Supplementary Information

Deciphering the effect of replacing thiophene with selenophene in the diketopyrrolopyrrole (DPP)-based low cost hole transport materials on the performance of perovskite solar cells

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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 in chloroform (CF) solutions and films were prepared by spin-coating CF solutions onto quartz substrates. Cyclic voltammograms (CV) were determined by using a Zahner IM6eX electrochemical workstation and at a scan rate of 50 mVs^{-1} at 25 °C under argon using 0.1 M tetrabutyl ammonium hexafluorophosphate (Bu$_4$NPF$_6$) 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 small molecules was drop casted on a carbon electrode used as the working

electrode. The electrochemical potential was calibrated against ferrocene/ferrocenium (Fc/Fc$^+$) system. The HTMs highest occupied molecular orbital (HOMO) levels were determined using the oxidation onset value. Meanwhile, LUMO levels were calculated from equation LUMO = E_g^{opt} – HOMO (where E_g^{opt} is the optical bandgap of HTMs from the thin film state).[1] 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- 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. Space-charge-limited-current (SCLC) hole mobility was studied by making hole-only 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.

Materials and Methods

All chemicals and solvents were purchased from Aldrich, Alfa Aesar and TCI Chemical Co. and used as received. The intermediate 2,5-dioctyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**1**)[2] and monomers 2,5-bis(trimethylstannyl)thiophene (**M2**)[3] and 2,5-bis(trimethylstannyl)selenophene (**M3**)[3] were prepared according to previous reported methods.
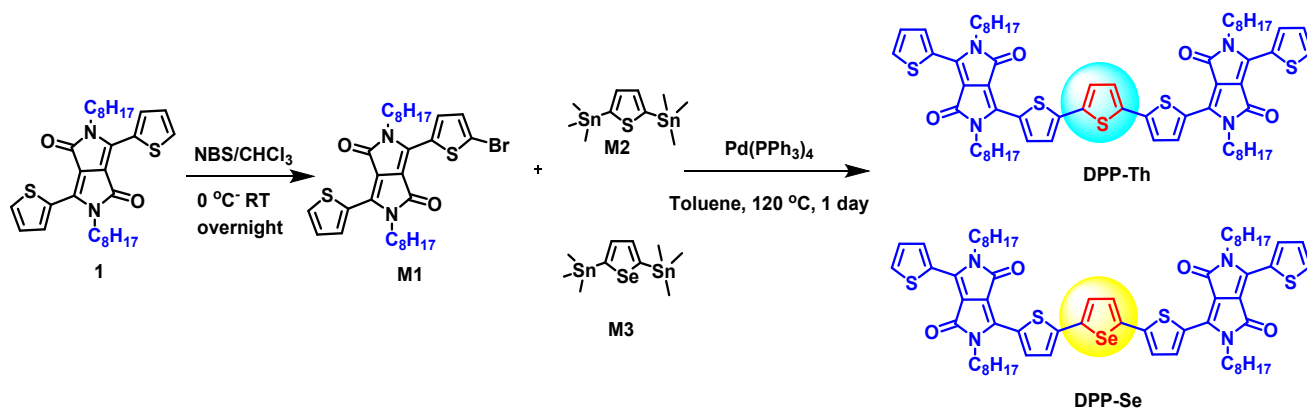
Scheme 1: Synthesis scheme of hole transporting materials

Synthesis of 3-(5-bromothiophen-2-yl)-2,5-dioctyl-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 CHCl$_3$ and a solution of NBS (0.19 g, 1.05 mmol) in 30 mL CHCl$_3$ was added dropwise to the solution at 0 – 5 °C. Then the mixture was warmed to room temperature and stirred overnight. CH$_2$Cl$_2$ was added and then the solution was washed with brine. The organic phase was dried (MgSO$_4$) and the solvent was evaporated under reduced pressure. and the crude product was purified by silica gel column chromatograph eluting with n-hexane/CHCl$_3$ (2:1 to 1:2, v : v) to afford a purple solid 3 (391 mg, 65%). **1H NMR** (400 MHz, CDCl3, ppm): δ 8.94 (d, *J* = 4.0 Hz, 1H), 8.68 (d, *J* = 4.4 Hz, 1H), 7.66 (d, *J* = 4.8 Hz, 1H), 7.29 (t, *J* = 4.4 Hz, 1H), 7.24 (d, *J* = 4.4 Hz, 1H), 4.09 (m, 4H), 1.78 (m, 4H), 1.44 (m, 20H), 0.89 F(m, 6H).

General process for synthesis of hole transporting materials

A solution of 3-(5-bromothiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**) (0.2 mmol), 2,5-bis(trimethylstannyl)thiophene (**M2**) or 2,5-

bis(trimethylstannyl)selenophene (**M3**) and Pd(PPh3)4 (5 mol%) was charged in 50 mL reaction flask, cycled with argon and dissolved in degassed solvent mixture of 15 mL of anhydrous toluene. The reaction mixture 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 minimum volume of chloroform and reprecipitated in methanol (200 mL) and the precipitate was filtered and dried. The dried solid was subjected to flash column purification using haxane:CH_3Cl as eluent. The desired products obtained as 80 – 85% of yield.

Synthesis of DPP-Th

Brown shining solid, **^{1}HNMR** (400 MHz, CDCl3) δ (ppm): 8.92-8.90 (m, 4H), 7.60-7.59 (d, J = 5.0 Hz, 2H), 7.37 (s, 2H), 7.25-7.20 (m, 4H), 4.07 (t, 4H), 1.75 (m, 8H), 1.45-1.24 (m, 48H), 0.87 (m, 12H). **^{13}CNMR** (100 MHz, CDCl3) δ (ppm): 161.22, 141.74, 139.65, 139.00, 136.69, 136.51, 135.35, 130.63, 129.82, 128.68, 128.60, 126.04, 125.27, 108.24, 107.89, 42.33, 42.25, 31.90, 30.04, 29.99, 29.63, 29.56, 29.41, 29.32, 29.28, 26.92, 22.69, 14.12.

Synthesis of DPP-Se

Brown shining solid, **^{1}HNMR** (400 MHz, CDCl3) δ (ppm): 8.92-8.89 (m, 4H), 7.59-7.58 (d, J = 5.1 Hz, 2H), 7.30-7.29 (d, J = 4.1 Hz, 2H), 7.25 (m, 4H), 4.05 (t, 4H), 1.75 (m, 8H), 1.47-1.22 (m, 48H), 0.87 (m, 12H). **^{13}CNMR** (100 MHz, CDCl3) δ (ppm): 161.22, 141.46, 139.67, 138.98, 136.58, 135.37, 130.66, 129.82, 128.82, 128.61, 126.14, 125.95, 108.31, 107.94, 42.34, 42.26, 31.90, 30.05, 29.99, 29.56, 29.31, 29.28, 26.92, 22.69, 14.12.

Fabrication of PVSCs

The glass/ITO substrates were thoroughly cleaned sequentially with soap, deionized water, acetone, and isopropyl alcohol, followed by oven drying for 1 h and UV/ozone treatment for 30 min for deposition of the PSCs. The SnO_2 ETL was then deposited on the glass/ITO substrates by spin coating at 3000 rpm and annealing at 150 °C for 30 min. The spin coating solution for the SnO_2 ETL was prepared by dissolving $SnCl_2·2H_2O$ (0.2 g) in ethanol (8 ml) and stirring for 24 h at 70 °C before use. To obtain the $MAPbI_3$ precursor solution, a 1.5:1.5 M mixture of methyl ammonium iodide (MAI) and lead iodide (PbI_2) was dissolved in a 7:3 mixture of dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) and stirred overnight at 60 °C. The perovskite precursor solution was spin-coated in two steps at 1000 and 5000 rpm for 10 and20 s, respectively. During the second step, 500 μL of CB was dropped onto the spinning substrate 5 s before the end of the program. The films were then annealed at 125 °C for 15 min at a relative humidity (RH) of 22%. The small-molecule DPP-Th and DPP-Se solutions were prepared with the concentration of 5 mg mL^{-1} in CB and stirred at 80 °C overnight to obtain clear solutions. Furthermore, the reference hole extracting solution was prepared by mixing spiro-MeOTAD (80 mg), 4- tert-butylpyridine/acetonitrile (28 μL), 18.5 μL of a stock solution of Li-TFSI (531 mg mL−1 in dimethyl sulfoxide), 21 μL of a stock solution of FK209 (300 mg mL−1 in acetonitrile), and anhydrous CB (1 mL) using a well-known formulation. All the HTM solutions were spin coated at 3000 rpm for 30 s to form the HTL. Finally, an Au (80 nm) anode was thermally deposited under high vacuum (<1 × 10−6 Torr) through a shadow mask to create devices with a total active area of 0.2 cm^2.
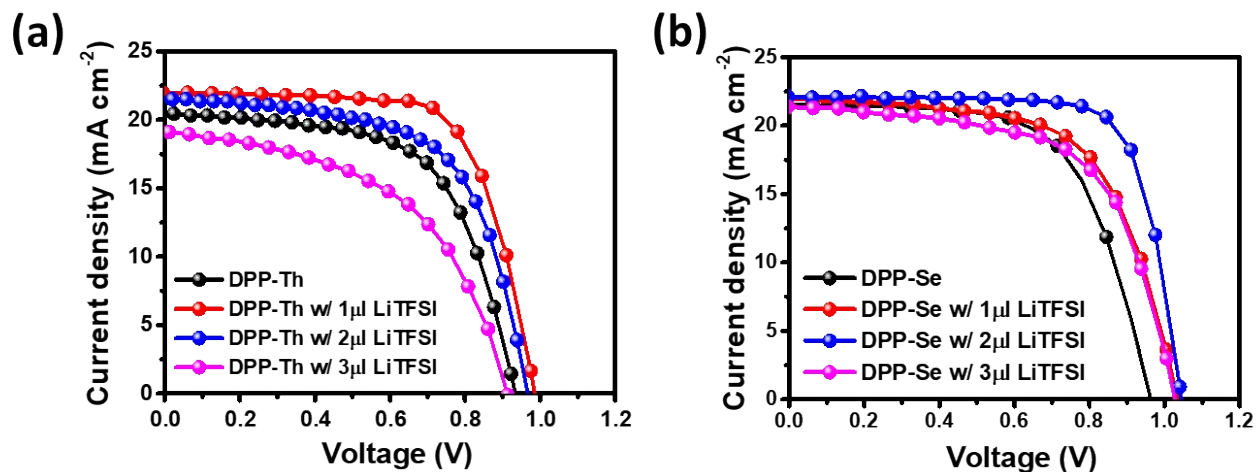
Figure S1. *J-V* characteristics of the PVSCs fabricated with (a) DPP-Th and (b) DPP-Se HTMs using different concentrations of Li-TFSI (The concentration of the Li-TFSI added from mother solution of Li-TFSI (530mg/ml in chlorobenzene) in μl (1 μl, 2 μl, and 3 μl) to the 1 ml solutions of the DPP-Th and DPP-Se).

Table S1. Photovoltaic parameters s of the PVSCs fabricated with different HTMs (DPP-Th, DPP-Se, DPP-Th w/ Li-TFSI, and DPP-Se 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 (1 μl, 2 μl, and 3 μl) to the 1 ml solutions of the DPP-Th and DPP-Se.

HTM	V_{OC} (V)	J_{SC} (mA-cm^{-2})	FF (%)	PCE (%)	R_S (Ω-cm^2)	R_{Sh} (Ω-cm^2)
DPP-Th	0.93±0.21	20.53±0.71	61.42±1.11	12.02±0.33	25.74±6.14	2532.5±969.7
DPP-Th + 1μl LiTFSI	1.00±0.03	22.08±0.86	66.53±1.76	14.32±0.37	24.23±5.09	3282.6±799.3
DPP-Th + 2μl LiTFSI	0.97±0.03	21.23±0.53	63.01±1.08	12.86±0.04	36.67±19.55	2621.7±837.3
DPP-Th + 3μl LiTFSI	0.91±0.02	19.10±0.43	56.07±1.27	9.74±0.74	39.17±9.15	2200.5±441.3
DPP-Se	0.96±0.01	21.70±0.39	63.37±3.55	13.51±0.91	22.35±2.52	4149.7±991.5
DPP-Se + 1μl LiTFSI	1.01±0.12	21.98±0.15	66.04±1.18	14.31±0.87	21.55±9.12	4661.1±152.4
DPP-Se + 2μl LiTFSI	1.02±0.07	22.18±0.25	74.42±4.23	16.42±0.41	16.69±5.97	7283.6±992.4
DPP-Se + 3μl LiTFSI	1.00±0.02	21.52±0.15	61.41±2.26	13.24±0.47	17.71±5.31	3183.5±491.7
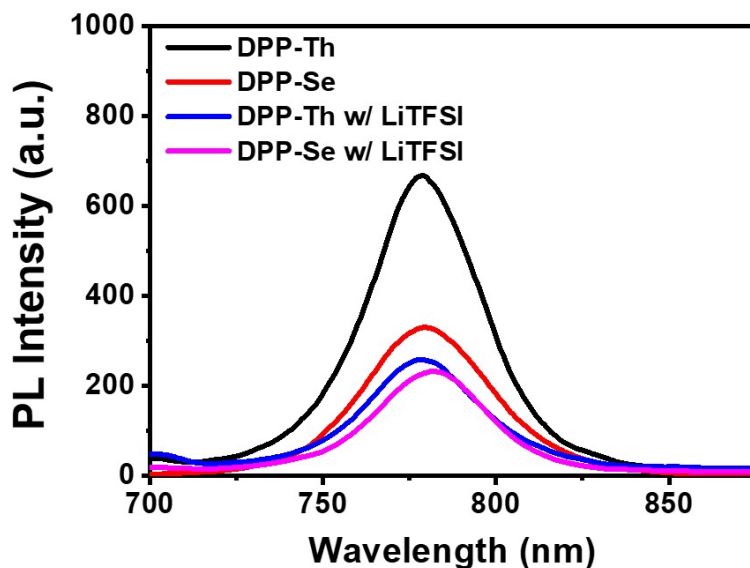
Figure S2. Photoluminescence (PL) spectra recorded for the samples glass/ITO/SnO$_2$/Perovskite:MAPbI$_3$/HTM when films were excited from glass side.
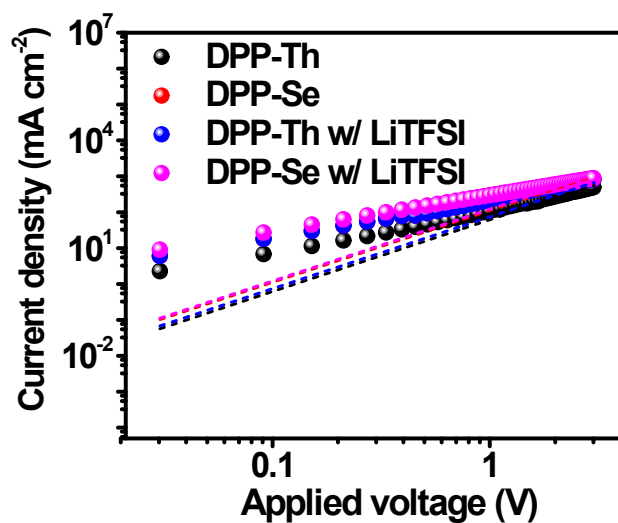
Table S2. Packing parameters derived from GIWAXS measurements for pristine **HTMs**.

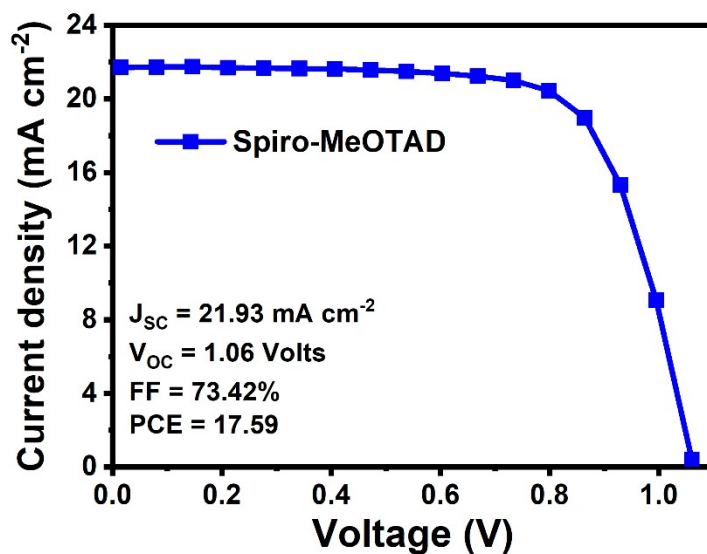| Film	IP[a]		OOP[b]	
	d-(100) [Å] / (q-(100) [Å^{-1}])	d-(010) [Å] / (q-(010) [Å^{-1}])	d-(100) [Å] / (q-(100) [Å^{-1}])	d-(010) [Å] / (q-(010) [Å^{-1}])
DPP-Th	24.16 (0.260)	3.65 (1.723)	25.22 (0.249)	-
DPP-Se	26.28 (0.239)	3.63 (1.73)	25.95 (0.242)	-

[a]Calculation from *xy*-axis (in-plane).

[b]Calculation from *z*-axis (out-of-plane).

Figure S3. Dark current density (J_d)-voltage curves for hole-only controlled devices (Glass/ITO/PEDOT:PSS /HTM/Au) fabricated with different HTMs.

Figure S4. Current density-voltage (J-V) characteristics of the MAPbI$_3$ based PVSC under 0.97 sun conditions. PVSC has device structure glass/ITO/SnO$_2$/perovskite MAPbI$_3$/spiro-MeOTAD/Au.
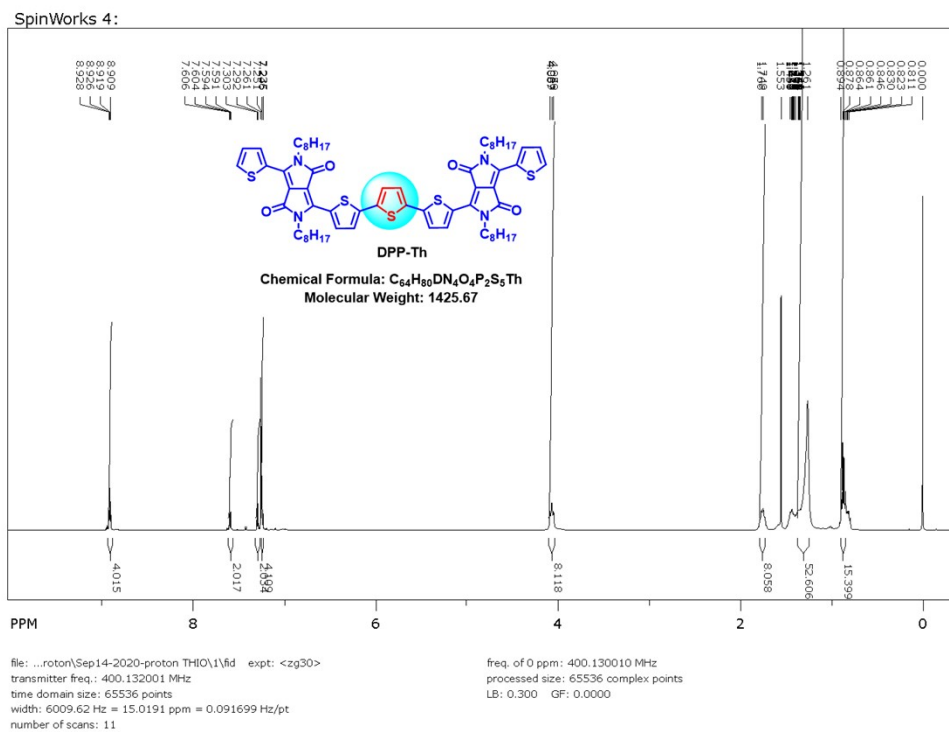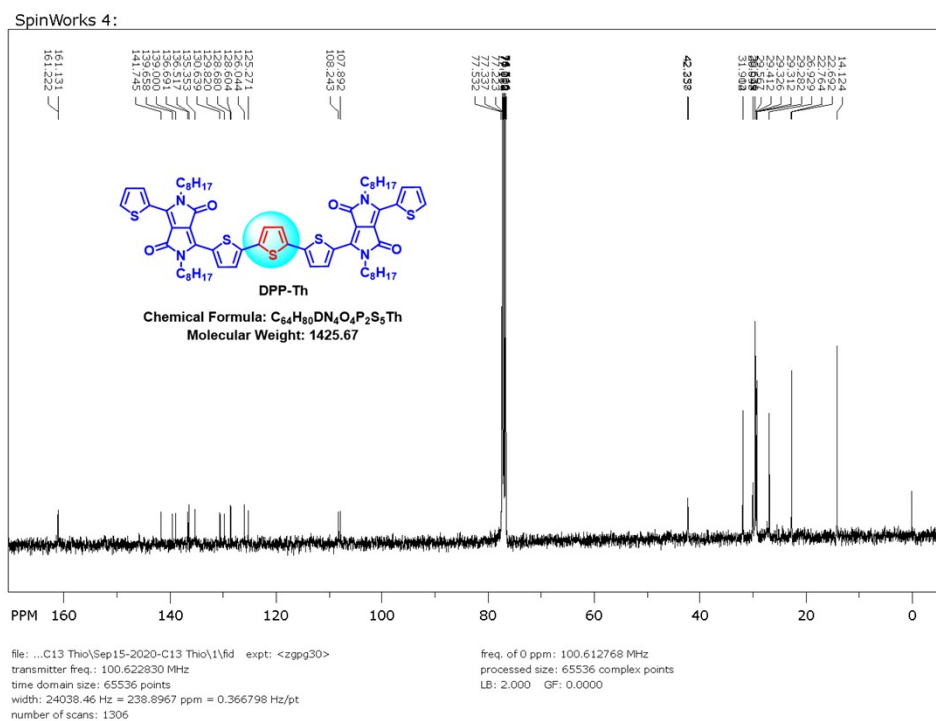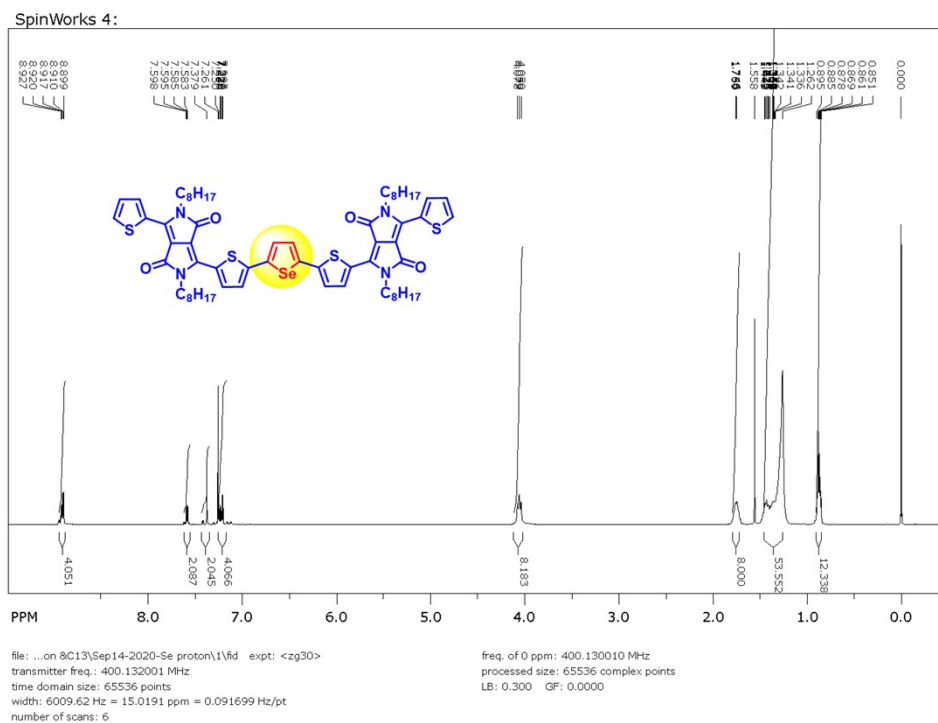
Figure S5. ^{1}H NMR of monomer **DPP-Th**.
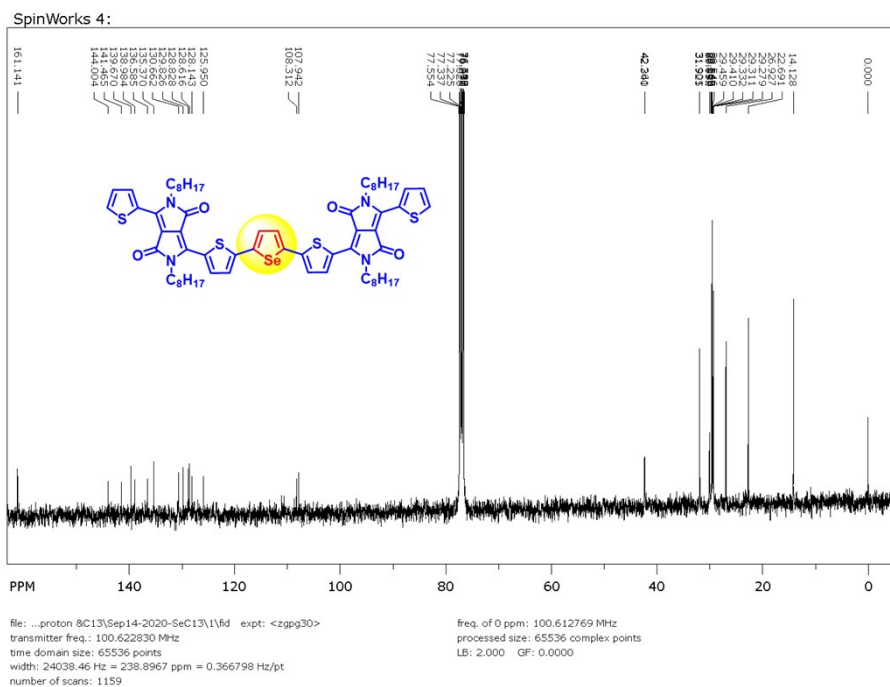

Figure S6. ^{13}C NMR of monomer **DPP-Th**.

Figure S7. ^{1}H NMR of monomer **DPP-Se**.

Figure S8. ^{13}C NMR of monomer **DPP-Se**.

Synthesis cost estimation of 1 gram DPP-Th and DPP-Se

We roughly estimated the synthesis cost of 1 gram DPP-Th and DPP-Se according to the model proposed by Osedach et al.[4] Such a model has been recently applied by many other groups to estimate the cost of many other hole-transporting materials.[5-7] 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[6] to get a more realistic estimation of lab synthesis costs of 225.64 $/g (152.43 x 1.5 = 225.64 $/g) and 240.89 $/g (160.59 x 1.5 = 240.89$/g) for DPP-Th and DPP-Se, respectively. Thus, both newly synthesized HTMs were found to be much cheaper than that of spiro-OMeTAD (~475.00 $/g, Sigma Aldrich Korea).[8]

Synthesis of 2,5-dioctyl-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		75		0.065	4.87	
n-Octylbromide	5.26		0.174		0.915	
$CHCl_3$		2000		0.0041	8.2	
magnesium sulphate	10g		0.003		0.03	
Silica gel	500g		0.0135		6.75	
Total					49.76	
Product step 1 (Yield = 85%, 4.5g)						**11.05**

Synthesis of 3-(5-bromothiophen-2-yl)-2,5-dioctyl-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		11.05		5.85	
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					25.47	
Product step 2 (Yield = 65%, 0.391g)						**64.94**

Synthesis of DPP-Th

Chemical	Reagent mass (g)	Solvent Vol. (ml)	Reagent cost ($/g)	Solvent cost ($/ml)	Reagent + solvent cost ($)	Product cost ($/g)
2, 5-Bis(trimethylstannyl)thiophene **(M2)**	0.2		63		12.6	
3-(5-bromothiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione **(M1)**	0.62g		64.94		40.26	
Pd catalyst*	0.028		30.32		0.85	
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					67.07	
Product step 3 (Yield = 80%, 0.44g)						**152.43**

Synthesis of **DPP-Se**

Chemical	Reagent mass (g)	Solvent Vol. (ml)	Reagent cost ($/g)	Solvent cost ($/ml)	Reagent + solvent cost ($)	Product cost ($/g)
2, 5-Bis(trimethylstannyl)selenophene **(M2)**	0.2		89		17.8	
3-(5-bromothiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione **(M1)**	0.62g		64.94		40.26	
Pd catalyst*	0.028		30.32		0.85	
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					72.27	
Product step 1 (Yield = 86%, 0.45g)						160.59

References:

1. 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 Applied Materials & Interfaces*, 2017, **9**, 12617-12628.
2. S. R. Suranagi, R. Singh and M. Kim, *Dyes and Pigments*, 2019, **163**, 525-532.
3. Z. Ni, H. Wang, Q. Zhao, J. Zhang, Z. Wei, H. Dong and W. Hu, *Advanced Materials*, 2019, **31**, 1806010.
4. T. P. Osedach, T. L. Andrew and V. Bulović, *Energy & Environmental Science*, 2013, **6**, 711-718.
5. M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *Journal of Materials Chemistry A*, 2015, **3**, 12159-12162.
6. 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, *Nature Energy*, 2016, **1**, 15017.
7. 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.
8. Cost of spiro-MeOTAD 2021, https://www.sigmaaldrich.com/KR/en/product/aldrich/792071.