

Supporting Information

Terthienyl Core Unit based Hole Transport Materials for Efficient Perovskite Solar Cells

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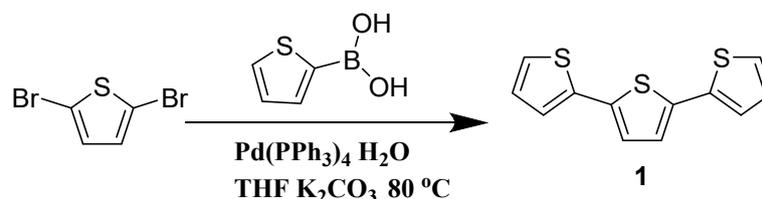
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Synthesis method

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

Synthesis of THP-1

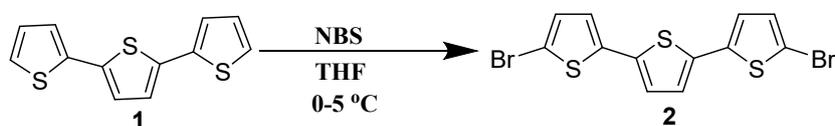


2,2':5',2''-terthiophene (1). In a 2-necked flask (250 mL) under nitrogen, 2,5-dibromothiophene (4.84 g, 20 mmol) and thiophen-2-ylboronic acid (5.63 g, 44 mmol) were dissolved in dry THF (140 mL), then added Pd(PPh₃)₄ (0.5 g, 0.43 mmol) and K₂CO₃ (10 mL) saturated aqueous solution. The mixture was degassed 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 under reduced pressure. The crude product was purified by column chromatography (petroleum ether) to obtain **1** (2.8 g, yield: 56.4%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.29 - 7.22 (m, 2H), 7.20 (dd, *J* = 3.6, 1.0 Hz, 2H), 7.11 (s, 2H), 7.05 (dt, *J* = 6.5, 3.2 Hz, 2H).

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

Reagent	Amount (g)	Amount (mL)	Price (RMB/g or RMB/mL)	Total price (RMB)
2,5-dibromothiophene	4.84	—	0.70	3.38
4-bromoanisole	5.63	—	7.12	40.11
Pd(PPh ₃) ₄	0.50	—	72.00	36.00
K ₂ CO ₃	10.00	—	0.06	0.62
THF	—	140.00	0.13	19.04

Dichloromethane	—	300.00	0.01	4.32
Silica gel	150.00	—	0.03	5.25
Petroleum ether	—	1000.00	0.01	10.40
Total cost	119.13 RMB			
Amount intermediate 1	2.80 g			
COST for intermediate 1	42.54 RMB/g			
Exchange rate	1 \$=6.61 RMB			

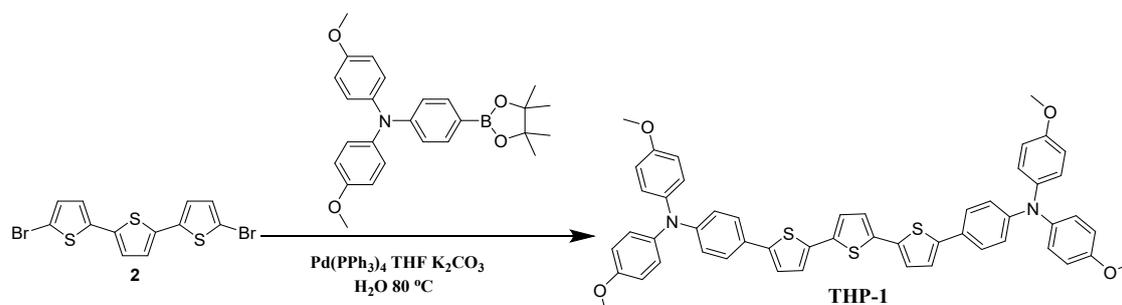


5,5''-dibromo-2,2':5,2''-terthiophene (2). *N*-bromo-succinimide (2.84 g, 15.95 mmol) was added in small portions to a solution of **1** (1.8 g, 7.25 mmol) in THF (100 mL) and the obtained mixture was stirred for 8 h at 0-5°C. Then extracted the mixture with dichloromethane and water. The organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether) to obtain **2** (2.62 g, yield: 89.1%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 2.6 Hz, 2H), 7.12 - 7.08 (m, 2H), 7.04 (d, *J* = 5.4 Hz, 2H).

Table S2 Synthesis cost of intermediate 2.

Reagent	Amount (g)	Amount (mL)	Price (RMB/g or RMB/mL)	Total price (RMB)
1	1.80	—	42.54	76.58
THF	—	100.00	0.13	13.60
<i>N</i> -Bromo-succinimide	2.84	—	0.13	0.39
Dichloromethane	—	300.00	0.01	4.32
Silica gel	130.00	—	0.03	4.55
Petroleum ether	—	800.00	0.01	8.32

Total cost	107.76 RMB
Amount intermediate 2	2.62 g
COST for intermediate 2	41.07 RMB/g
Exchange rate	1\$=6.61 RMB

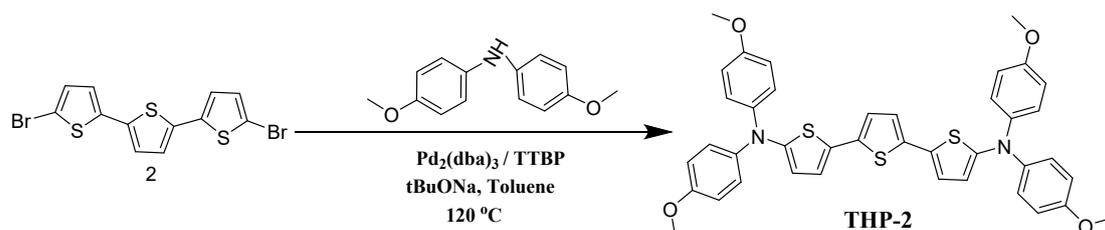


4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) (THP-1). In a 2-necked flask, **2** (0.86 g, 2.12 mmol) and 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (2.28 g, 5.3 mmol) were dissolved in dry THF (80 mL), then Pd(PPh₃)₄ (0.13 g, 0.11 mmol) and K₂CO₃ (10 mL) saturated aqueous solution were added in the solution. The mixture was degassed for 10 minutes and then refluxed at 80°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 Na₂SO₄, the organic layer was collected and evaporated under 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 THP-1 (0.92 g, yield: 50.8%) as an orange solid. ¹H-NMR (400 MHz, DMSO) δ 7.58 - 7.53 (m, 1H), 7.53 - 7.46 (m, 6H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.14 - 7.00 (m, 9H), 6.99 - 6.89 (m, 9H), 6.76 (t, *J* = 10.8 Hz, 4H), 3.76 (s, 12H). ¹³C-NMR (101 MHz, CDCl₃) 156.78, 156.05, 154.96, 141.23, 141.09, 140.03, 130.93, 128.87, 125.81, 125.74, 125.60, 125.48, 125.12, 125.07, 124.83, 124.77, 123.18, 122.67, 122.50, 122.35, 122.10, 120.46, 119.65, 116.63, 116.50, 114.81, 114.61, 114.50, 77.39, 77.07, 76.75, 55.63, 55.54, 17.03. HR-MS: calculated: C₅₂H₄₂N₂O₄S₃, 854.2307, found: 854.413.

Table S3 Synthesis cost of intermediate **THP-1**.

Reagent	Amount (g)	Amount (mL)	Price (RMB/g or RMB/mL)	Total price (RMB)
2	0.86	—	41.07	35.32
4-methoxy- <i>N</i> -(4-methoxyphenyl)- <i>N</i> -(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline	2.28	—	144.00	328.32
THF	—	80.00	0.13	10.88
Pd(pph ₃) ₄	0.13	—	72.00	9.36
K ₂ CO ₃	5.00	—	0.06	0.31
Silica gel	100.00	—	0.03	3.50
Petroleum ether	—	900.00	0.01	9.36
Dichloromethane	—	500.00	0.01	7.20
Ethyl acetate	—	150.00	0.01	2.16
Total cost	406.41 RMB			
Amount THP-1	0.92 g			
COST for THP-1	441.75 RMB/g			
Exchange rate	1\$=6.61 RMB			

Synthesis of THP-2



***N*₅,*N*₅,*N*_{5''},*N*_{5''}-tetrakis(4-methoxyphenyl)-[2,2':5,2''-terthiophene]-5,5''-diamine (THP-2).** A mixture of **2** (0.812 g, 2.00 mmol), 4,4-dimethoxydiphenylamine (1.12 g, 4.40 mmol), Pd₂(dba)₃ (0.092 g, 0.1 mmol), tri-tert-butylphosphonate (0.20 mmol) and sodium tert-butoxide (0.577 g, 6.00 mmol) in toluene (100 mL) was stirred at 110 °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 under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 8:1 vol/vol) to obtain THP-2 (0.680 g, yield: 48.4%) as an orange red solid. ¹H-NMR (400 MHz, Acetone) δ 7.19 - 7.03 (m, 8H), 7.00 - 6.85 (m, 12H), 6.39 - 6.24 (m, 2H), 3.80 (d, *J* = 7.1 Hz, 12H). ¹³C-NMR (101 MHz, CDCl₃) 156.28, 156.08, 149.00, 148.41, 143.88, 142.61, 140.59, 140.32, 137.75, 134.83, 133.16, 132.36, 130.93, 129.75, 128.87, 126.97, 126.83, 126.74, 126.28, 126.15, 126.03, 125.97, 125.92, 124.79, 124.49, 123.87, 123.26, 114.85, 114.79, 77.39, 77.07, 76.75, 55.51. HR-MS: calculated: C₄₀H₃₄N₂O₄S₃, 702.1681, found: 702.1674.

Table S3 Synthesis cost of intermediate **THP-2**.

Reagent	Amount (g)	Amount (mL)	Price (RMB/g or RMB/mL)	Total price (RMB)
2	0.81	—	41.07	33.35
4,4-Dimethoxydiphenylamine	1.12	—	38.40	43.01
Pd ₂ (dba) ₃	0.09	—	130.00	11.96
Tri-tert-butylphosphonate	0.05	—	11.00	0.64

sodium tert-butoxide	0.57	—	0.45	0.26
Toluene	—	100.00	0.04	4.10
Silica gel	100.00	—	0.03	3.50
Petroleum ether	—	800.00	0.01	8.32
Ethyl acetate	—	200.00	0.01	2.88
Total cost	108.01 RMB			
Amount THP-2	0.68 g			
COST for THP-2	223.17 RMB/g			
Exchange rate	1\$=6.61 RMB			

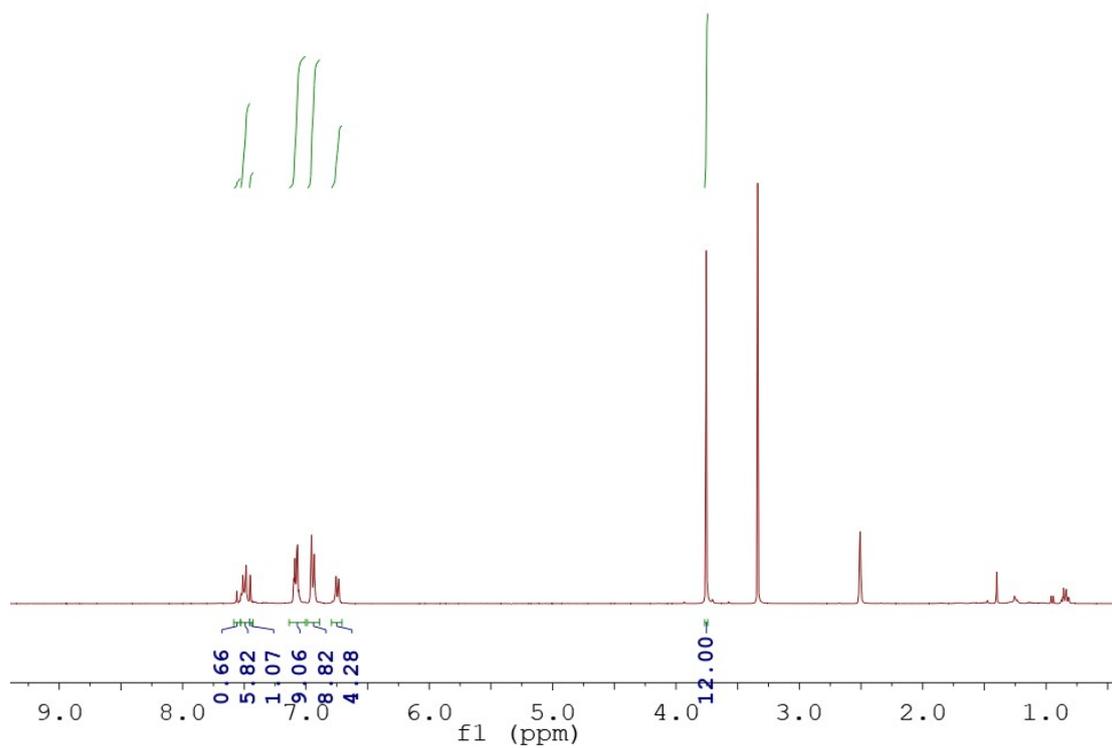


Figure S1. ¹H-NMR spectrum of THP-1 recorded in DMSO.

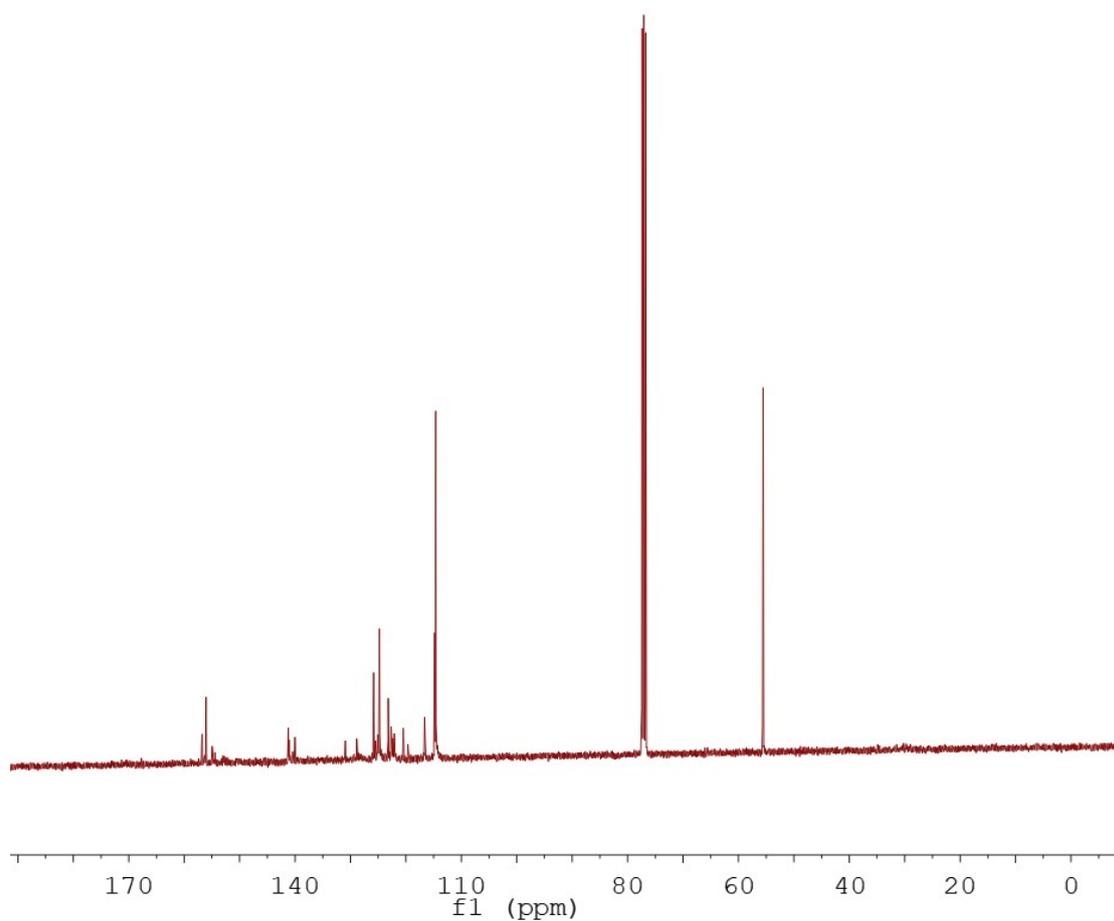


Figure S2. ^{13}C -NMR spectrum of THP-1 recorded in CDCl_3 .

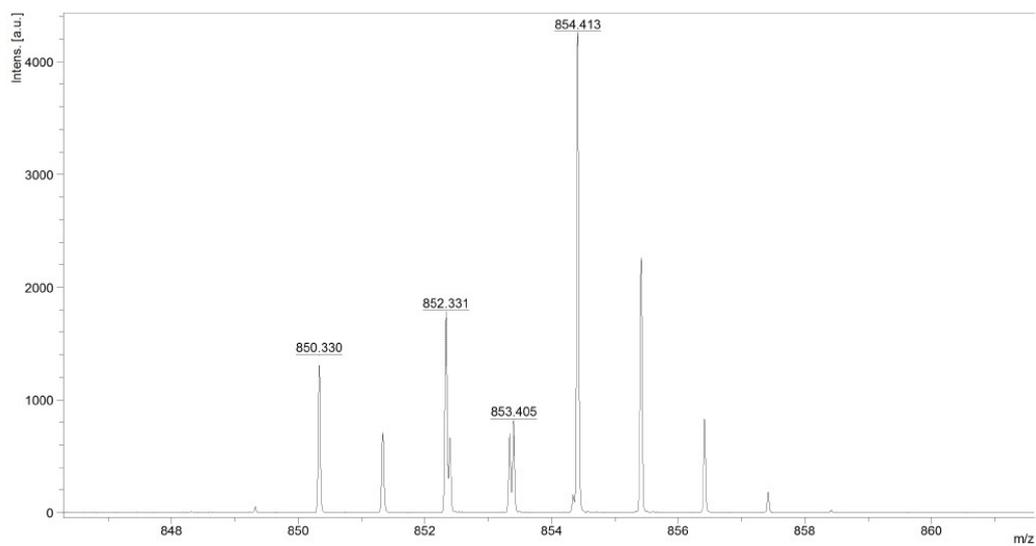


Figure S3. HR-MS spectrum of THP-1 in THF.

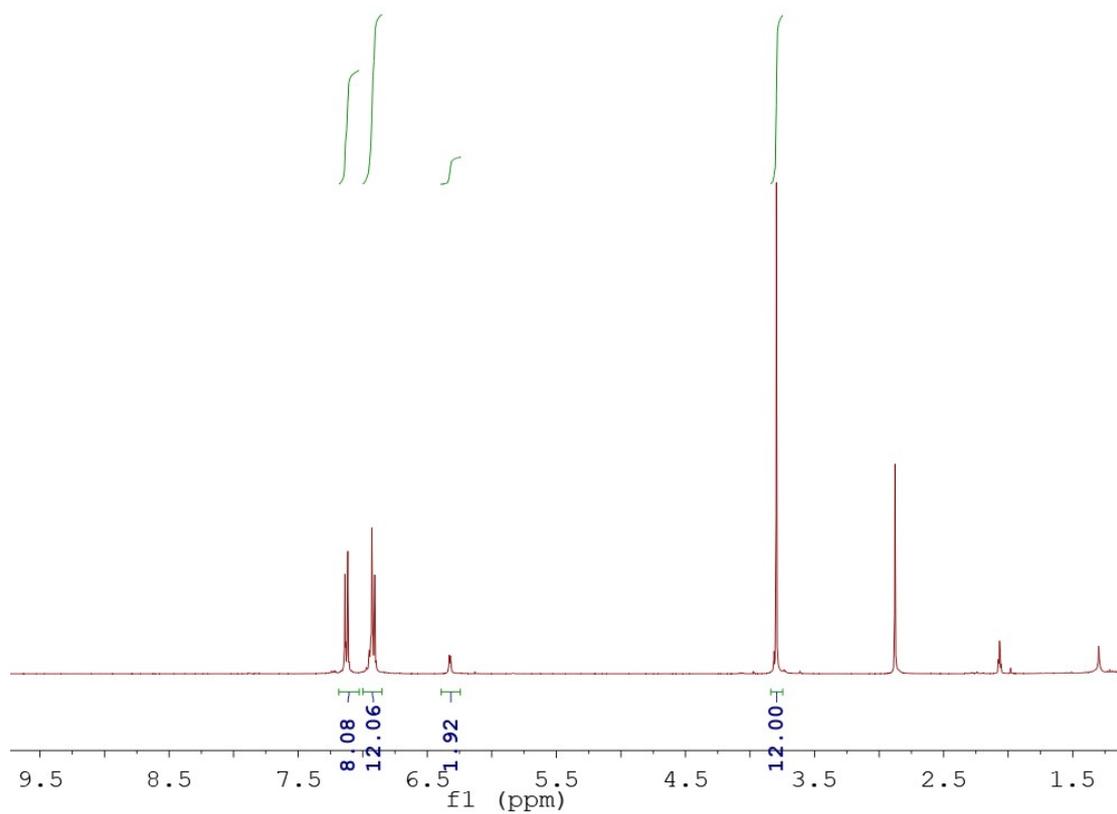


Figure S4. $^1\text{H-NMR}$ spectrum of THP-2 recorded in acetone.

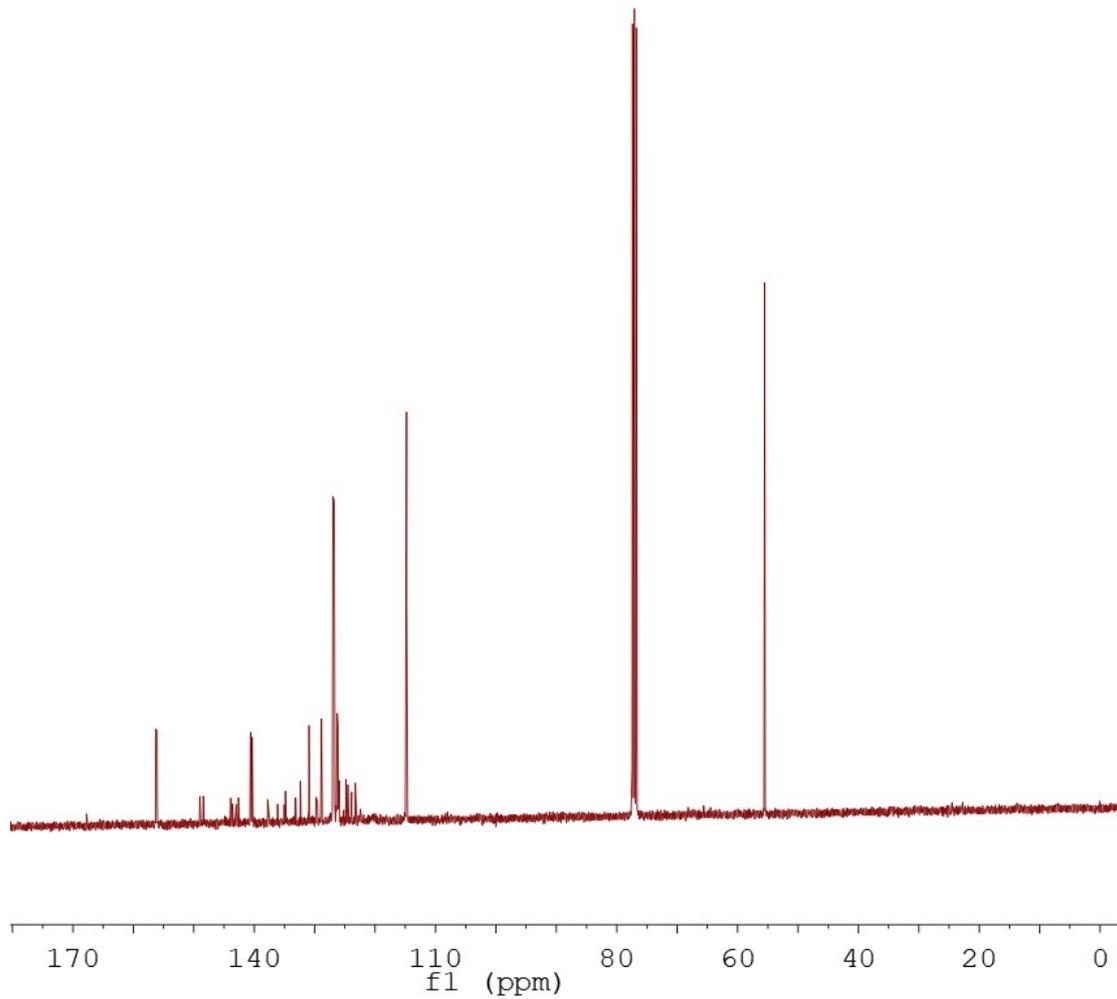


Figure S5. ^{13}C -NMR spectrum of THP-2 recorded in CDCl_3 .

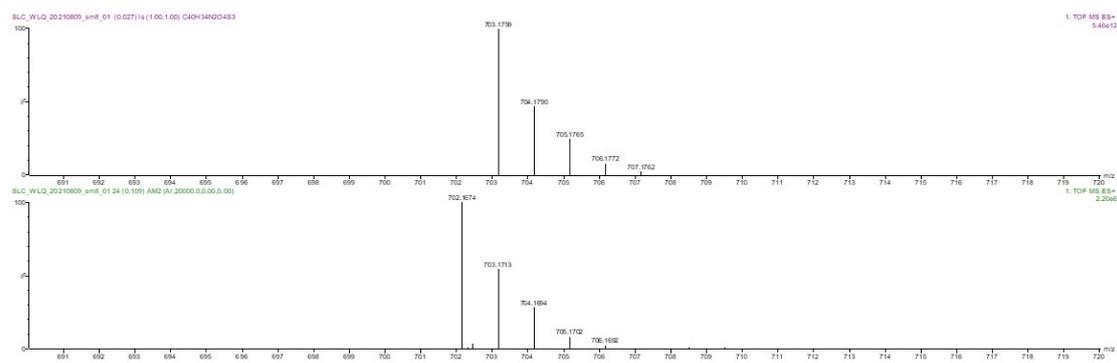


Figure S6. HR-MS spectrum of THP-2 in THF.

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 TBAPF₆ as the supporting electrolyte, a Ag⁺/AgNO₃ 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*⁺) 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⁻² calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.0625 cm². 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. Space-charge-limited current can be described by equation below:

$$J = \frac{9}{8} \mu \varepsilon_0 \varepsilon_r \frac{V^2}{D^3}$$

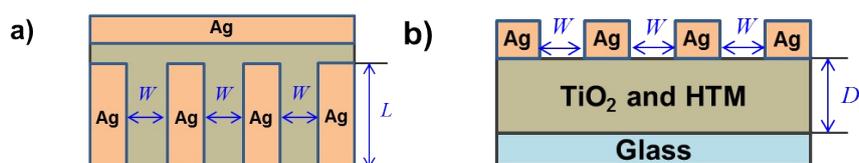
where *J* is the current density, μ is the hole mobility, ε_0 is the vacuum permittivity (8.85×10⁻¹² F / m), ε_r is the dielectric constant of the material (normally taken to

approach 3 for organic semiconductors), V is the applied bias, and D is the film thickness.

For conductivity, the electrical conductivities of the HTM films were determined by using two-probe electrical conductivity measurements. The electrical conductivity (σ) 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 TiO₂ 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 SnO₂: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 sequentially in 2% RBSTTM50 solution (Fluka) for 30 minutes, deionized water, acetone and ethanol for 15 minutes each. A thin and dense layer of TiO₂ (b1-TiO₂) 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 acetylacetone (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 TiO₂ 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 (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} perovskite solution we mixed PbI₂ (TCI), FAI (Dyename), PbBr₂ (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 TiO₂. 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 µl 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 (Spiro-OMeTAD: 80 mg Spiro-OMeTAD, 30 mM LiTFSI, 250 mM TBP and 4 mM FK209; THP-1: 40 mg THP-1, 30 mM LiTFSI, and 4 mM FK209; THP-2: 40 mg THP-2, 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 ~20 mm².

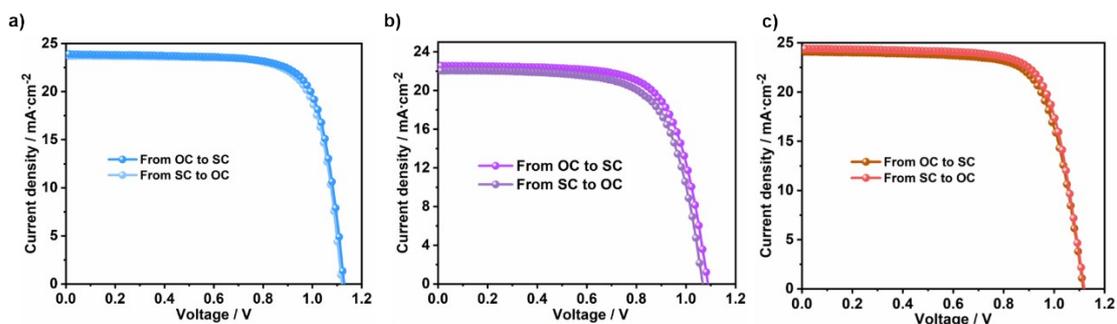


Figure S7. J - V characteristic curves of the PSCs containing a) THP-1, b) THP-2 and c) Spiro-OMeTAD as HTMs.

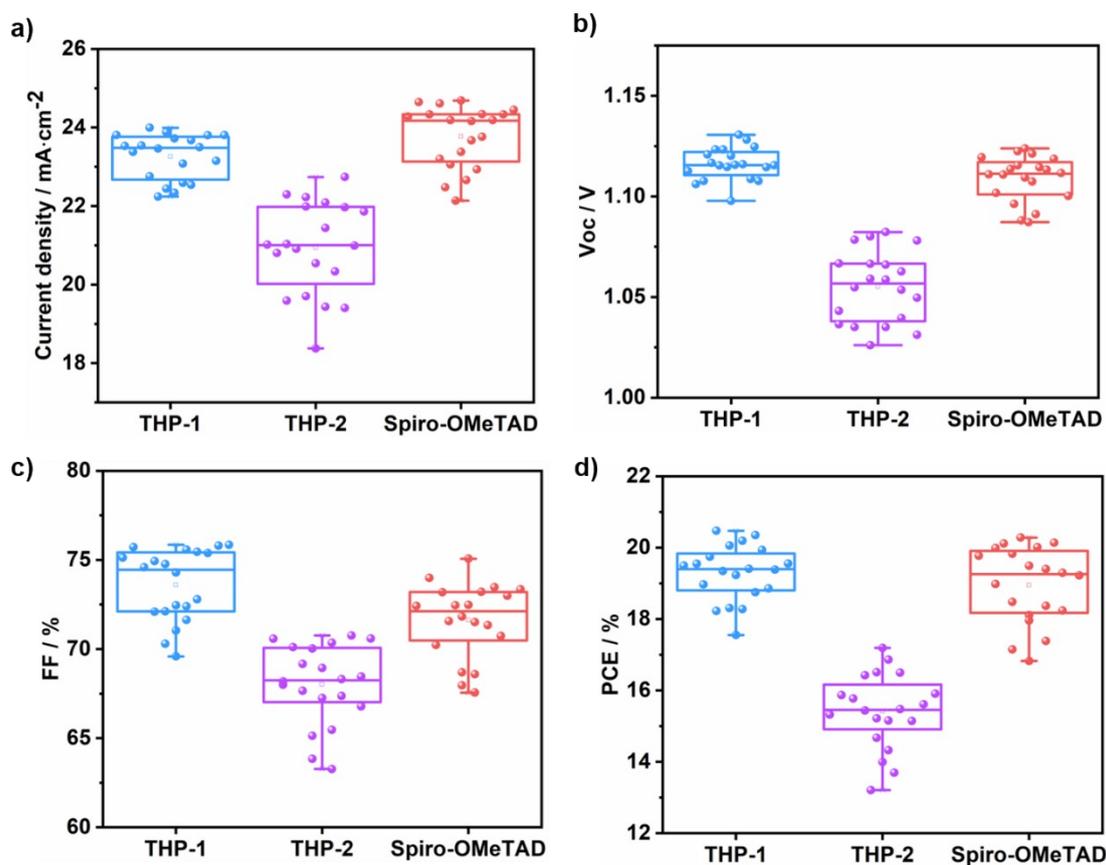


Figure S8. The statistical photovoltaic parameters a) J_{SC} , b) V_{OC} , c) FF , and d) PCE distributions of 20 devices obtained from different HTMs-based devices fabricated in one batch.

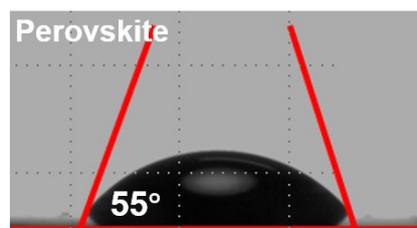


Figure S9. The water contact angle of the perovskite film.