl, 1µl, and 2µl) to the 1 ml solutions of the DPP-Th and DPP-Se.

HTM	**V_{OC} (V)**	**J_{SC} (mAcm^{-2})**	**FF (%)**	**PCE (%)**
DPP-TT	0.94 ± 0.19	21.38 ± 0.91	61.12 ± 2.14	12.25 ± 0.42
DPP- TT + 0.5µl LiTFSI	0.93 ± 0.15	20.69 ± 0.47	62.37 ± 3.15	13.34 ± 0.84
DPP- TT + 1µl LiTFSI	0.98 ± 0.14	21.74 ± 0.59	69.52 ± 1.15	15.57 ± 0.63
DPP- TT + 2µl LiTFSI	0.94 ± 0.07	21.22 ± 0.82	68.96 ± 2.18	14.46 ± 0.39
DPP-DTT	0.92 ± 0.13	19.92 ± 0.71	58.66 ± 3.17	11.29 ± 0.91
DPP- DTT + 0.5µl LiTFSI	0.93 ± 0.05	21.49 ± 0.47	62.93 ± 1.17	12.83 ± 0.51
DPP- DTT + 1µl LiTFSI	0.97 ± 0.12	20.34 ± 0.63	69.89 ± 1.31	14.23 ± 0.34
DPP- DTT + 2µl LiTFSI	0.96 ± 0.03	19.97 ± 0.27	68.80 ± 2.13	13.93 ± 0.49

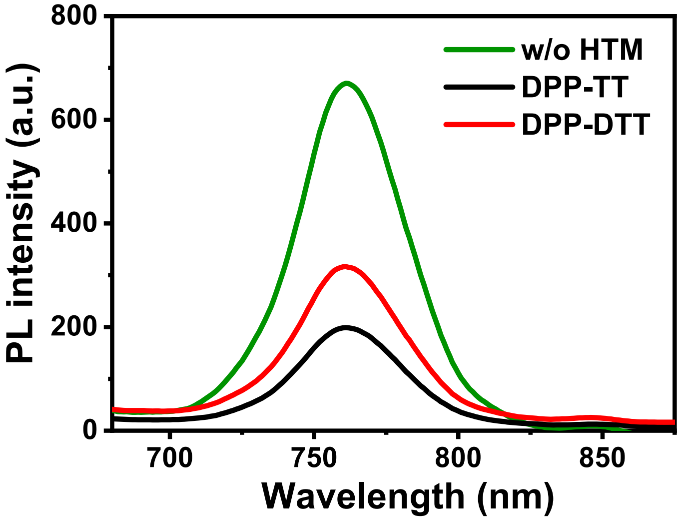


Figure. S3 Photoluminescence (PL) spectrum recorded for the samples ITO/SnO_2/$MAPbI_3$ (w/o HTM) and ITO/SnO_2/$MAPbI_3$/HTM where films were excited from ITO side.

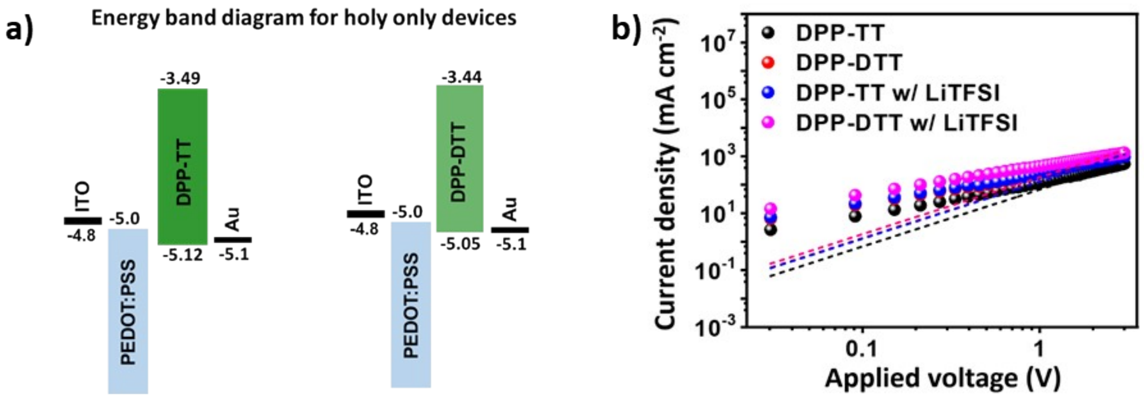


Figure S4. a) Energy level alignment of hole only devices with structure (Glass/ITO/PEDOT:PSS/Perovskite/HTM/Au) and b) corresponding dark current density (J_d)-voltage curves for hole carrier controlled devices fabricated with different HTMs.

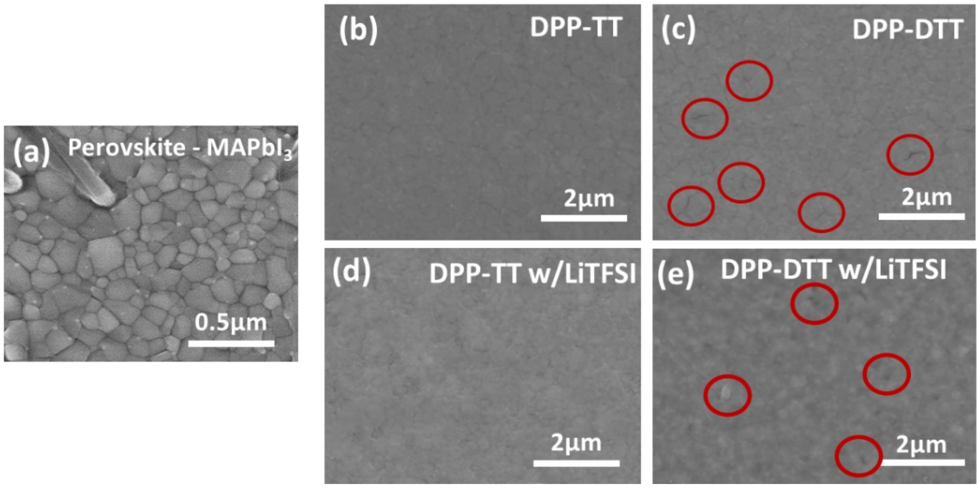


Figure S5. Morphological characterization: FE-SEM images of the (a) pristine perovskite - $MAPbI_3$ (without HTM), (b) DPP-TT, (c) DPP-DTT, (d) DPP-TT w/LiTFSI, and (e) DPP-DTT w/LiTFSI) HTMs coated on the perovskite film (Red circle indicates cracks or pinholes).

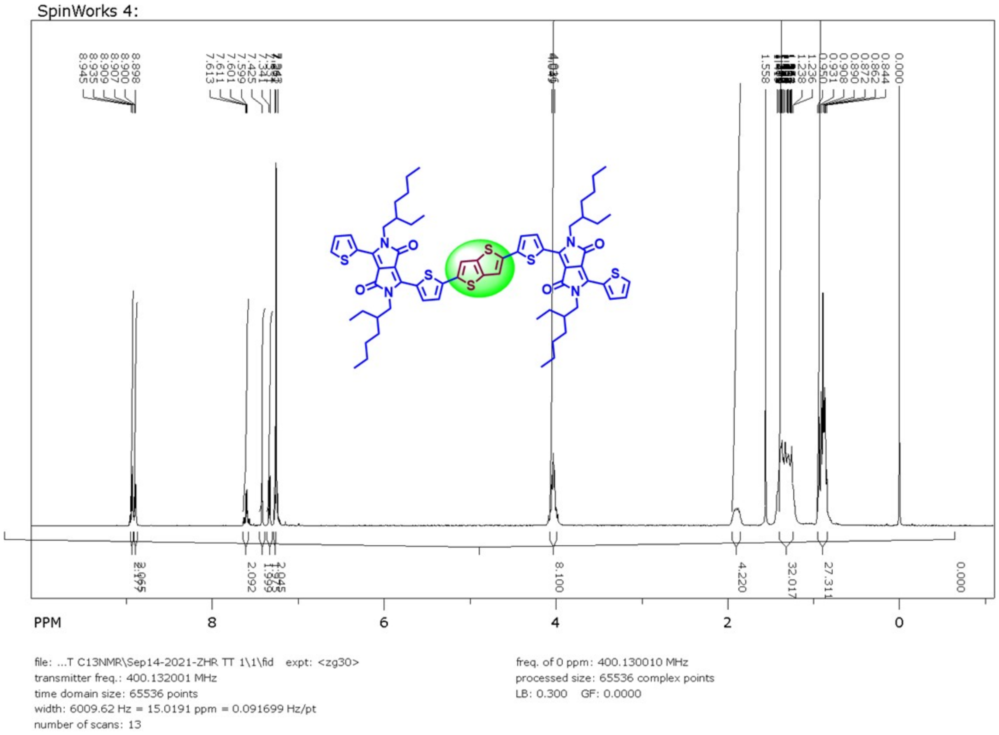
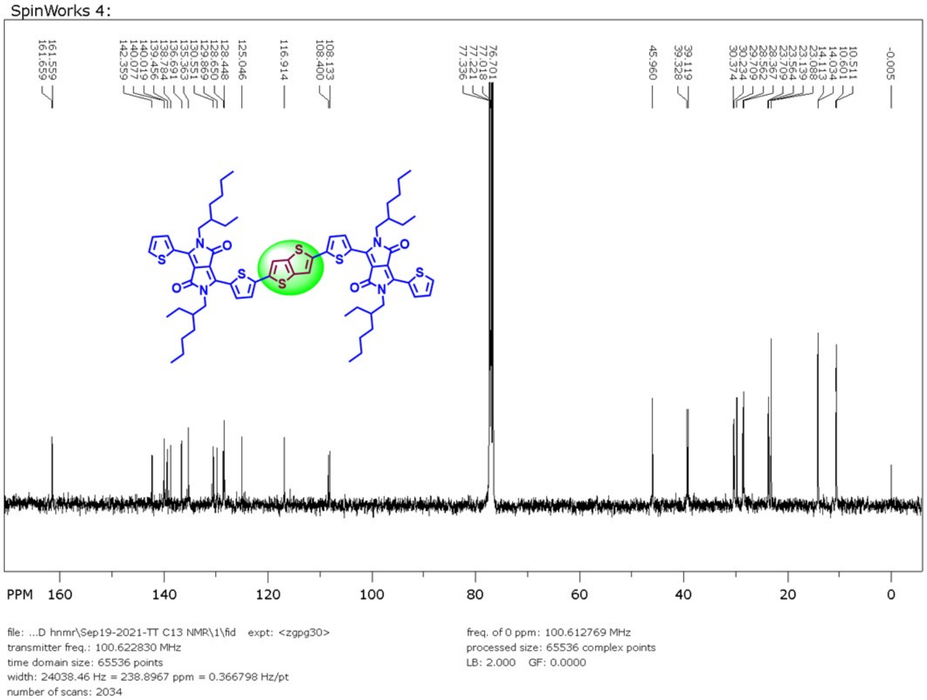


Figure S6. ^{1}HNMR (Top)and ^{13}CNMR of DPP-TT(bottom).



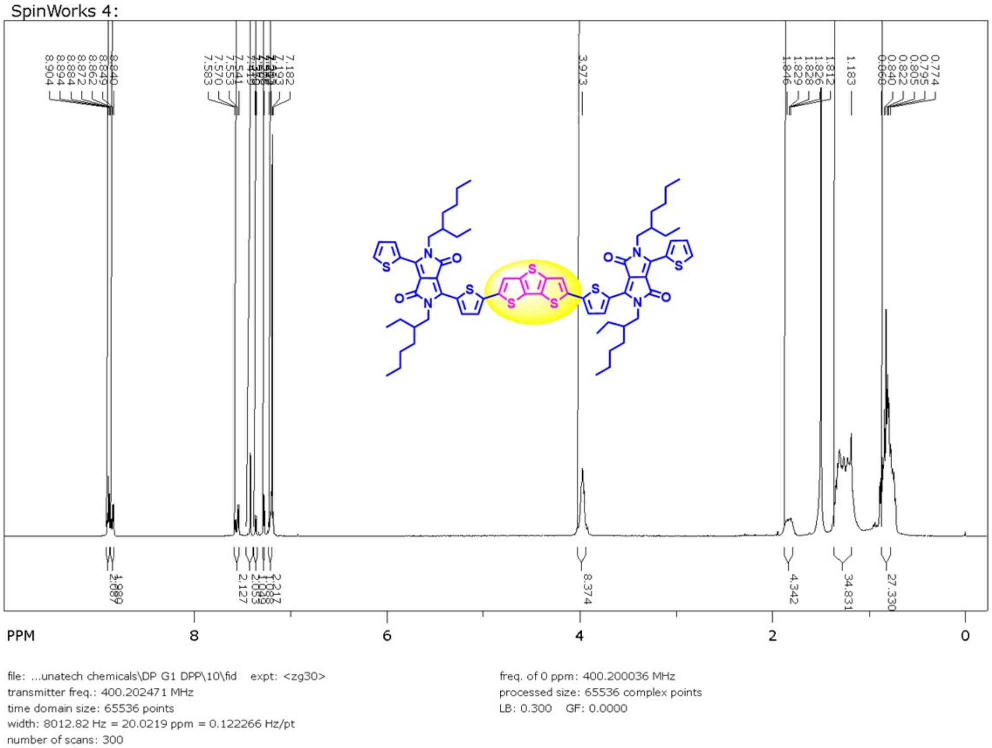
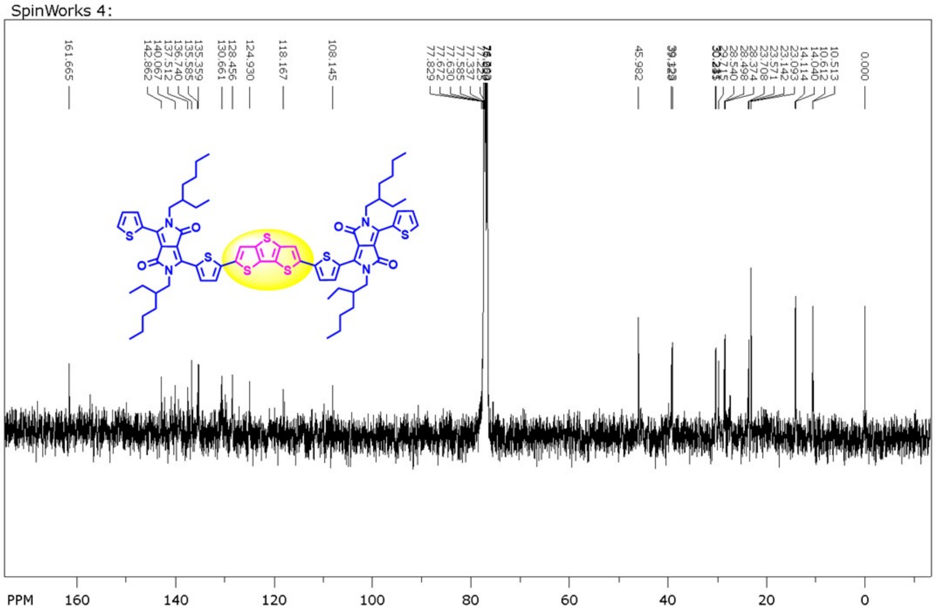


Figure S7. ^{1}H NMR (Top)and ^{13}C NMR of DPP-DTT(bottom).



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References:

1. S. R. Suranagi, R. Singh and M. Kim, *Dyes and Pigments*, 2019, **163**, 525-532.
2. G. P. Kini, S. Oh, Z. Abbas, S. Rasool, M. Jahandar, C. E. Song, S. K. Lee, W. S. Shin, W.-W. So and J.-C. Lee, *ACS. Appl. Mater. Interfaces*, 2017, **9**, 12617-12628.
3. T. P. Osedach, T. L. Andrew and V. Bulović, *Energy Environ. Sci.*, 2013, **6**, 711-718.
4. M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159-12162.
5. M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K.-H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel and M. K. Nazeeruddin, *Nat. Energy*, 2016, **1**, 15017.
6. F. Zhang, Z. Wang, H. Zhu, N. Pellet, J. Luo, C. Yi, X. Liu, H. Liu, S. Wang, X. Li, Y. Xiao, S. M. Zakeeruddin, D. Bi and M. Grätzel, *Nano Energy*, 2017, **41**, 469-475.
7. Cost of spiro-MeOTAD 2021, https://www.sigmaaldrich.com/IN/en/product/aldrich/792071.