Supporting Information

Cyclopentadithiophene-based Hole-Transporting Material for Highly Stable Perovskite Solar Cells with Stabilized Efficiencies approaching 21%

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Experimental Details

Materials and methods

All materials were used as received unless stated otherwise. Tetrahydrofuran (THF), isopropanol (*i*PrOH), dichloromethane (DCM), petrol ether (PE), and ammonium chloride (NH₄Cl) were purchased at VWR International. THF was purified and dried with a MB SPS-800 solvent purification equipment from MBraun. Magnesium sulphate (MgSO₄) was bought at Grüssing GmbH. Boron trifluoride etherate (48% BF₃) and *n*-butyl lithium (n-BuLi, 1.6 M in hexane) were ordered from Acros Organics. *N*-Bromsuccinimide (NBS) was ordered at Alfa Aeser and 2-bromotriphenylamine at TCI. Bis(trimethylsilyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4-one was synthesized from 3-bromothiophene (Fluorochem) with trimethylsilyl chloride (Merck) and dimethyl carbamoyl chloride (Sigma Aldrich) in three steps after a literature-known procedure.

Characterization and analytics

NMR spectra were measured on a Bruker Avance 400 spectrometer (1H-NMR: 400 MHz, 13C-NMR: 101 MHz). High resolution MALDI mass spectra were recorded on a Bruker (FT-ICR)-SolariX with *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. The optical properties of HTM-1 were determined by UV-vis absorption spectroscopy. CV were measured in dichloromethane (DCM) at room temperature with tetrabutylammonium hexafluorophosphate (0.1 M) as conducting salt. Three cycles were measured with a scan speed of 100 mV/s. The second scan of each measurement is shown. All potentials are internally referenced to the ferrocene/ferricenium (Fc/Fc⁺) redox pair. The HOMO energy level was determined by the onset value of the oxidation and Fc set to -5.1 eV vs vacuum. Photoelectron spectroscopy in air (PESA) was measured on spin-coated glass substrates (DCM, 10 mg/ml, 1200 rpm) with an RKI model-AC2 photoelectron spectrometer. Three films were measured each and the mean work function was used. For the thermogravimetric analysis (TGA), small samples (1-2 mg) of the HTMs were heated to 1000 °C with a heating rate of 10 °C/min and the mass loss was determined. All measurements were carried out under nitrogen atmosphere. For the differential scanning calorimetry (DSC), the sample of HTM-1 underwent three heating and cooling cycles from 30 °C to 360 °C. The measurements were carried out under argon atmosphere and the scans are recorded downwards. The diffraction data of a crystal of **HTM-1** were collected in a stream of nitrogen at 180 K on a Agilent SuperNova, Cu at zero, Atlas CCD using graphite-monochromated Cu Kα radiation. Data collection strategy was performed with the APEX2 software, data reduction, absorption correction and cell refinement with CrysAlisPro171. The structure was solved by direct methods with SHELXL-2016/6, revealing all atoms of **HTM-1**. H atoms were discernible from difference Fourier maps during refinement on F2 with SHELXL-97. For the final model, all atoms were refined anisotropically.

Synthetic procedures

10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b']dithiophene] (3): The reaction was carried out under argon atmosphere. 2-Bromo-N,N-diphenylaniline 1 (1.0 g, 3.0 mmol) was dissolved in 130 ml dry THF and cooled to -78 °C. A solution of *n*-butyl lithium in *n*-hexane (1.6M, 2.5 ml, 4.0 mmol) was slowly added. The solution was stirred for 60 min at -78 °C. A solution of 2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one 2 (1.21 g, 3.33 mmol) in 20 ml THF was cooled to -78 °C and slowly added to the lithiated species until the red color no longer vanished. The reaction was directly quenched by addition of 2 ml iPrOH and warmed to room temperature. Saturated NH₄Cl-solution was added, and the product was three times extracted with DCM. The combined organic fractions were dried with MgSO₄ and the solvent was evaporated under reduced pressure. The crude product was purified by a short filtration column with an eluent mixture PE:DCM 2:1, which was changed to PE:DCM 1:4 as soon as the red fractions began to elude. The fraction with ketone 2 and product 3 was collected and the solvent was removed in vacuo. A reddish solid (1.46 g, 2.40 mmol, 77% of 95% GC-purity) was obtained. The mixture was directly dissolved in 50 ml dry DCM and cooled to 0 °C. BF₃-etherate (50% in Et₂O, 3.3 ml 15.1 mmol) was added at once. The solution was stirred at 0 °C for 1 h. The reaction was quenched by addition of saturated NaHCO₃ solution. The organic phase was three times extracted with DCM and dried with MgSO₄. The crude product was purified by column chromatography on silica gel and an eluent mixture of PE:DCM 8:1. Cyclopentadithiophene 3 (911 mg, 2.2 mmol) was obtained as a white solid in 72% yield.

Mp. 260.0-262.0 °C (1 °C/min); ¹H NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.75 – 7.66 (m, 2H), 7.63 – 7.55 (m, 1H), 7.50 – 7.41 (m, 2H), 7.22 (d, *J* = 4.9 Hz, 2H), 7.01 (d, *J* = 4.9 Hz, 2H), 6.96 (ddd, *J* = 8.3, 6.5, 2.3 Hz, 2H), 6.72 – 6.57 (m, 4H), 6.37 (ddd, *J* = 8.3, 1.1, 0.5 Hz, 2H); ¹³C NMR (101 MHz, CD₂Cl₂): δ [ppm] = 162.82, 142.36, 141.33, 136.34, 131.57, 129.07, 128.05, 126.89, 126.20, 122.94, 122.89, 121.20, 115.26; FTICR-MALDI-MS: m/z=419.07976 (calc.: 419.08024, \Box m/m= 1.1 ppm).

2',6'-Dibromo-10-phenyl-10H-spiro[acridne-9,4'-cyclopenta[2,1-b:3,4-b']dithiophene] (4): 10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b']dithiophene] **3** (500 mg, 1.19 mmol) was dissolved in 45 ml dry DCM and cooled to 0 °C. N-bromosuccinimide (424 mg, 2.38 mmol) was added portion wise and the solution was stirred for 4 h. The precipitate was filtered, washed with cold PE and dried under vacuum. The filtrate was washed with saturated Na₂SO₃ solution, washed with water, and dried over MgSO₄. Petrol ether was added, and the solvent was evaporated under slight vacuum, until a precipitate formed. The solution was cooled to 0 °C and the precipitate was filtered off, and washed with cold methanol. Cyclopentadithiophene **4** (673 mg, 1.17 mmol) was obtained as a slightly greyish solid in 98 % yield.

Mp. 265-270 °C (2 °C/min); ¹H NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.70 (m, 2 H), 7.59 (m, 1 H,), 7.44 (m, 2 H,), 7.01 (m, 4 H), 6.71 (m, 2 H,), 6.65 (m, 2 H,), 6.36 (dd, *J* = 8.4, 1.1 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃): δ [ppm] = 160.56, 141.62, 140.71, 135.52, 131.22, 131.14, 128.77, 128.08, 126.07, 125.64, 121.07, 120.92, 115.06, 112.75, 53.58; FTICR-MALDI-MS: m/z= 581.17141 (calc.: 581.16986, \Box m/m= 2.6 ppm).

4,4'-(10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b']dithiophene]-2',6'-diyl)bis(N,Nbis(4-methoxyphenyl)aniline) (HTM-1): 2',6'-Dibromo-10-phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b']dithiophene] 4 (25 mg, 43 µmol), 4-methoxy-N-(4-methoxyphenyl)-N-[4-(4,4, 5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]aniline 5 (47 mg, 108 µmol), and tetrakis(triphenylphosphine)palladium(0) (5 mg, 4 µmol) in a Schlenk tube were evacuated for 1 h, and THF (2.5 ml) was added and the solution was degassed with argon for 2 minutes. The tube was sealed, and the solution was heated to 75 °C for 90 h. After cooling, water was added, and the organic phase was extracted three times with Et₂O. The collected organic fractions were dried over MgSO₄ and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on with NEt₃-deactivated silica gel. An eluent mixture PE: Et₂O of 3:1, which was gradually changed to 1:1, was used. The obtained solid was crystallized from PE/DCM. The target HTM-1 (32 mg, 31 µmol) was obtained as a yellow-orange solid in 72 % yield. $T_g = 165 \text{ °C}; T_{dec} (TGA, onset) = 417 \text{ °C}; ^1H NMR (400 \text{ MHz}, CDCl_3): \delta [ppm] = 7.74 - 7.67 (m, 100 \text{ MHz})$ 2H), 7.62 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 7.39 – 7.33 (m, 4H), 7.11 (s, 2H), 7.08 – 7.02 (m, 8H), 6.98 (ddd, J = 8.5, 7.1, 1.6 Hz, 2H), 6.92 – 6.87 (m, 4H), 6.86 – 6.79 (m, 10H), 6.69 (ddd, J = 7.9, 7.1, 1.2 Hz, 2H), 6.37 (dd, J = 8.3, 1.1 Hz, 2H), 3.80 (s, 12H); ¹³C NMR (101 MHz, CDCl₃): δ [ppm] = 162.72, 156.01, 148.06, 145.89, 141.81, 141.05, 140.81, 134.15, 131.27, 131.18, 128.63, 127.62, 127.34, 126.64, 126.46, 125.87, 122.61, 121.02, 120.92, 117.30, 114.82, 114.75, 55.63, 54.21; FTICR-MALDI-MS: m/z= [M⁺] 1025.33136 (calc. [M⁺]: 1025.33002, □m/m=1.31 ppm).

¹H-, ¹³C-NMR-spectra



Figure S1. ¹H-NMR-spectrum of cyclopentadithiophene 3.



Figure S2. ¹³C-NMR-spectrum of cyclopentadithiophene 3.



Figure S3. ¹H-NMR-spectrum of cyclopentadithiophene 4.



Figure S4. ¹³C-NMR-spectrum of cyclopentadithiophene 4.



Figure S5. ¹H-NMR-spectrum of HTM-1.



Figure S6. ¹³C-NMR-spectrum of HTM-1.

High resolution mass spectra



Figure S7. FTICR-MALDI MS of cyclopentadithiophene 3.



Figure S8. FTICR-MALDI MS of cyclopentadithiophene 4.



Figure S9. FTICR-MALDI MS of HTM-1.

Single crystal X-ray structure analysis

4,4'-(10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b']dithiophene]-2',6'-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) **HTM-1** (CCDC number: 1979010)

Bond precision: C-C = 0.0030 AWavelength=1.54184 Cell: a=10.2586(1) b=18.1730(2) c = 29.9845(3)beta=92.7628(9) gamma=90 alpha=90 Temperature: 143 K Calculated Reported 5583.50(10) Volume 5583.52(10) Space group P 21/C P 1 21/c 1 Hall group -P 2ybc -P 2ybc C67 H51 N3 O4 S2 [+ Moiety formula C67 H51 N3 O4 S2 solvent](CCl₂H₂) C67 H51 N3 O4 S2 [+ Sum formula C67 H51 N3 O4 S2 solvent](CCl₂H₂) Mr 1026.23 1026.22 1.221 1.221 Dx,g cm-3 Z 4 4 1.270 Mu (mm-1) 1.270 F000 2152.0 2152.0 F000' 2160.39 h,k,lmax 12,22,37 12,22,37 Nref 11344 11024 Tmin,Tmax 0.871,0.910 0.594,1.000 Tmin' 0.709 Correction method= # Reported T Limits: Tmin=0.594 Tmax=1.000 AbsCorr = MULTI-SCAN Dete completeness 0.070 \square (max) $\neg 4$ 117

Data completeness= 0.972	Theta(max) = 74.117
R(reflections) = 0.0431(9103)	wR2(reflections) = 0.1225(11024)
S = 1.067 Np	ar= 785



Figure S10. Single crystal X-ray structure analysis of **HTM-1** showing the individual molecule with atomic labels a) and side view b). Thermal ellipsoids are setted at 50% probability.

Conjugated π -System						
Atom1	Atom2	Length (Å)	Atom1	Atom2	Length (Å)	
C62	016	1.415(3)	C14	C2	1.415(3)	
016	C27	1.372(2)	C2	C8	1.373(3)	
C27	C4	1.388(3)	C8	S2	1.752(2)	
C4	C6	1.380(3)	S2	C15	1.703(2)	
C6	C29	1.397(3)	C20	C5	1.546(3)	
C29	C42	1.389(3)	C5	C14	1.531(3)	
C42	C33	1.392(3)	C8	C13	1.470(3)	
C33	C27	1.382(3)	C13	C49	1.397(3)	
C29	N11	1.413(3)	C49	C48	1.382(3)	
C59	02	1.429(3)	C48	C45	1.384(3)	
02	C22	1.367(3)	C45	C31	1.393(3)	
C22	C23	1.383(3)	C31	C26	1.385(3)	
C23	C38	1.393(3)	C26	C13	1.392(3)	
C38	C21	1.384(3)	C45	N40	1.423(3)	
C21	N11	1.425(3)	N40	C30	1.414(3)	
C21	C47	1.384(3)	C30	C39	1.387(3)	
C47	C43	1.378(3)	C54	C14	1.385(3)	
C45	C22	1,367(5)	C14	C24	1,200(5)	
(28	C25	1 305(3)	C34	C55	1 377(3)	
C25	C7	1 381(3)	C55	C30	1 388(3)	
C7	C11	1.393(3)	C44	038A	1.38(1)	
C11	C40	1.397(3)	038A	C74	1.44(1)	
C40	C36	1.384(3)	N40	C41	1.419(3)	
C36	C28	1.395(3)	C41	C58	1.395(3)	
C11	C12	1.467(3)	C58	C61	1.380(4)	
C12	C3	1.373(3)	C61	C60	1.383(4)	
C3	C20	1.412(3)	C60	C46	1.380(4)	
C20	C9	1.366(3)	C46	C51	1.392(3)	
C9	S1	1.714(2)	C51	C41	1.387(3)	
S1	C12	1.749(2)	C60	059	1.39(2)	
C9	C15	1.442(3)	059	C75	1.56(4)	
C15	C14	1.379(3)				
L		Acridir	ne unit 			
Atom1	Atom2	Length (Å)	Atom1	Atom2	Length (Å)	
C5	C18	1.519(3)	C50	C37	1.388(3)	
C18	C57	1.386(3)	C37	C19	1.385(3)	
C57	C52	1.392(3)	C19	C1	1.385(3)	
C52	C35	1.374(3)	N20	C10	1.46(1)	
C35	C32	1.374(3)	C10	C53	1.38(2)	
C32	C16	1.399(3)	C53	C64	1.38(1)	
C16	C18	1.406(3)	C64	C65	1.39(2)	
C5	C1	1.522(3)	C65	C63	1.38(2)	
C1	C24	1.408(3)	C63	C56	1.39(2)	
C24	C17	1.398(3)	C56	C10	1.38(2)	
C17	C50	1.382(3)				

 Table S1. Relevant bond length distances in HTM-1.



Figure S11. Single crystal X-ray structure analysis: Unit cell containing four HTM-1 molecules. Hydrogen atoms have been omitted for clarity.

Table S2. Relevant angles and torsion angles of HTM-1

Angles: Spiro unit							
Atom1	Atom2	Atom3	Angle (degrees)	Atom1	Atom2	Atom3	Angle (degrees)
C12	S1	C9	90.58(9)	C1	C5	C18	110.7(1)
S1	C12	C3	111.9(1)	C18	C16	C32	119.3(2)
C12	C3	C20	111.8(2)	C16	C32	C35	121.0(2)
C3	C20	C9	113.3(2)	C32	C35	C52	120.2(2)
C20	C9	S1	112.5(1)	C35	C52	C57	119.3(2)
C3	C20	C5	135.7(2)	C52	C57	C18	121.7(2)
S1	C9	C15	138.3(1)	C57	C18	C16	118.4(2)
C9	C15	S2	137.6(1)	C24	C1	C19	118.7(2)
C15	S2	C8	91.12(9)	C1	C19	C37	122.1(2)
S2	C8	C2	111.1(1)	C19	C37	C50	118.8(2)
C8	C2	C14	112.8(2)	C37	C50	C17	120.3(2)
C2	C14	C15	112.2(2)	C50	C17	C24	120.8(2)
C14	C15	S2	112.8(1)	C17	C24	C1	119.1(2)
C2	C14	C5	136.9(2)	C16	N20	C10	115.3(7)
C14	C5	C18	112.3(1)	C24	N20	C10	118.1(7)
C20	C5	C18	110.0(1)	N20	C10	C53	120(1)
C14	C5	C1	115.7(2)	C10	C53	C64	120(1)
C20	C5	C1	107.8(1)	C53	C64	C65	120(1)
C5	C18	C16	119.4(2)	C64	C65	C63	120(1)
C18	C16	N20	119.6(2)	C65	C63	C56	119(1)
C16	N20	C24	120.4(2)	C63	C56	C10	121(1)
N20	C24	C1	119.9(2)	C56	C10	C53	120(1)
C24	C1	C5	119.2(2)		010	000	120(1)
			Torsion	angles			
	Atom1	Atom2	Atom3	Ato		Torsion angle (degrees)	
	C14	C5	C1	C10	a	27 6(3)	
	C14 C14	C5	C18	(15	,	-22 5(2)	
	C14 C20	C5	C10	C10	,	-23.3(2)	
	C20	C5	C18	C13	,	86.6(2)	
	C20	C18	C16	N2('n	-9.6(2)	
	C5	C18	C10	N20	5	5 9(3)	
	C16	N2O	C10	C53	2	75(1)	
	C24	N20	C10	C56	5	107(1)	
	S1	C12	C10	C40	,)	-32 9(3)	
	\$2	(8	C13	C76	5	8 8(3)	
	C28	N11	C21	C47	,	50.8(3)	
	C28	N11	C29	C47	,	40.4(3)	
	C45	N40	C41	C58	-	40 5(3)	
	C45	N40	C30	C39)	35.2(3)	



Figure S12. Molecular packing in the single crystal X-ray structure analysis of **HTM-1** showing intermolecular short contacts (green lines) between atoms perpendicular to the (100) a) and (001) planes b). Hydrogen atoms have been omitted for clarity. The triphenylamine units have been softened up for clarity in b).

Atom M1	Atom M2	Distance (Å)	Symm. M1	Symm. M2
C4	H59C	2.760	x,y,z	-1+x,y,z
016	H59C	2.562	x,y,z	-1+x,y,z
C27	H59C	2.866	x,y,z	-1+x,y,z
H43	C64	2.753	x,y,z	-x,-1/2+y,1/2-z
02	H37	2.471	x,y,z	1-x,-1/2+y,1/2-z
H25	038	2.680	x,y,z	-x,1-y,1-z
H25	C67	2.812	x,y,z	-x,1-y,1-z
C26	H35	2.889	x,y,z	-x,1-y,1-z
C33	H67C	2.803	x,y,z	-x,1-y,1-z
C42	H67C	2.832	x,y,z	-x,1-y,1-z
C22	H59A	2.885	x,y,z	1-x,1-y,-z
C43	H59A	2.769	x,y,z	1-x,1-y,-z
C22	H67B	2.832	x,y,z	1-x,1-y,1-z
H34	C43	2.790	x,y,z	1-x,1-y,1-z
C62	H26	2.884	x,y,z	-1+x,1.5-y,-1/2+z
H62A	S2	2.974	x,y,z	-1+x,1.5-y,-1/2+z
C63	H55	2.764	x,y,z	-1+x,1.5-y,-1/2+z
C4	C19	3.367	x,y,z	x,1.5-y,-1/2+z
016	H53	2.560	x,y,z	x,1.5-y,-1/2+z
C42	H49	2.806	x,y,z	x,1.5-y,-1/2+z
H49	C42	2.806	x,y,z	x,1.5-y,1/2+z

 Table S3. Relevant intermolecular short contacts (below the sum of the Van der Waals radii) in the X-Ray structure analysis of HTM-1.

Device fabrication

Fluorine-doped tin oxide (FTO) glass with a sheet resistance of ~10 ohm/square was employed as a transparent conductive substrate. Prior to use, substrates were ultrasonically cleaned in Hellmanex (2% in deionized water) for 20 min, followed by sequential rinsing with de-ionized water, ethanol, and acetone. The substrates were treated with UV-O₃ for 15 min to remove the last traces of organic residues. A ~30 nm-thick compact layer of TiO₂ (c-TiO₂) was subsequently deposited via aerosol spray pyrolysis at 450 °C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) (75% in 2-propanol) diluted in ethanol (1:9, volume ratio) with oxygen as a carrier gas. A diluted paste of (30NRD) mesoporous TiO₂ (mp-TiO₂) layer was then deposited onto the c-TiO₂ by using spin-coating at a spin speed of 5000 rpm, for 15 s (the weight ratio of TiO₂: ethanol is 1:5.5). This was followed by sintering of the substrates at 450 °C for 30 min. The substrates were transferred into a glove-box for perovskite deposition. The perovskite deposition was carried out in a glove-box under controlled atmospheric conditions with humidity <2%. We note that 10% excess PbI₂ and PbBr₂ were used for (FAPbI₃)_{0.9} (MAPbBr₃)_{0.1} perovskite precursor solution. The perovskite solutions were deposited from a precursor solution containing FAI 1.2 M, PbI₂ 1.3 M, MABr 0.13 M and PbBr₂ 0.14 M in anhydrous dimethylformamide (DMF) / dimethylsul-

foxide (DMSO) (4:1 / v:v). CsI was dissolved in DMSO at concentration of 1.5 M and added to the mixed perovskite precursor (5% volume) to make Cs/FA/MA triple cation perovskite. The perovskite solution was spin coated in a two-step program at 1000 and 4000 rpm for 10 s and 30 s, respectively. During the second step, 200 μ L of chlorobenzene was poured on the spinning substrate 15 s prior to the end of the program. The substrates were then annealed at 100 °C for 45-50 min in a glove-box. Subsequently, HTM solutions prepared by dissolving 73 mM of spiro-MeO-TAD and 30 mM of **HTM-1** in 1 mL of chlorobenzene were spin coated at 4000 rpm for 20 s. Spiro-MeOTAD and **HTM-1** were doped with Li-TFSI and *t*BP. The molar ratio of additives for each HTM was 0.5 and 3.3 for Li-TFSI and *t*BP, respectively. Finally, ~80 nm thick gold layer was thermally evaporated under high vacuum.

Device characterization

The hydrophilicity of HTM-containing surfaces as a function of time was assessed by the contact angle measurement by drop shape analyzer (KRÜSS, DSA100) at ambient temperature. To record time-integrated photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra, pristine and HTM containing samples were excited with the second harmonic (~425 nm) of a picosecond mode-locked Ti/sapphire laser (80.5 MHz). The collected emission spectra were spectrally and temporally analysed using a 32-cm focal length monochromator equipped with a charge-coupled device (CCD) (resolution of >1 meV) and a streak camera (resolution of ~ 20 ps), respectively. For hole injection study, the samples were excited from the top side. The perovskite films were excited at room temperature with a picosecond laser emitting at 420 nm to determine the hole extraction ability of HTM. The field-emission scanning electron microscope (FE-SEM, Carl Zeiss, Merlin) was used to characterize the spiro-MeOTAD and HTM-1 containing devices and thicknesses of various layers. The current density-voltage (J-V) curves of fabricated devices were measured with a digital source meter (Keithley, 2400) using 450 W xenon lamp (Oriel) under the AM 1.5 G illumination of 100 mW.cm⁻² as the light source. External quantum efficiency (EQE) measurements of the devices were recorded using a LED light source EQE system (Ariadne) in the DC mode without any voltage bias. The J-V and EQE curves of all devices were measured by masking the active area with a metal mask having an area of 0.16 cm². Operational stability measurements were performed with a Biologic MPG2 potentiostat under AM 1.5. The devices with a metal aperture mask were mounted in the sample holder flushed with nitrogen. The devices were measured with a maximum power point tracking (MPPT) under constant illumination. Thermal stability tests were carried out by aging the cells with increasing temperature (60 to 80 °C) on a hot plate under nitrogen atmosphere. Photovoltaic performance of the cells was periodically recorded under 1 sun illumination.

Thermal properties



Figure S13. TGA measurement of HTM-1.



Figure S14. DSC measurement of HTM-1.

Optoelectronic properties



Figure S15. UV-vis solution spectra of HTM-1 (green curve) in comparison to spiro-MeOTAD (brown curve).



Figure S16. UV-vis film absorption spectra of HTM-1 (green curve) in comparison to spiro-MeOTAD (brown curve).

	$\lambda_{max, sol}$	$\lambda_{max, film}$	3	$\lambda_{ons, sol}$	E _{gap,opt}	E ⁰ _{ox1}	E ⁰ _{ox2}	E ⁰ _{ox3}	НОМО	LUMO	WF
	[nm]	[nm]	$[M^{-1}cm^{-1}]$	[nm]	[eV]	[V]	[V]	[V]	[eV]	[eV]	[eV]
HTM-1	445	449	65 000	506	2.45	-0.01	0.13	0.69	-5.01	-2.57	-4.99
Spiro-MeOTAD	386	375	75 700	418	2.97	-0.01	0.12	0.33	-5.04	-2.07	-5.01

Table S4. Optoelectronic properties of HTM-1 and spiro-MeOTAD.

Photovoltaic properties



Figure S17. Dependence of photovoltaic performance on the concentration of HTM-1 (4 devices for each case).



Figure S18. Statistics of the solar cell efficiencies obtained from 25 samples of the spiro-MeOTAD and **HTM-1**-based perovskite solar cells.

HTMs	V _{oc} (V)	J _{SC} (mA.cm ⁻²)	FF	PCE (%)
Spiro-MeOTAD	1.14	24.35	0.76	21.09
	(1.11±0.01)	(24.40±0.25)	(0.76±0.01)	(20.64±0.27)
HTM-1	1.10	24.74	0.77	20.95
	(1.09±0.01)	(24.70±0.16)	(0.77±0.01)	(20.43±0.25)

Table S5. The best and average (25 cells for each conditions) photovoltaic parameters of different HTM based PSCs.

ToF device preparation and measurement

ITO substrates (15 Ohm/sq.) were cleaned using standard procedures (ultrasonication in chloroform, acetone, Hellmanex and water). Depending on the HOMO of the HTM bare ITO was used or modified with a layer of PEDOT, or semitransparent old, aluminum or chromium with a thickness of 15 to 25 nm. To obtain reference samples comparable to literature, thick films of spiro-MeOTAD were spin-coated from a 100 mg/mL solution in toluene or drop-coated from a 10 mg/mL solution to yield about 3 μ m thick films. Additionally, spiro-MeOTAD layers were fabricated by sublimation in vacuum at a rate of 2 A/s.

In order to approach the thickness of the HTM layer in a solar cell (< 1 μ m), thinner films were fabricated by spin-coating spiro-MeOTAD and **HTM-1** from benzene solution. **HTM-1** was dissolved at a nominal concentration of 50 mg/mL at about 60 °C and filtrated prior to spin-coating through ab 0.45 μ m PTFE syringe filter. The spin-coater was saturated with benzene vapor before spin-coating. To adjust the **HTM-1** thickness, spin speeds were varied from 150 rpm to 1000 rpm. At low spin speed the rotation serves just a step to yield homogeneous films, but the film formation is more like drop casting (very slow drying). For experiments with films thinner than 2 μ m a 30 nm ZnPc film was evaporated to serve as charge generation layer (CGL). Film thickness was measured by a Dektak surface profiler or by interference fringes in the NIR-vis transmission spectra. The ToF devices were completed by evaporation of a metal contact being either opaque or semi-transparent Au, Ag, or Al depending on excitation wavelength.

Devices were mounted in a sample holder and biased using a Keithley 2400 source meter or an Agilent pulse generator. Current transients were detected by a LeCroy Wavesurfer oscilloscope after passing either a load resistor or a Femto DHPCA-100 amplifier. Reference devices were excited with the third harmonic (355 nm) of a Nd-YAG laser. Devices with a CGL were excited using

an OPO operating at 645 nm, pumped by the third harmonic (355 nm) of a Nd-YAG laser. The excitation intensity was adjusted using neutral density filter wheels and kept to a minimum, typically below 5 nJ per pulse in order to satisfy the CU limit (generated charge should be below 5 % of the capacitor charge). The laser pulses were about 5 ns long. The maximum time resolution of the experiment is about 100 ns.

<u>ToF measurement results</u>

Reference spiro-MeOTAD: for thick spiro-MeOTAD devices typical ToF transients are shown in Figure S19 proving hole transport in equilibrium without severe trapping. Besides initial electromagnetic noise the transients feature a current plateau and a trailing edge after transit. The transit time can be obtained in a standard way for these non-dispersive transients as depicted. Although this overestimates the mobility compared with MC simulations, it has been the established method. However, for thinner films the excitation at 355 nm cannot be used due to the penetration depth of the light. Moreover, small device thickness can contribute to dispersion as illustrated with two spiro-MeOTAD films obtained by sublimation (Figure S20). For the 2 µm device the transit time can only be obtained in log-log representation. Thus, to exclude device thickness and volume charge generation the charge generation zone should be limited to 10 % of the total film thickness to obtain a well-defined transit time. For this reason, we used ZnPc as charge generation layer. This allowed the excitation charge in ZnPc with light (645 nm) transmitted through spiro-MeOTAD and HTM-1 (sub-gap). Figure S21 depicts the mobility vs. electric field for different spiro-MeOTAD devices. Shown are measurements from devices with and without CGL, varying thickness and solution-processed devices as well as devices obtained by sublimation in vacuum. The field dependence is more or less identical despite variation in devices parameters which proves the dominance of volume mobility. The spread in mobility is a good representation of the variance due to variation in preparation parameters.

However, for **HTM-1** the ToF signals are dispersive, examples are shown in Figure S22. This allows transit time (and thus mobility) determination only on log-log scale. This implies dispersive transport, *i.e.*, non-equilibrium transport. Since in all cases a CGL was used, the dispersion is a material/device characteristic and not due to volume charge generation. A characteristic of dispersive transport is the dependence of mobility on the device and thus on device fabrication details. Hence, we investigated different devices to obtain a reliable result. In Figure S23 the mobility of different devices is shown. Apparently, the mobility and its functional dependence are similar but showed a

larger variation compared with non-dispersive transport in spiro-MeOTAD. However, as expected from dispersive transport the turn over to a negative field dependence is different.



Figure S19. ToF transients of a 2.9 μ m thick spiro-MeOTAD device at U = 10 V (black), 20 V (green) and 30 V (blue), respectively. Marked is the transit time obtained by intersection of two tangents to plateau and trailing edge of the current transient. The transients are offset for clarity.



Figure S20. ToF transients of a 2.00 µm and 4.26 µm thick spiro-MeOTAD device at approximately the same electric field to illustrate the effect of film thickness on dispersion.



Figure S21. The log hole mobility vs square root of electric field for different spiro-MeOTAD devices. Black square: 2.9 µm drop casted identical to data shown in the main paper, black dot: 2.9 µm spin coated, blue dot: bottom CGL, 0.9 µm HTL, blue circle: top CGL; 1.8 µm HTL, red circle: bottom CGL; 1.6 µm HTL.



Figure S22. ToF transients of **HTM-1** (1.14 μ m thick) using a CGL. The hole mobility can only be obtained by applying tangents to the current plateau and tail in a log-log plot. The applied voltage increases from 12 V to 50 V with decreasing transit time.



Figure S23. The log hole mobility vs square root of electric field for different **HTM-1** devices with top CGL. Black square: 0.6 μ m spin coated, black dot: 1.17 μ m spin coated, black circle: 1.14 μ m HTL, red dot: 0.84 μ m, identical to data shown in the main paper.