

## Supporting Information

### **Molecular Engineering of Methoxy-Substituted Terthienyl Core Unit Based Hole Transport Materials for Perovskite Solar Cell**

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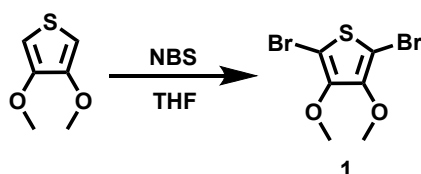
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## Synthesis method

**Chemicals:** All of the solvents and chemicals were used as received unless specially stated.

### Synthesis of DTP-1

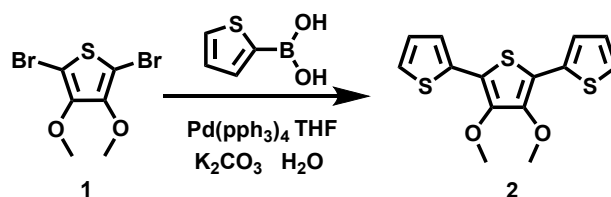


**2,5-dibromo-3,4-dimethoxythiophene (1).** N-Bromo-succinimide (8.15 g, 45.8 mmol) was slowly added to a solution of tetrahydrofuran (100 mL) containing 3,4-dimethoxythiophene (3 g, 20.8 mmol), and the resulting mixture was stirred at 0-5 °C for 4 h. The reaction solution was then extracted with ethyl acetate and water. The organic layer was collected and evaporated reduced pressure. The crude product was purified by column chromatography (petroleum ether : dichloromethane = 8 : 1 v/v) to obtain **1** (5.6 g, yield: 89%) as a slightly yellow liquid. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  3.85 (s, 6H).

**Table S1.** Synthesis cost of intermediate **1**.

Reagent	Amount /g	Amount /mL	Price (RMB/g or RMB/mL)	Total price (RMB)
3,4-dimethoxythiophene	3.00		3.500	10.500
THF		100.00	0.136	13.600
N-Bromo-succinimide	8.15		0.138	1.128
Dichloromethane		100.00	0.0144	1.440
Ethyl acetate		150.00	0.0144	2.160
Silica gel	130.00		0.035	4.550
Petroleum ether		800.00	0.0104	8.320

<b>Total cost</b>	41.698 RMB
<b>Amount intermediate 2</b>	5.600 g
<b>Cost for intermediate 2</b>	7.446 RMB/g
<b>Exchange rate</b>	1\$=7.076 RMB

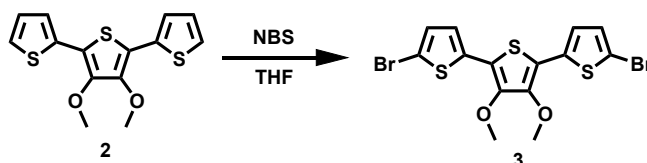


**3',4'-dimethoxy-2,2':5',2''-terthiophene (2).** In a 2-necked flask (250 mL) under nitrogen, **1** (3 g, 8.98 mmol) and 2-thienoborate acid (2.53 g, 19.76 mmol) were dissolved in dry THF (100 mL), then added Pd(pph<sub>3</sub>)<sub>4</sub> (0.52 g, 0.45 mmol) and K<sub>2</sub>CO<sub>3</sub> (10 mL) saturated aqueous solution. The mixture was degassed for 10 minutes and then refluxed at 80 °C for 15 h under nitrogen. After cooling down the reaction to room temperature, the mixture was diluted with dichloromethane and washed with water. The organic layer was collected and evaporated reduced pressure. The crude product was purified by column chromatography (petroleum ether : dichloromethane = 10 : 1 v/v) to obtain **2** (1.87 g, yield: 73%) as a slightly yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO) δ: 7.37 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.75 (s, 6H).

**Table S2.** Synthesis cost of intermediate 2.

Reagent	Amount /g	Amount /mL	Price(RMB/g or RMB/mL)	Total price(RMB)
<b>1</b>	3.00		7.446	22.388
2-Thienoborate acid	2.53		3.560	9.007
Pd(pph <sub>3</sub> ) <sub>4</sub>	0.52		72.000	37.440
K <sub>2</sub> CO <sub>3</sub>		10.00	0.062	0.620
THF		100.00	0.136	13.600

Dichloromethane		250.00	0.0144	3.600
Silica gel	200.00		0.035	7.000
Petroleum ether		1000.00	0.0104	10.400
<b>Total cost</b>	104.055 RMB			
<b>Amount intermediate 1</b>	1.87 g			
<b>Cost for intermediate 1</b>	55.644 RMB/g			
<b>Exchange rate</b>	1\$=7.076 RMB			

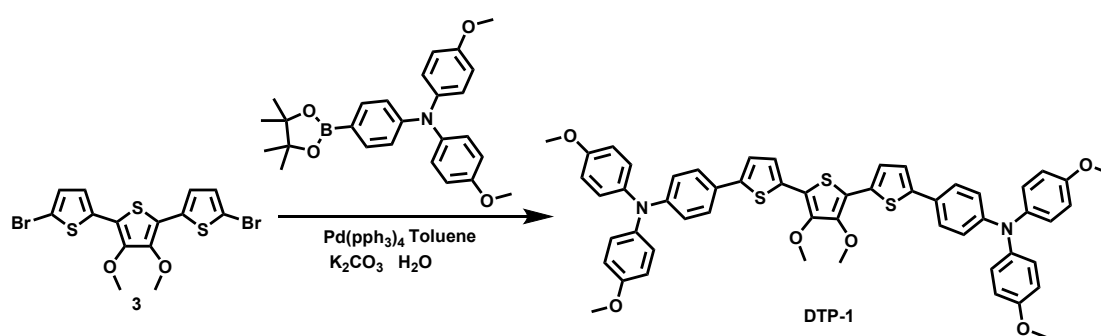


**5,5''-dibromo-3',4'-dimethoxy-2,2':5',2''-terthiophene (3).** N-Bromo-succinimide (1.83 g, 10.27 mmol) was slowly added to a solution of tetrahydrofuran (100 mL) containing **2** (1.44 g, 4.67 mmol), and the resulting mixture was stirred at 0-5 °C for 8 h. The reaction solution was then extracted with ethyl acetate and water. The organic layer was collected and evaporated reduced pressure. The crude product was purified by column chromatography (petroleum ether : dichloromethane = 12 : 1 v/v) to obtain **3** (1.81 g, yield: 87%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.36 (d, *J* = 3.9 Hz, 2H), 7.22 (d, *J* = 3.9 Hz, 2H), 3.99 (s, 6H). Retardation factor (*R<sub>f</sub>*) = 0.49.

**Table S3.** Synthesis cost of intermediate **3**.

Reagent	Amount /g	Amount /mL	Price (RMB/g or RMB/mL)	Total price (RMB)
<b>2</b>	1.44		55.644	80.127
THF		100.00	0.136	13.600
N-Bromo-succinimide	1.83		0.138	0.253

Dichloromethane		100.00	0.0144	1.440
Ethyl acetate		150.00	0.0144	2.160
Silica gel	180.00		0.035	6.300
Petroleum ether		1200.00	0.0104	12.480
<b>Total cost</b>	116.360 RMB			
<b>Amount intermediate 2</b>	1.81 g			
<b>Cost for intermediate 2</b>	64.287 RMB/g			
<b>Exchange rate</b>	1\$=7.076 RMB			



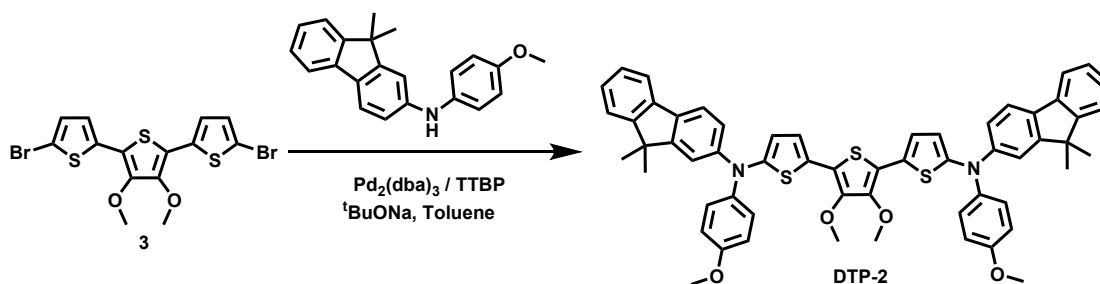
**4,4'-(3',4'-dimethoxy-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (DTP-1).** In a 2-necked flask, **3** (0.86 g, 1.93 mmol) and 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1.83 g, 4.25 mmol) were dissolved in dry THF (80 mL), then Pd(pph<sub>3</sub>)<sub>4</sub> (0.12 g, 0.10 mmol) and K<sub>2</sub>CO<sub>3</sub> (10 mL) saturated aqueous solution were added in the solution. The mixture was degassed for 10 minutes and then refluxed at 115 °C for 15 h under nitrogen. After cooling to the room temperature, the mixture is washed several times with ethyl acetate and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer was collected and evaporated reduced pressure. The crude product was purified by column chromatography (petroleum ether : dichloromethane = 2 : 1 vol/vol) and (petroleum ether : ethyl acetate = 6 : 1 vol/vol) to obtain **DTP-1** (0.92 g, yield: 50.8%) as an orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.51 - 7.34 (m, 4H), 7.31 -

7.20 (m,  $J = 3.8$  Hz, 2H), 7.12 (m,  $J = 8.5$  Hz, 10H), 6.93 (t,  $J = 8.6$ , 4H), 6.91 - 6.78 (m,  $J = 4.6$  Hz, 8H), 3.98 (s, 6H), 3.82 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.23, 156.03, 148.91, 148.29, 147.50, 145.08, 144.10, 143.52, 140.65, 140.39, 132.06, 126.90, 126.78, 126.67, 126.28, 126.18, 125.07, 125.01, 124.37, 121.67, 120.55, 120.07, 119.86, 114.82, 114.76, 108.94, 108.41, 77.36, 77.04, 76.72, 60.36, 60.28, 55.51, 29.72, 14.14, 1.04. HR-MS: calculated:  $\text{C}_{54}\text{H}_{46}\text{N}_2\text{O}_6\text{S}_3$ , 914.2518, found: 914.2485.

**Table S4.** Synthesis cost of intermediate **DTP-1**.

Reagent	Amount /g	Amount /mL	Price (RMB/g or RMB/mL)	Total price (RMB)
<b>3</b>	0.86		64.287	55.287
4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline	1.83		144.000	263.520
THF		80.00	0.136	10.880
$\text{Pd}(\text{pph}_3)_4$	0.12		72.000	8.640
$\text{K}_2\text{CO}_3$		10.00	0.062	0.620
Silica gel	100.00		0.035	3.500
Petroleum ether		800.00	0.0104	8.320
Dichloromethane		100.00	0.0144	1.440
Ethyl acetate		200.00	0.0144	2.880
<b>Total cost</b>	354.769 RMB			
<b>Amount DTP-1</b>	0.92 g			
<b>Cost for DTP-1</b>	385.618 RMB/g			
<b>Exchange rate</b>	1\$=7.076 RMB			

**Synthesis of DTP-2**



**N5,N5''-bis(9,9-dimethyl-9H-fluoren-2-yl)-3',4'-dimethoxy-N5,N5''-bis(4-methoxyphenyl)-[2,2':5',2''-terthiophene]-5,5''-diamine (DTP-2).** A mixture of **3** (0.80 g, 1.8 mmol), *N*-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (1.46 g, 4.60 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.084 g, 0.09 mmol), Tri-tert-butylphosphonate (0.053 g, 0.18 mmol) and sodium tert-butoxide (0.52 g, 5.41 mmol) in toluene (80 mL) was stirred at 115 °C for 24 h. After cooling down the reaction to room temperature, the mixture was diluted with ethyl acetate and washed with water. The organic layer was collected and evaporated reduced pressure. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 9 : 1 vol/vol) to obtain **DTP-2** (0.52 g, yield: 55.7%) as an orange red solid. <sup>1</sup>H NMR (400 MHz, DMSO) δ: 7.69 (dd, J = 7.6, 3.1 Hz, 4H), 7.62 (d, J = 7.3 Hz, 2H), 7.54 – 7.39 (m, 6H), 7.23 (d, J = 8.8 Hz, 6H), 6.78 (d, J = 2.0 Hz, 2H), 6.58 (dd, J = 11.4, 5.4 Hz, 4H), 6.25 (d, 2H), 3.75 (s, 12H), 1.32 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.08, 155.06, 153.57, 153.49, 139.97, 139.02, 138.78, 127.04, 126.98, 126.72, 126.37, 122.51, 122.45, 122.37, 121.57, 120.63, 120.43, 119.55, 119.36, 118.74, 116.91, 114.90, 114.75, 114.38, 77.37, 77.06, 76.74, 60.22, 55.53, 46.94, 46.87, 34.71, 31.62, 29.09, 27.13, 27.10, 26.95, 25.32, 22.69, 22.66, 20.74, 14.15, 11.47, 1.05. HR-MS: calculated: C<sub>58</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>, 934.2933, found: 934.2892.

**Table S5.** Synthesis cost of intermediate **DTP-2**.

Reagent	Amount /g	Amount /mL	Price (RMB/g or RMB/mL)	Total price (RMB)
<b>3</b>	0.80		64.287	51.429
<i>N</i> -(4-methoxyphenyl)-9,9-	1.46		45.950	67.087

dimethyl-9H-fluoren-2-amine				
$\text{Pd}_2(\text{dba})_3$	0.084		130.000	10.920
Tri-tert-butylphosphonate	0.053		11.000	0.583
sodium tert-butoxide	0.52		0.450	0.234
Toluene		80.00	0.041	3.280
Silica gel	100.00		0.035	3.500
Petroleum ether		900.00	0.0104	9.360
Ethyl acetate		250.00	0.0144	3.600
<b>Total cost</b>	149.993 RMB			
<b>Amount DTP-2</b>	0.52 g			
<b>Cost for DTP-2</b>	288.448 RMB/g			
<b>Exchange rate</b>	1\$=7.076 RMB			

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 7.37 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.75 (s, 6H).

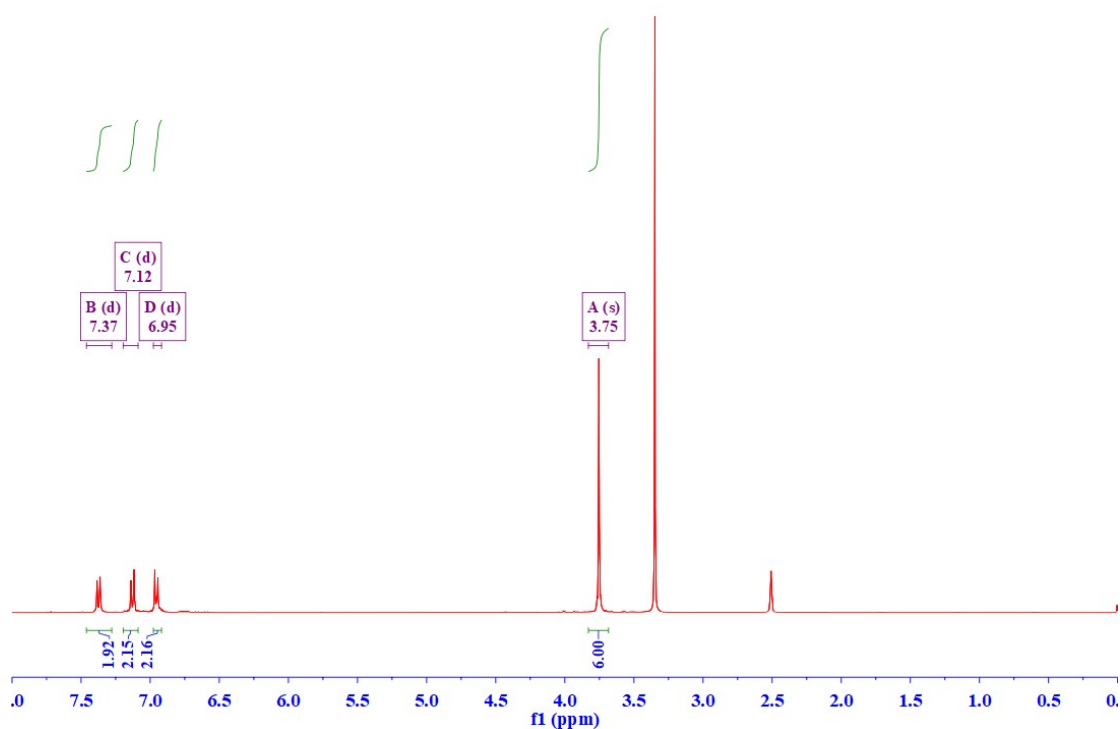


Figure S1.  $^1\text{H}$ -NMR spectrum of compound 2 recorded in DMSO.



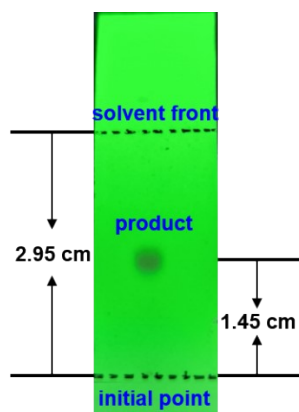


Figure S2. Rf value test of the intermediate compound 3.

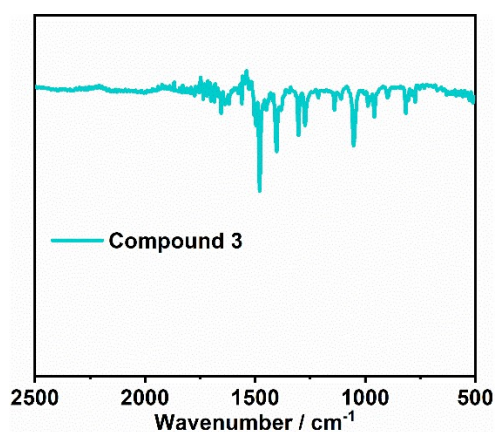


Figure S3. FT-IR spectrum of the intermediate compound 3.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.34 (m, 4H), 7.31 – 7.20 (m,  $J = 3.8$  Hz, 2H), 7.12 (m,  $J = 8.5$  Hz, 10H), 6.93 (t,  $J = 8.6$ , 4H), 6.91 – 6.78 (m,  $J = 4.6$  Hz, 8H), 3.98 (s, 6H), 3.82 (s, 12H).

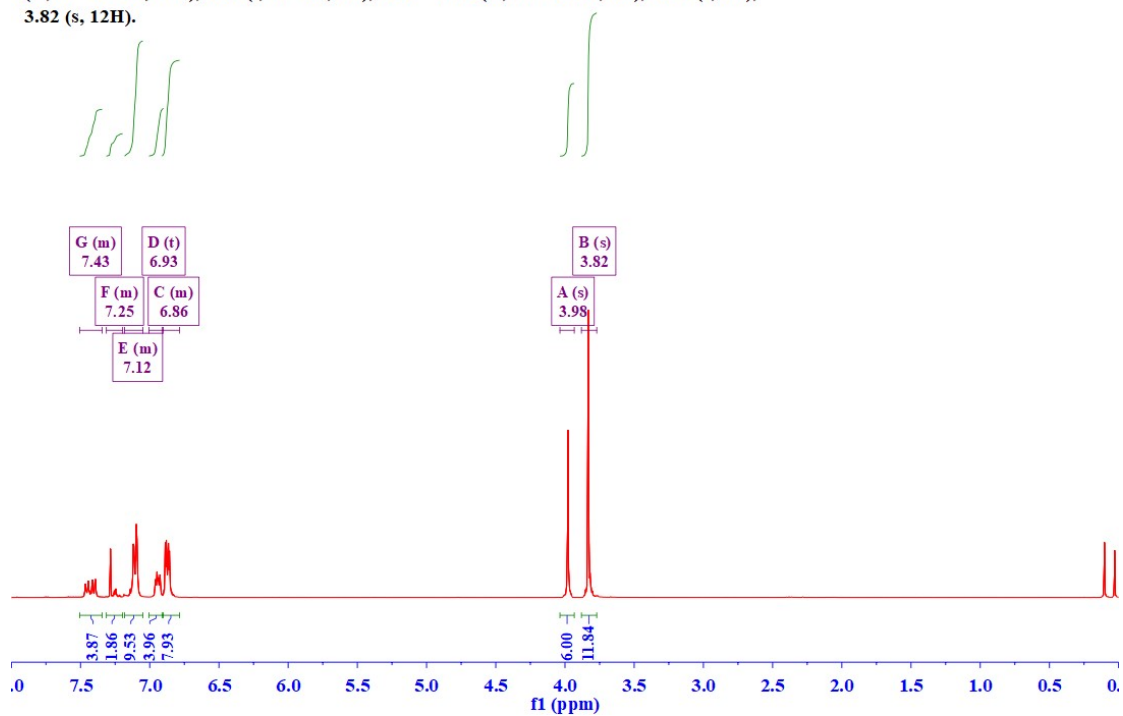


Figure S4.  $^1\text{H-NMR}$  spectrum of DTP-1 recorded in  $\text{CDCl}_3$ .

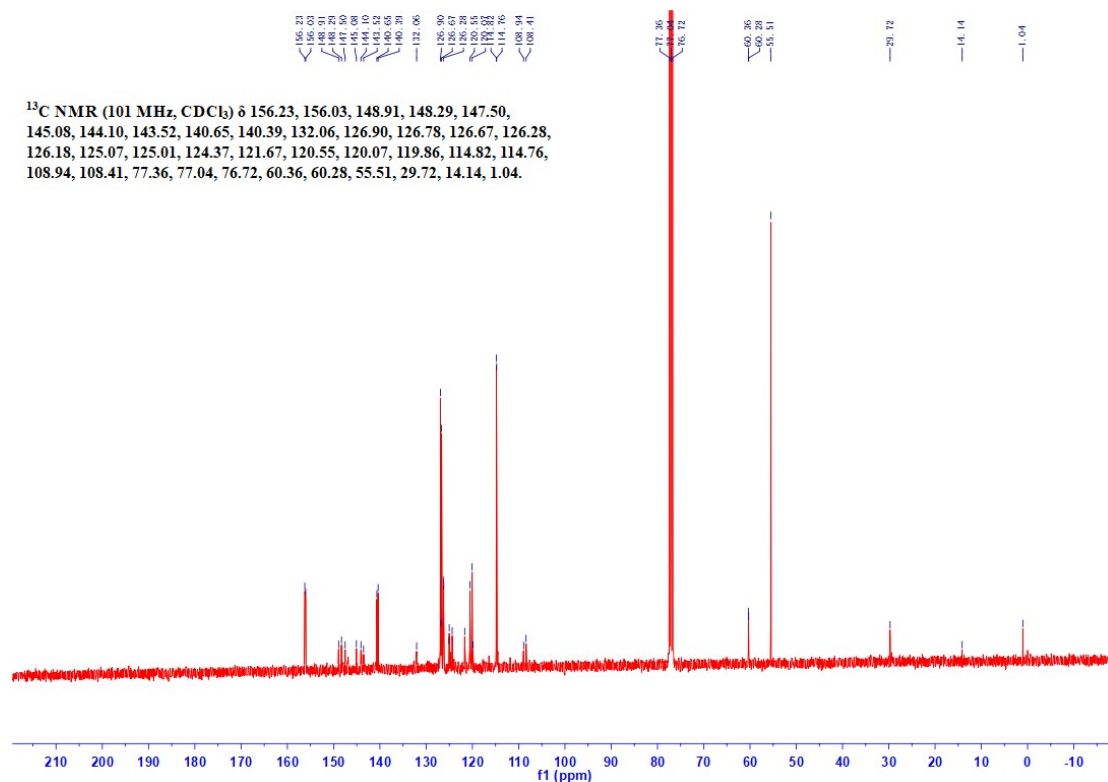


Figure S5.  $^{13}\text{C}$ -NMR spectrum of DTP-1 recorded in  $\text{CDCl}_3$ .

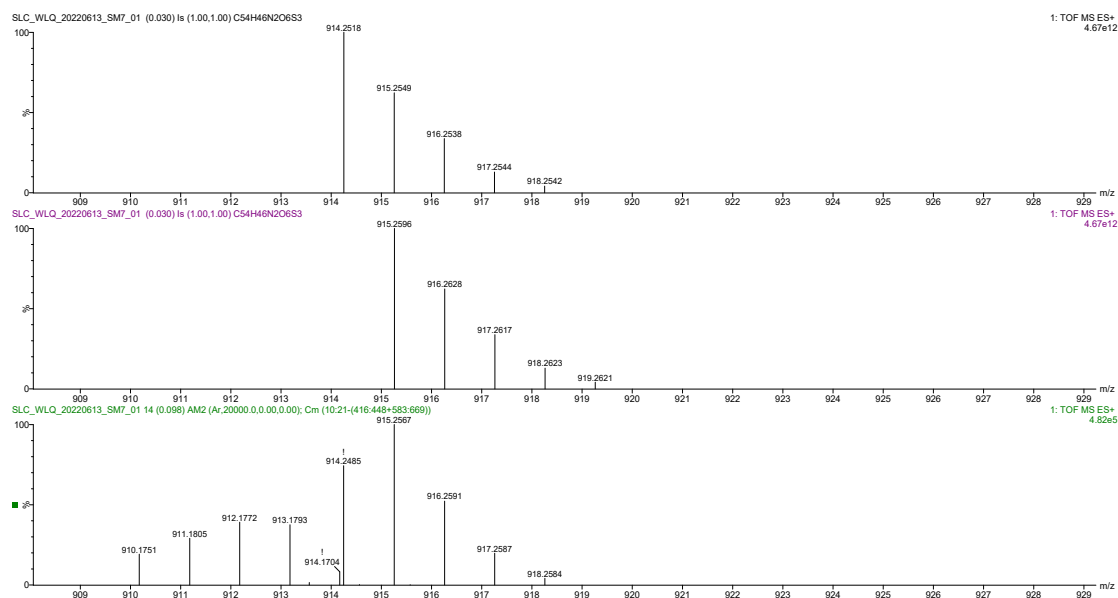


Figure S6. HR-MS spectrum of DTP-1 in THF.

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.69 (dd,  $J = 7.6, 3.1$  Hz, 4H), 7.62 (d,  $J = 7.3$  Hz, 2H), 7.54 – 7.39 (m, 6H), 7.23 (d,  $J = 8.8$  Hz, 6H), 6.78 (d,  $J = 2.0$  Hz, 2H), 6.58 (dd,  $J = 11.4, 5.4$  Hz, 4H), 6.25 (d, 2H), 3.75 (s, 12H), 1.32 (s, 12H).

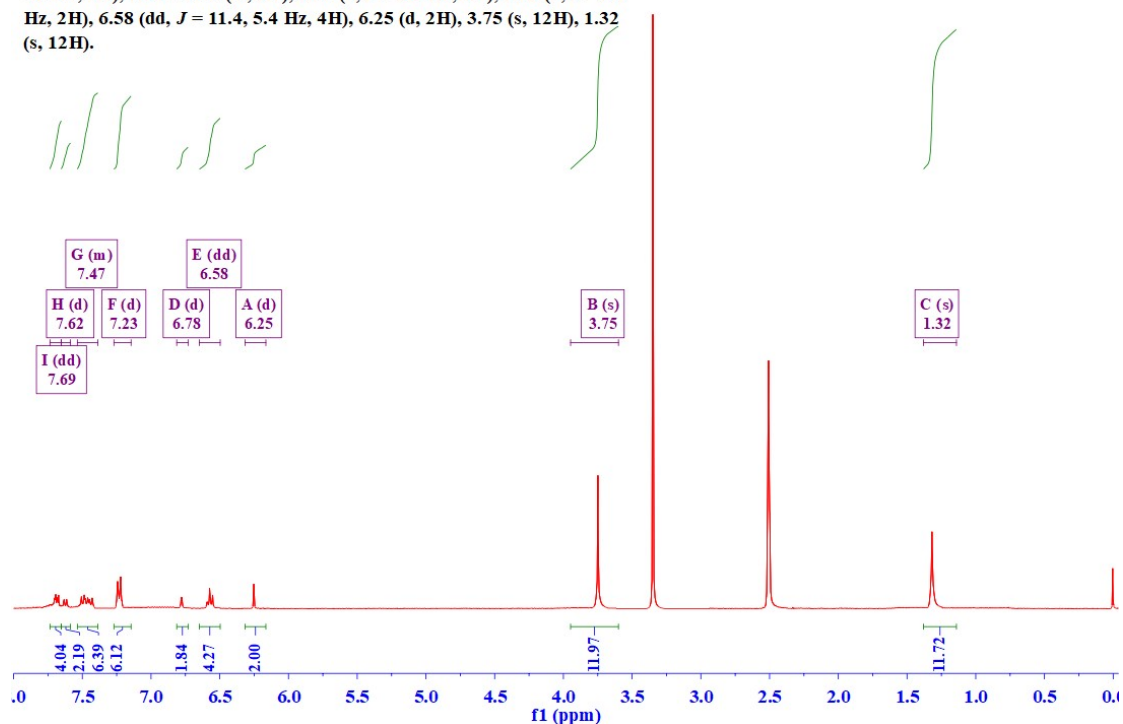


Figure S7.  $^1\text{H}$ -NMR spectrum of DTP-2 recorded in DMSO.

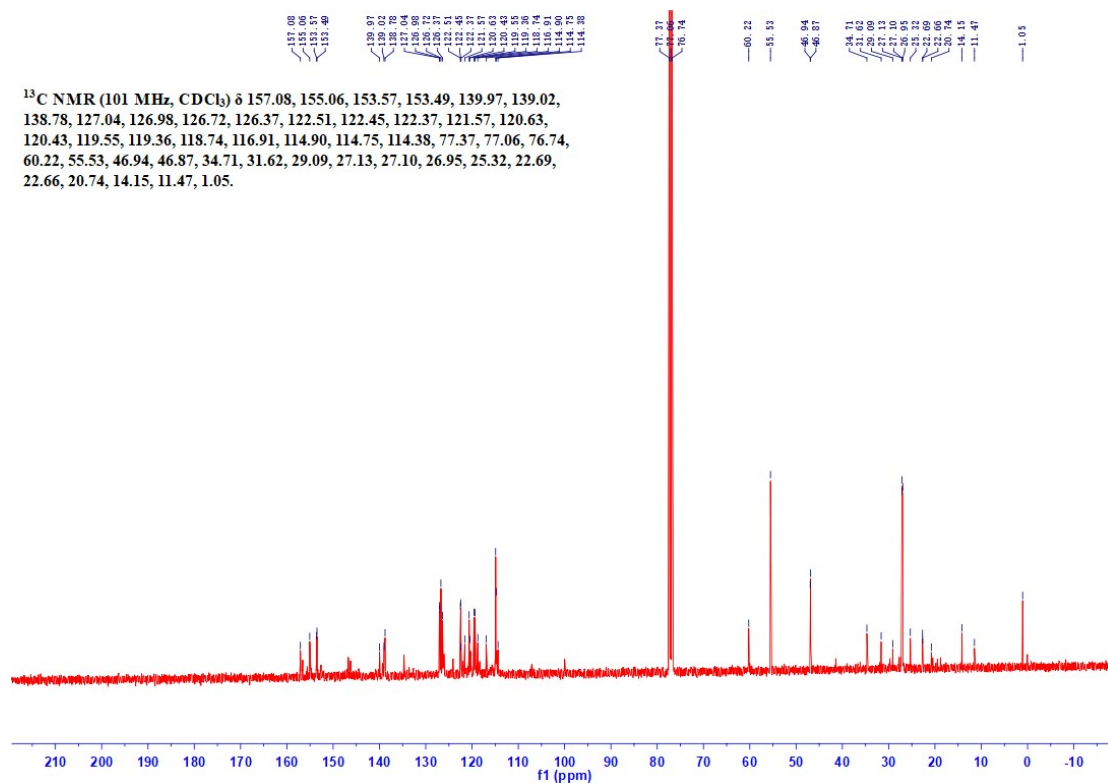


Figure S8.  $^{13}\text{C}$ -NMR spectrum of DTP-2 recorded in  $\text{CDCl}_3$ .

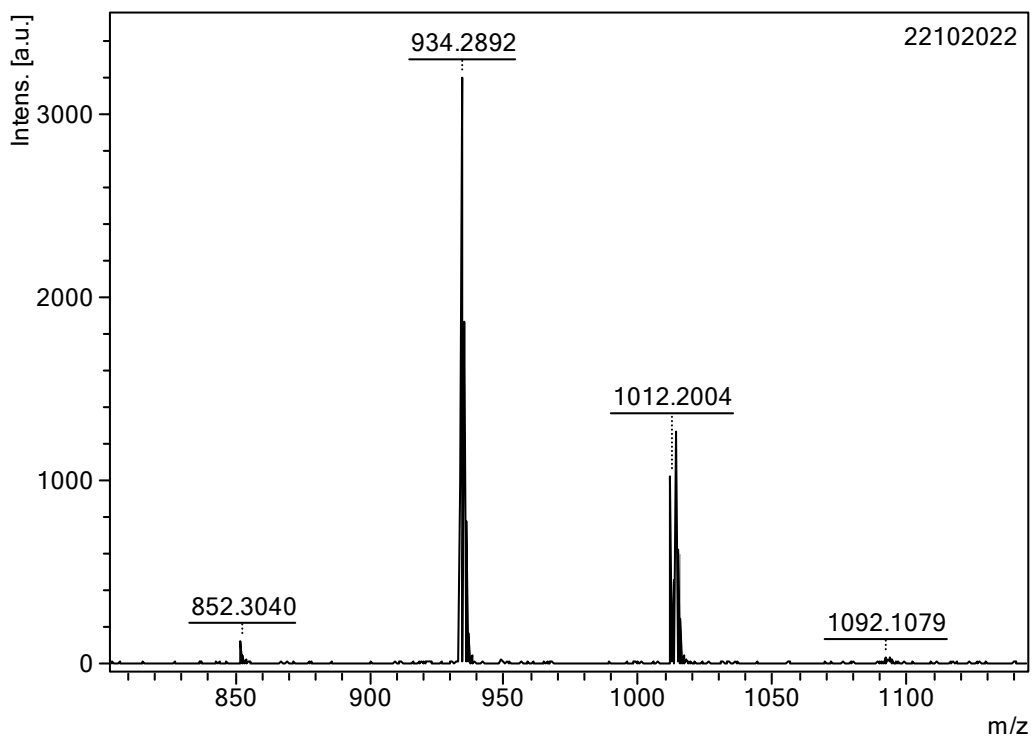


Figure S9. HR-MS spectrum of DTP-2 in THF.

## Measurement

The absorption spectra were recorded on an Agilent 8453 spectrophotometer using a 1 cm cuvette. Cyclic voltammetry (CV) was performed in dichloromethane with 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte, a Ag<sup>+</sup>/AgNO<sub>3</sub> electrode as the reference electrode, a carbon-glass electrode as the working electrode, a Pt electrode as the counter electrode and ferrocene/ferrocenium (*Fc*/*Fc*<sup>+</sup>) as an internal reference with a CH Instruments electrochemical workstation (model 660 A). The SEM images were taken on a JEOL JSM-S4800. Light source for the photocurrent-voltage (*J-V*) measurement is an AM 1.5G solar simulator. The incident light intensity was 100 mW·cm<sup>-2</sup> calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.126 cm<sup>2</sup>. The *J-V* curves were obtained by the linear sweep voltammetry (LSV) method using a Keithley 2400 source-measure unit. The

measurement of the incident-photon-to-current conversion efficiency (IPCE) was performed with CEL-QPCE3000 photoelectric chemical quantum efficiency testing and analysis system.

Hole mobility was measured by using the space-charge-limited current (SCLC) method with the device structure of FTO/PEDOT:PSS/HTM/Au. Two devices (eight groups of data) are tested and the data shown in Figure is an average data. Space-charge-limited current can be described by equation below:

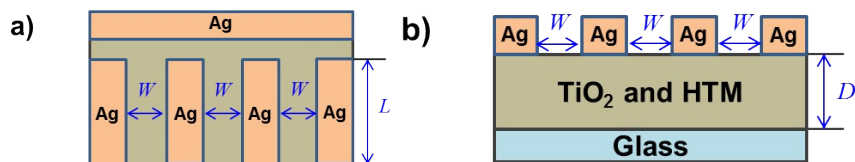
$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{D^3}$$

where  $J$  is the current density,  $\mu$  is the hole mobility,  $\epsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12}$  F / m),  $\epsilon_r$  is the dielectric constant of the material (normally taken to approach 3 for organic semiconductors),  $V$  is the applied bias, and  $D$  is the film thickness.

For conductivity, two devices (six groups of data) are tested and the data shown in Figure is also an average data. The electrical conductivities of the HTM films were determined by using two-probe electrical conductivity measurements. The electrical conductivity ( $\sigma$ ) was calculated by using the following equation:

$$\sigma = \frac{W}{R L D}$$

where  $L$  is the channel length 10 mm,  $W$  is the channel width 2 mm,  $D$  is the film thickness of the  $\text{TiO}_2$  and HTM, and  $R$  is the film resistance calculated from the gradients of the curves.



Scheme S1. Schematic illustrations of the conductivity device: (a) top-sectional view; (b) cross-sectional view.

### Perovskite Solar Cell Fabrication

The perovskite and hole-transport material solutions were prepared inside an Argon glovebox. Conducting SnO<sub>2</sub>:F glass substrates (Pilkington, TEC15) were cut (15 mm x 15 mm) and patterned by chemical etching using zinc powder and hydrochloric acid. The substrates were washed by sonication subsequently in 2% RBST<sup>TM</sup>50 solution (Fluka) for 30 minutes, deionized water, acetone and ethanol for 15 minutes each. A thin and dense layer of TiO<sub>2</sub> (bl-TiO<sub>2</sub>) was applied on the glass using spray-pyrolysis at 500°C from a solution of 0.2 M titanium (IV) tetraisopropoxide (Aldrich) and 2 M acetylacetonate (Aldrich) in isopropanol (Aldrich). The 15% Tin Oxide colloid precursor was diluted to 2.67% by deionized water. And the solution was spun onto the glass/compact TiO<sub>2</sub> substrate surface at 3000 rpm for 30 s, and then baked on a hotplate in ambient atmosphere at 120 °C for 20 min. To yield a (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> perovskite solution we mixed PbI<sub>2</sub> (TCI), FAI (Dyename), PbBr<sub>2</sub> (Alfa Aesar), MABr (Dyename), in molar concentrations of 1.1, 1, 0.2, 0.2, respectively, in 4:1 DMF:DMSO (anhydrous, Aldrich). The solutions were heated to dissolve the inorganic salts but otherwise kept at room temperature at all times. 40 µl of the perovskite solution spread onto the TiO<sub>2</sub>. The substrate was the spin-coated at 1000 rpm for 10 seconds and 4000

rpm for 30 seconds with a ramp speed of 2000 rpm/s. During the second spin-coating step an anti-solvent was injected onto the film after 15 seconds using 200  $\mu$ l of chlorobenzene (anhydrous, Aldrich). The perovskite films were then annealed at 100°C for 30 minutes on a hotplate. Subsequently, the HTM layer was then spin coated on top of the perovskite film. The HTL was deposited by spin coating at 4000 rpm for 30 s with chlorobenzene solutions (THP-1: 40 mg THP-1, 30 mM LiTFSI, 250 mM TBP and 4 mM FK209; DTP-1: 40 mg, 30 mM LiTFSI, and 4 mM FK209; DTP-2: 40 mg, 30 mM LiTFSI, 250 mM TBP and 4 mM FK209). Finally, a layer of 100 nm Au was deposited sequentially under high vacuum ( $<4 \times 10^{-4}$  Pa) by thermal evaporation through a shadow mask to form an active area of  $\sim 20$  mm<sup>2</sup>.

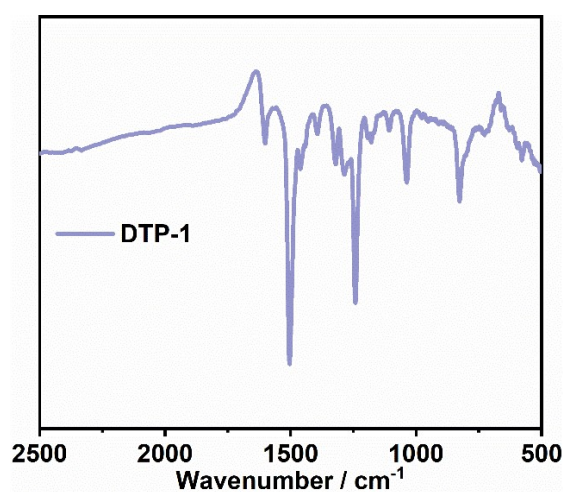


Figure S10. FT-IR spectrum of the compound DTP-1.

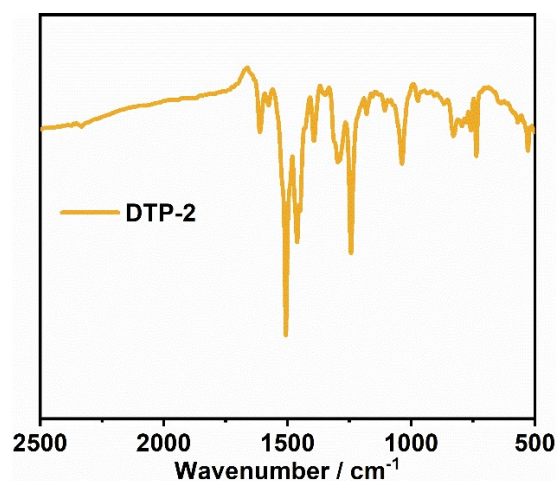


Figure S11. FT-IR spectrum of the compound DTP-2.

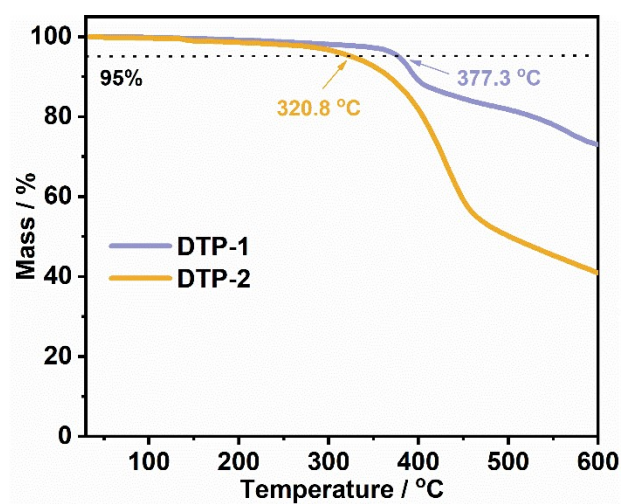


Figure S12. Thermogravimetric analysis of DTP-1 and DTP-2 measured with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .

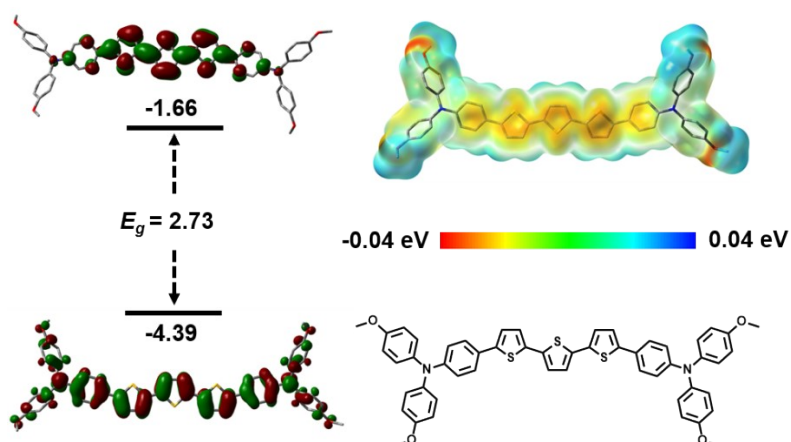


Figure S13. Optimized molecular structures and DFT calculation results of the THP-1.



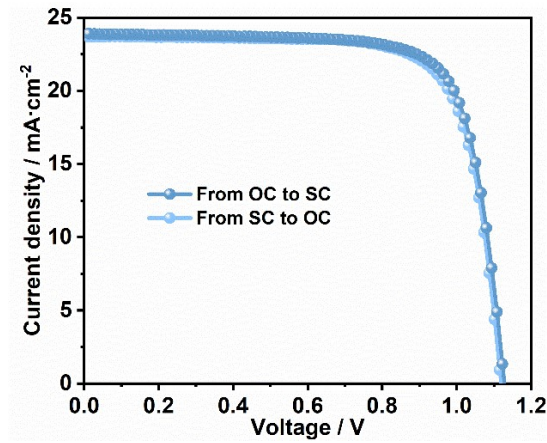


Figure S14.  $J$ - $V$  characteristic curves of the PSCs containing THP-1 as HTMs.

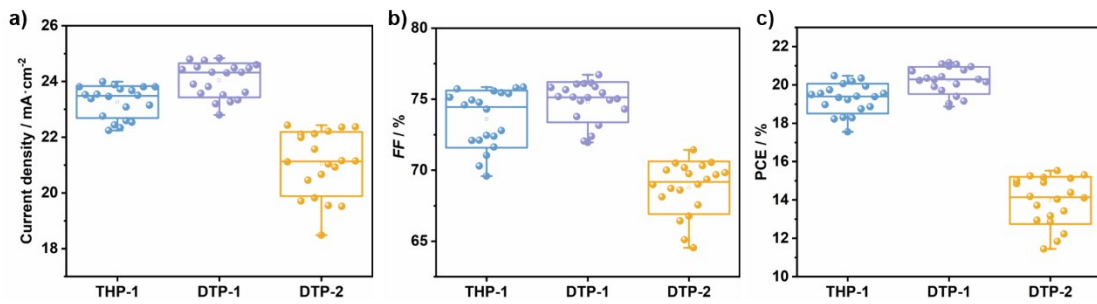


Figure S15. The statistical photovoltaic parameters a)  $J_{SC}$ , b)  $FF$  and c)  $PCE$ . Distributions of 20 devices obtained from different HTMs-based devices fabricated in one batch.

**Table S6.** The TRPL decay data for PSCs of perovskite and perovskite/HTMs films.

Films	$\tau_{avg}$ (ns)	$\tau_1$ (ns)	$\tau_2$ (ns)	A1	A2
Perovskite	1150.3	10.1	1155.7	342.4	632.5
DTP-1	12.6	1.3	19.3	932.0	106.1
DTP-2	55.8	7.4	65.8	626.7	339.3
THP-1	36.4	3.9	45.8	746.7	219.0

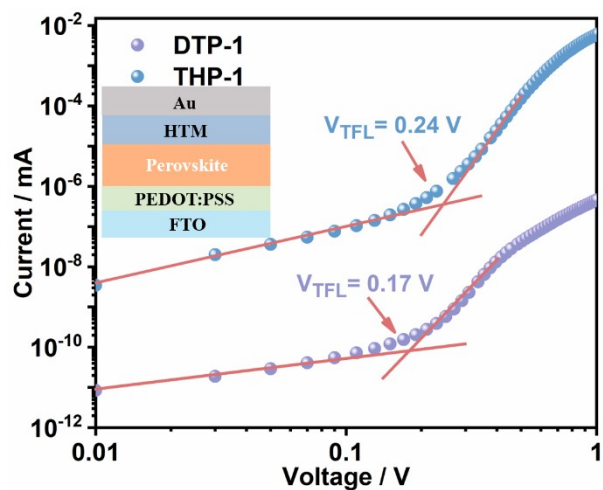


Figure S16. Space-charge-limited current measurements of hole-only devices.

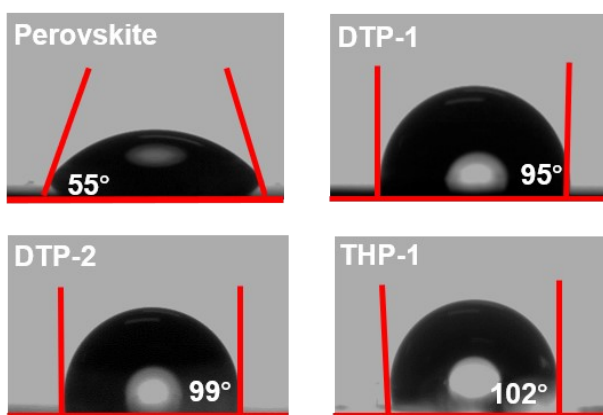


Figure S17. Water contact angles of the perovskite films covered with DTP-1, DTP-2 and THP-1.