Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

A Dopant-free Spirobi[cyclopenta[2,1-b;3,4-b']dithiophene] based Hole-Transport Material for Efficient Perovskite Solar Cells

Marius Franckevičius,[a,c] Amaresh Mishra,[b]* Franziska Kreuzer,[b] Jingshan Luo,[a] Shaik Mohammed Zakeeruddin,[a]* and Michael Grätzel[a]*

[a]Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

[b]Institute of Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany. Email amaresh.mishra@uni-ulm.de

[c]Center for Physical Sciences and Technology, Savanorių Ave. 231, LT-02300 Vilnius, Lithuania.

Experimental

Instrument and Measurements: NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). Chemical shift values (δ) are expressed in parts per million using residual solvent protons (^{1}H NMR: $\delta_H = 7.26$ for $CDCl_3$; $\delta_H = 1.72$ for THF-d_8; ^{13}C NMR: $\delta_C =$ 77.0 for $CDCl_3$; $\delta_C = 67.21$ for THF-d_8) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). Melting points were determined using a Büchi Melting Point B-545. Preparative column chromatography was performed on glass columns packed with silica gel, Merck Silica 60, particle size 40−63 µm. High resolution MALDI-TOF mass spectra (HRMS) experiments were performed using a MS Bruker Reflex 2 (Bruker Daltonik GmbH, Bremen, Germany) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Cyclic voltammetry experiments were performed with a computer-controlled

Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferrocenium couple.

Optical measurements: UV-Vis absorption spectra in dichloromethane solution were recorded on a Perkin Elmer Lambda 19 spectrometer. Optical absorption spectra of all investigated materials in thin films spin coated on the top of amorphous glass, TiO_2 and TiO_2/perovskite were recorded with a CARY-5 UV-Vis-NIR spectrophotometer in transmission mode within the 180-1000 nm range. For film measurements HTMs were spin coated from chloroform solution of concentration of 5mg/ml at 1500 r.p.m. on top of amorphous glass/TiO_2/ $CH_3NH_3PbI_3$.

Device fabrication: Devices were prepared on conductive fluorine-doped tin oxide (FTO) coated glass substrates. The substrates were cleaned by sonication for 30 min in Hellmanex (2% by volume in water) and then rinsed extensively by deionized water, acetone and isopropanol. Prior to further processing, oxygen plasma was used for 15 min. A compact titanium dioxide (TiO_2) layer of about 20 nm was deposited by spray pyrolysis of 4.5 ml ethanol solution containing 0.3 mL titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) and 0.2 mL acetylacetone at 450 ^oC in air. On top of this layer, a 300-350 nm-thick mesoporous titanium dioxide was formed by spin-coating 30 nm sized nanoparticles (Dyesol 30NRT, Dyesol) diluted in ethanol (1:3.5 *w*/*v*) at 5000 r.p.m. for 20 s. The formed layer was heated to 500 degrees and sintered for 1 hour in oxygen atmosphere. Afterwards, lead iodide (PbI_2) was dissolved in *N,N*-dimethylformamide by vigorous stirring at 130° C to make 1.2 M stock solution. Pb salt was spin coated on the top of mesoporous TiO_2 layer at 6500 r.p.m. for 20 s and left for drying for 10 min at 85 ^oC. In order to assure better film coverage and pore filling, the deposition of lead iodide was performed two times. Subsequently, on the top of a led salt 0.05 M CH_3NH_3I ethanol solution was sprayed and left for 20 s before spin coating at 3000 r.p.m. for 30 s. Formed perovskite films were dried at 85 ^oC for 15 min. Subsequently, for devices with hole transporting materials Spiro-MeOTAD and HTM **1** compounds were dissolved in chlorobenzene at the concentrations 0.06M and 0.03 M and deposited on the top of perovskite by spin coating at 3000 r.p.m. for 20 s while keeping solutions at ambient environment during the whole procedure. Devices were finalized by thermal evaporation of 60-nm thick gold layer on the top of the pure perovskite and perovskite with hole transporting materials.

J-V Characterization: The J-V characteristics of the devices were measured under 100mW/cm^2 conditions using a 450 W Xenon lamp (Oriel), as a light source, equipped with a Schott K113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectra to the AM1.5G standard in the region of 350-750 nm. The current–voltage characteristics of the devices were obtained by applying external potential bias to the cell while recording the generated photocurrent using a Keithley (Model 2400) digital source meter. The J–V curves of all devices were measured by masking the active area with a metal mask of area 0.16 cm^2.

IPCE: The internal photon to current conversion efficiency of the devices was measured by focusing light from the 300W Xenon lamp (ILC Technology, U.S.A.) through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.) while chopping at 3 Hz before illuminating onto the photovoltaic cell. The monochromator was incremented through the visible spectrum to generate the IPCE dependence on wavelength.

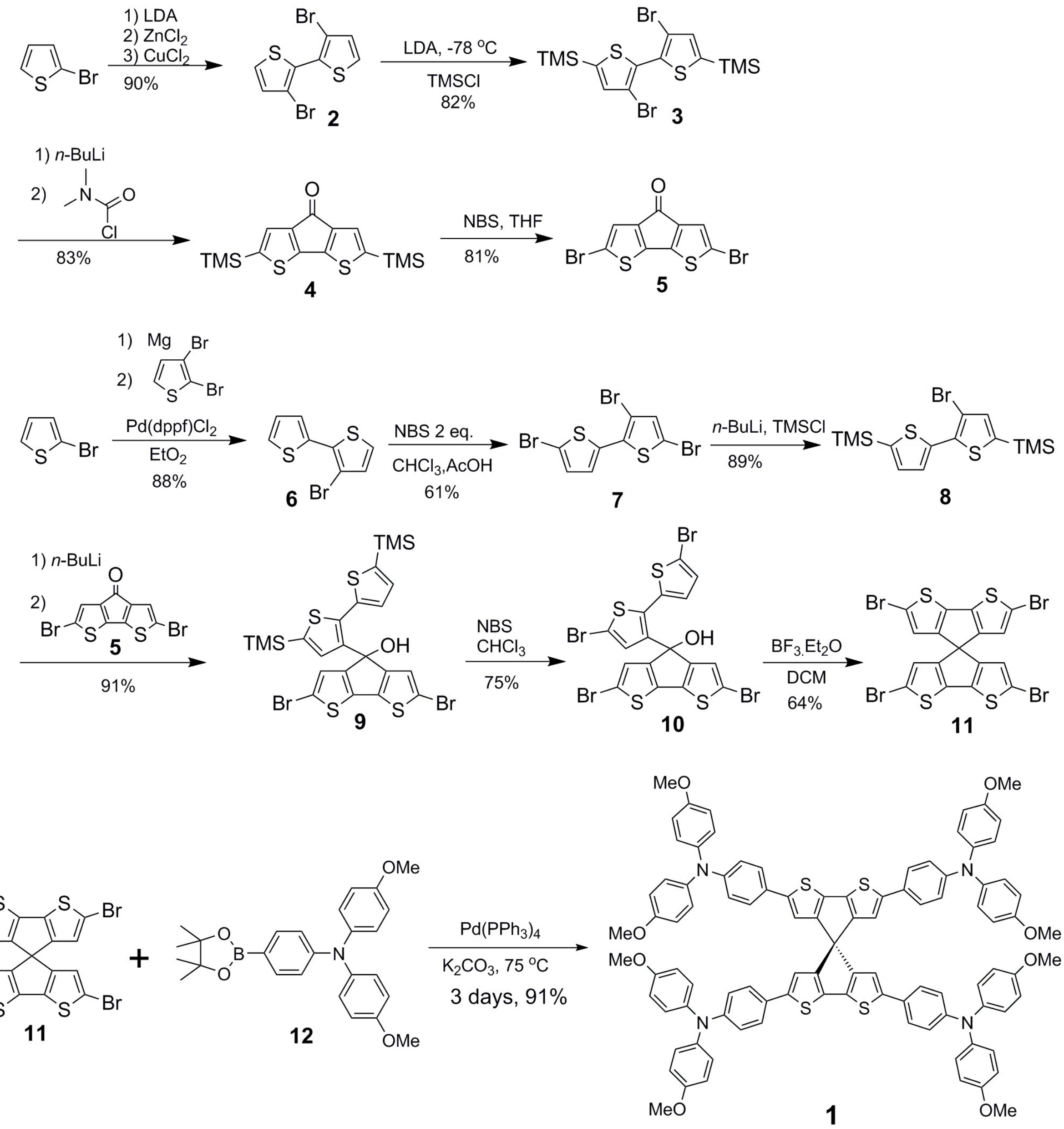
Mobility measurements: The mobility of hole transporting materials were measured by applying space charge limited current (SCLC) method. The Bio-Logic SP-300 potentiostat was used for the *J-V* measurements in the dark while scanning current change from 0 to 6V at 100mV/s scan rate. The current density is limited by the space charge, so that it can be calculated with the following equation:

$$I = \frac{9}{8}\frac{\varepsilon\varepsilon_0\mu U^2}{d^3} \qquad (1)$$

where I is current, U is voltage and d is thickness of hole transporting material are measured directly. The ε is dielectric constant of the material, which for organic semiconductors equals to 3 and ε_0 is electric constant. As is seen, hole mobility indicated as μ can be extracted from the first equation when all other parameters are known.

The samples for hole mobility measurements were prepared as follows. Fluorine-doped tin oxide (FTO) coated glass substrates (Tec15, Pilkington) were cleaned by sonication for 30 min in Hellmanex (2% by volume in water) and then rinsed extensively by deionized water, acetone and isopropanol. Prior to further processing, oxygen plasma was used for 15 min. Alumina oxide (Al_2O_3) particles were spin cast on the top of FTO substrates to make planar surface for HTM. Afterwards thin layer (~30nm) of PEDOT:PSS was spin coated on the top of the alumina oxide particles. Different thickness of hole transporting materials were deposited by spin-coating 10 mM precursor solution in chloroform. Samples were completed by thermal evaporation of about 50 nm thick gold layer on the top of the hole transporting materials.

Synthesis.



Scheme 1. Synthetic route of spiro-CPDT based HTM **1**.

3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (3). Diisopropylamine (3.7 mL, 2.66 g, 26.3 mmol) in dry THF (100 mL) was cooled to 78 °C under argon and then *n*-BuLi (1.6 M, 15.5 mL, 24.73 mmol) was added at once. The resulting solution was allowed to warm to 0 °C, kept at this temperature for 20 min and again cooled to -78 °C. A solution of 3,3'-dibromo-2,2'-bithiophene **2**

(3.60 g, 11.11 mmol) in dry THF (56 mL) was added dropwise over 30 min. The white suspension was allowed to warm to -10 °C and stirred for 30 min, cooled to -78 °C again and trimethylsilyl chloride (4.07 mL, 3.47 g, 32.0 mmol) was added dropwise. The reaction mixture was allowed to warm to rt and stirred overnight. Water was added to quench the reaction and extracted with diethyl ether (3 × 30 mL). The organic phase was washed 3 times with brine and dried over $MgSO_4$. The title compound **3** was obtained as a white solid in a yield of 82% (4.25 g, 9.08 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.15 (s, 1H), 0.35-0.32 (m, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 143.03, 137.15, 134.07, 113.08, -0.23.

2,6-bis(trimethylsilyl)-cyclopenta[2,1-b;3,4-b']dithiophen-4-one (4) A solution of **3** (4.00 g, 8.54 mmol) in 33 mL dry THF was cooled to -78 °C under argon. *n*-BuLi (1.6 M, 10.6 mL, 16.96 mmol) was added dropwise over 10 min and stirred for further 15 min. A solution of *N,N*-dimethylcarbamyl chloride (0.78 mL, 0.91 g, 8.46 mmol) in dry THF (6,6 mL) was added dropwise. Then the mixture was allowed to warm up to 0 °C and stirred for 2.5 h at 0 °C. An aqueous NH_4Cl solution (1.66 g in 12,5 mL water) was added to end the reaction and the dark orange-brown solution became immediately intensely red. The red organic phase was separated from the aqueous phase, which was extracted with petroleum ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was rotary evaporated. The red residue was purified by column chromatography (SiO_2, DCM/petroleum ether 1:3) to get the keton **4** as a red solid in a yield of 83% (2.35 g, 6.99 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.07 (s, 2H), 0.31 (s, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 183.33, 154.51, 145.04, 144.31, -0.09.

2,6-dibromo-cyclopenta[2,1-b;3,4-b']dithiophen-4-one (5) Ketone **4** (3.74 g, 11.13 mmol) was dissolved in 77 mL THF and cooled to 0 °C under argon. NBS (3.44 g, 19.32 mmol) was added at once, stirred for 30 min at 0 °C, warm up to rt and stirred for an additional hour. The reaction was controlled by thin layer chromatography. After completion, THF was removed and the residue was dissolved in DCM, washed with water (2 × 50mL), brine (1 × 50) and dried over $MgSO_4$. The solvent was evaporating and boiled for 1 h in methanol and filtered over a buchner funnel to receive the brominated keton **5** as dark violet powder in a ylied of 81% (3.16 g, 9.03 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.00 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 180.66, 148.82, 139.67, 124.56, 114.10.

3-bromo-2,2'-bithiophene (6). At first a Grignard reagent was prepared by the reaction of 2-bromothiophene (10 mL, 16.84 g, 103.29 mmol) and Mg (4.16 g, 171.08 mmol) in 100 mL dry diethyl ether refluxing under argon for 45 min. This solution was added dropwise over 1 h to a stirring suspension of Pd(dppf)Cl_2. DCM-complex (637.14 mg, 0.78 mmol), 2,3-dibromothiophene (10 mL, 21.37 g, 99.4 mmol) in 100 mL dry diethyl ether at -5 °C. The reaction was stirred for 3 h at 0 °C. Finally 10 mL methanol was added to quench the reaction. The mixture was filtered over a short (~3 cm) Na_2SO_4/SiO_2 double layer eluting with diethyl ether. The combined organic layer was rotary evaporated. The oily liquid was purified by column chromatography (SiO_2, petroleum ether) affording 3-bromo-2,2'-bithiophene **6** as slightly green oil (19.0 g, 77.5 mmol, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.3 (m, 1H), 7.36 (d, J = 5.1 Hz, 1H), 7.19 (d, J = 5.4 Hz, 1H), 7.09 (dd, J = 4.9, 3.8 Hz, 1H), 7.02 (d, J = 5.3 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 134.43, 132.38, 131.93, 127.36, 126.88,126.22, 124.50, 107.99.

3,5,5'-tribromo-2,2'-bithiophene (7). NBS (7.39 g, 41.52 mmol) was added at once to a stirred solution of 3-bromo-2,2'-bithiophene **6** (5.03 g, 20.5 mmol) in a solvent mixture of $CHCl_3$ (44 mL) and AcOH (34 mL) under argon. The solution was stirred 24 h at room temperature and protected from light. The solvents were rotary evaporated. The residue was dissolved in DCM, washed with water (2 × 50 mL), 5% aqueous $NaHCO_3$ (1 × 50 mL), water (50 mL) and finally with brine (50 mL). After drying over Na_2SO_4 and removal of the solvent at reduce pressure the residue was purified by column chromatography (SiO_2, petroleum ether). 3,5,5'-tribromo-2,2'-bithiophene **7** was obtained as a white solid (61%, 5.05 g, 12.5 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.05 (d, J = 3.9 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 6.98 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 134.91, 133.93, 133.27, 130.16, 127.21, 113.92, 111.70, 107.44.

3-bromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (8). 3,5,5'-tribromo-2,2'-bithiophene **7** (2.14 g, 5.31 mmol) was dissolved in 45 mL dry diethyl ether under argon at rt. The milky suspension was cooled down to -78 °C, *n*-BuLi in hexane (1.6 M, 6.25 mL, 10 mmol) was added dropwise over 15 min and stirred for 30 min at -78 °C. After changing the bath to a ice-salt-bath at -10 °C the resulting mixture was again stirred for 5h. TMSCl (1.27 mL, 1.08 g, 10 mmol) was added and the suspension become slightly yellow. The mixture was stirred at rt overnight and finally quenched by adding water. The mixture was extracted with 150 mL diethyl ether and the combined organic layer was washed two times with water (50 mL), brine (2 × 50 mL) and dried over $MgSO_4$. After the solvents was rotary evaporated, the residue was purified by column chromatography (SiO_2, petroleum ether), affording TMS-capped bithiophene **8** as a pale yellow oil in a yield of 89% (1.74 g, 4.47 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.50 (d, J = 3.5 Hz, 1H), 7.19 (d, J = 3.5 Hz, 1H), 7.09 (s, 1H), 0.34 (s, 9H), 0.32 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm 138.29, 134.35, 127.78, 0.04, -0.26. (quaternary carbon atoms not visible).

4-(5,5'-Bis(trimethylsilyl)-2,2'-bithiophen-3-yl)-2,6-dibromo-4-hydroxycyclopenta[2,1-b;3,4-b']dithiophene (9). *n*-BuLi in hexane (1.6 M, 1.8 mL, 2.88 mmol) was added dropwise over 10 min to a stirred solution of **8** (1.20 g, 3.09 mmol) in 46 mL dry diethyl ether at -78 °C under argon. The reaction mixture was allowed to warm to -30 °C and stirred for an additional hour. At this point solid ketone **5** (1.05 g, 3.00 mmol) was added at once and the reaction mixture was stirred for further 30 min at -30 °C, then allowed to warm to rt. After 6 h aqueous NH_4Cl was added to quench the reaction.

The organic layer was immediately separated and washed with water (2 × 20 mL), brine (1 x 20 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, petroleum ether/DCM 5:4) affording carbinol **9** as a white fluffy solid (1.73 g, 2.62 mmol 91% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (s, 1H), 6.88 (d, J = 3.4 Hz, 1H), 6.80 (s, 2H), 6.42 (d, J = 3.4 Hz, 1H), 0.38-0.30 (m, 9H), 0.30-0.25 (m, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 154.07, 142.85, 140.86, 138.48, 138.08, 137.29, 136.20, 134.43, 133.55, 129.69, 125.54, 112.44, 78.48, 0.07, 0.05. HRMS (MALDI-TOF) m/z: [M^+] caclcd for $C_{23}H_{24}Br_2OS_4Si_2$: 657.86; found [M^+]: 657.86; [M^+-OH]: 658.59.

2,6-Dibromo-4-(5,5'-dibromo-2,2'-bithiophen-3-yl)-4-hydroxy-cyclopenta[2,1-b;3,4-b']dithiophene (10). Carbinol **9** (1.00 g, 1.52 mmol) was dissolved in DCM (20 mL), cooled to -78 °C and NBS (0.61 g, 3.4 mmol) was added under argon. The mixture was allowed to warm to -30 °C, stirred for further 2 h and finally brought to rt. Aqueous $Na_2S_2O_3$ was added to quench the reaction. The reaction mixture was extracted with DCM and the organic layer was washed with water (2 x 10 mL), brine (1 x 10 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2, petroleum ether/DCM 1:1). The brominated alcohol **10** was obtained as a white fluffy solid in a yield of 75% (0.77 g, 1.14 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.35 (s, 1H), 6.84 (s, 2H), 6.75 (d, J = 3.8 Hz, 1H), 6.23 (d, J = 3.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 153.48, 139.16, 137.45, 133.64, 131.07, 130.84, 129.70, 129.66, 114.76, 113.18, 112.65, 78.03. HRMS (MALDI-TOF) m/z: [M^+] calcd. for $C_{17}H_6Br_4OS_4$: 673.60; found [M^+]: 673.60; [M^+-OH]: 642.86.

2,2',6,6'-Tetrabromo-4,4'-spirobi[cyclopenta[2,1-b;3,4-b']dithiophene] (11). A solution of boron trifluoride diethyl ether (BF3·Et_2O) (0.48 mL, 0.552 g, 3.88 mmol) in dry DCM (8 mL) was added to a solution of alcohol **10** (200 mg, 0.30 mmol) in dry DCM (150 mL). The resulting mixture was stirred for 10 min and ethanol (10 mL) and water (50 mL) were added. The phases were separated and the aqueous phase was extracted with DCM. The combined DCM layers were washed and dried over $MgSO_4$. After removal of the solvent, the remaining crude product was purified by chromatography (SiO_2, petroleum ether/DCM 3:1). Tetrabromo derivative **11** was isolated in 64% yield (116.6 mg, 0.17 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.35 (s, 1H), 6.84 (s, 2H), 6.75 (d, J = 3.8 Hz, 1H), 6.23 (d, J = 3.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 147.02, 138.91, 124.29, 112.65, 58.67. HRMS (MALDI-TOF) m/z: [M^+] calcd. for $C_{17}H_4Br_4S_4$: 655.59; found [M^+]: 655.59.

4,4',4'',4'''-(4,4'-spirobi[cyclopenta[2,1-b:3,4-b']dithiophene]-2,2',6,6'-tetrayl)tetrakis(*N*,*N*-bis(4-methoxyphenyl)aniline) 1. THF (5 mL) was degased with argon for 20 min, **11** (100 mg, 0.15 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxabor-olan-2-yl)-phenyl)aniline **12** (298 mg, 0.69 mmol) and $Pd(PPh_3)_4$ was added at once. The degased potassium carbonate solution (2 M, 0.76 mL) was added and stirred for 3 days at 110 °C. The reaction was controlled by thin layer chromatography. The reaction mixture was extracted with ethyl acetate (2 x 30 mL), the combined organic layers was washed with water (2 x 40 mL), brine (40 mL) and dried over $MgSO_4$. The solvent was evaporating by reduce pressure. The product was purified by chromatography (SiO_2, petroleum ether/ethyl acetate/ trietyhlamine, 75:25:1) affording spiro **1** as an orange solid in a yield of 91% (216 mg, 0.14 mmol). ^1H-NMR (500 MHz, THF-d_8) δ ppm 7.35 (d, J = 8.8 Hz, 8H), 6.98 (d, J = 8.9 Hz, 16H), 6.84-6.78 (m, 28H), 3.73 (s, 24H). ^{13}C-NMR (125 MHz, THF-d_8) δ ppm 157.48, 152.11, 149.25, 146.66, 141.72, 137.57, 128.16, 127.52, 126.63, 121.46, 117.42, 115.62, 68.10, 55.74. HRMS (MALDI-TOF) m/z: [M^+] calcd. for $C_{97}H_{76}N_4O_8S_4$: 1553.458; found [M^+] 1553.455.

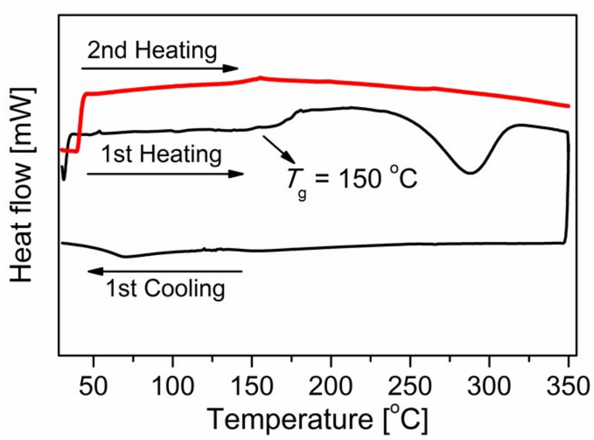


Figure S1. Differential scanning calorimetry (DSC) trace of HTM **1** measured under Ar flow at heating and cooling rate of 10 °C/min.

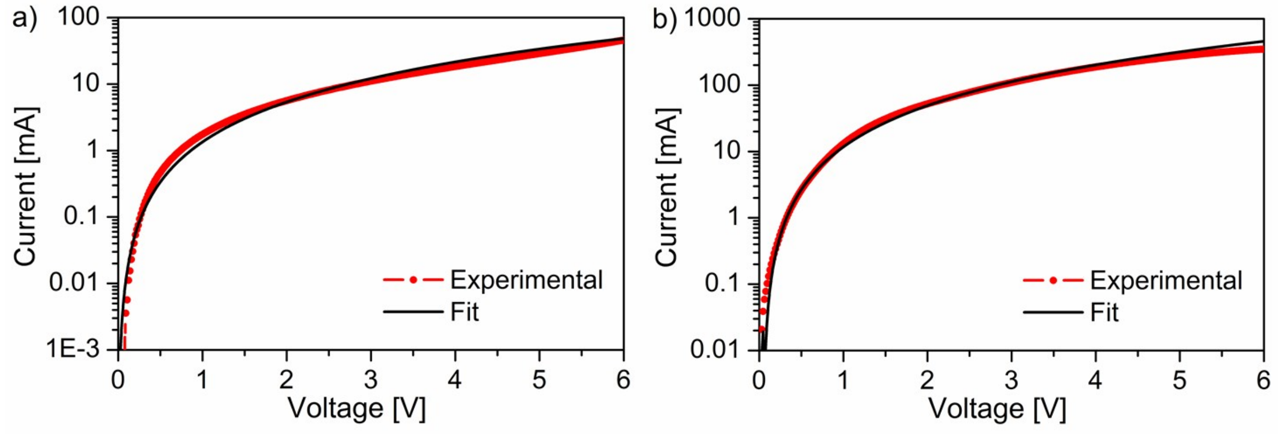


Figure S2. Experimental and fitted J-V curves of the hole-only devices for (a) HTM **1** and (b) spiro-MeOTAD hole transporting materials.

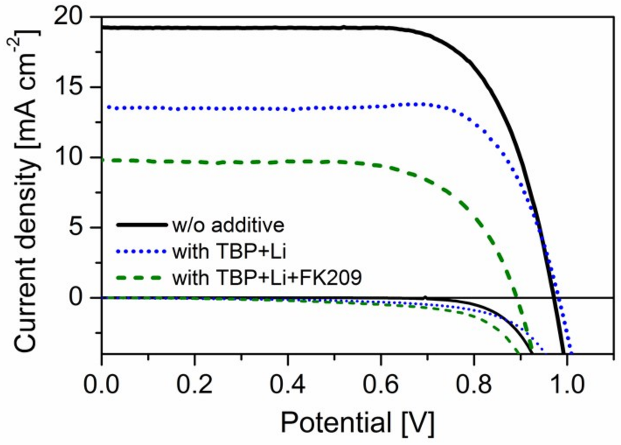


Figure S3. *J*-*V* curves of devices using HTM **1** with additives and dopant. The best device without additives and dopant is included for comparison.

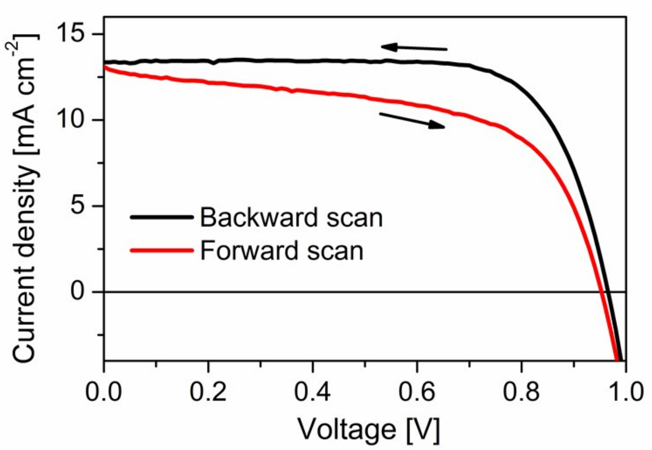


Figure S4. Current voltage hysteresis curves of perovskite solar cell device based HTM **1** containing *t*BP+Li as additives.

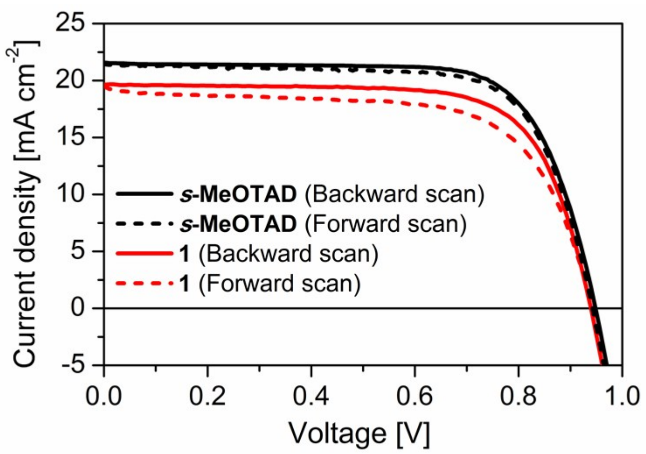


Figure S5. Current-voltage hysteresis curves of perovskite solar cells comprising champion devices with HTMs spiro-MeOTAD and spiro-CPDT **1** measured starting with backward scan and continuing with forward scan. The *J*-*V* characteristics were measured with 50 mV s^{-1} scan rate at 1 sun illumination.

Table S1. Photovoltaic data of devices based on HTM **1** and spiro-MeOTAD.

HTM	Additives+dopant	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	PCE [%]
1	-	20.2	948	68.6	13.1
		18.9	961	70.1	12.7
		19.5	931	71.4	13.3
		19.3	**971**	**71.6**	**13.4**
		18.8	994	71.4	13.3
Aver. ± std dev [%]		19.3±0.56	961±23.7	70.6±1.3	13.2±0.28
s-MeOTAD	-	**17.6**	**835**	**48.8**	**7.2**
		17.5	855	45.0	6.7
		17.7	868	44.6	6.9
		17.3	856	47.6	7.0
		16.9	846	49.3	7.1
Aver. ± std dev [%]		17.4±0.3	852±12.3	47.1±2.2	6.98±0.19
1	*t*BP+Li	11.4	976	81.4	9.0
		13.8	**982**	**75.6**	**10.3**
		13.4	965	74.1	9.6
Aver. ± std dev [%]		12.8±1.3	974±8.6	77.9±3.85	9.6±0.6
1	*t*BP+Li+FK209	9.4	871	68.5	5.6
		8.2	862	69.6	4.9
		10.0	**891**	**67.2**	**6.0**
Aver. ± std dev [%]		9.2±0.9	875±14.8	68.4±1.2	5.5±0.55
s-MeOTAD	*t*BP+Li+FK209	20.8	947	75.0	14.8
		20.0	946	74.7	14.1
		19.8	990	75.1	14.9
		21.1	955	74.0	14.9
		21.6	**952**	**73.3**	**15.0**
Aver. ± std dev [%]		20.66±0.75	958±18.3	74.4±0.76	14.74±0.36

Table S2. Photovoltaic data of perovskite solar cells containing spiro-MeOTAD and HTM **1** measured at backward and forwards scans.

HTM	Scan direction	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	PCE [%]
1	backward	19.6	939	72	13.1
	forward	19.5	941	66	12.1
1	backward	19.3	971	72	13.4
	forward	19.3	968	66	12.3
Spiro-MeOTAD	backward	21.6	948	73	14.9
	forward	21.4	942	72	14.5
Spiro-MeOTAD	backward	21.5	953	73	14.9
	forward	21.2	945	72	14.4

Table S3. Photovoltaic data for HTM **1** device with light soaking effect at forward bias. Light soaking was performed at 1.1V.

HTM	Light soaking time [min]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	PCE [%]
1	0	18.2	955	49	8.6
1	1	18.5	981	62	11.2
1	3	18.8	985	67	12.4
1	5	18.8	987	71	13.1
1	9	18.9	985	72	13.2
Spiro-MeOTAD	0	19.8	998	75	15.0
Spiro-MeOTAD	1	19.5	998	75	14.8
Spiro-MeOTAD	3	19.5	995	76	14.7
Spiro-MeOTAD	5	19.4	993	76	14.6
Spiro-MeOTAD	10	19.4	994	76	14.6