Supporting information

A star-shaped carbazole-based hole-transporting material with triphenylamine side arms for perovskite solar cells

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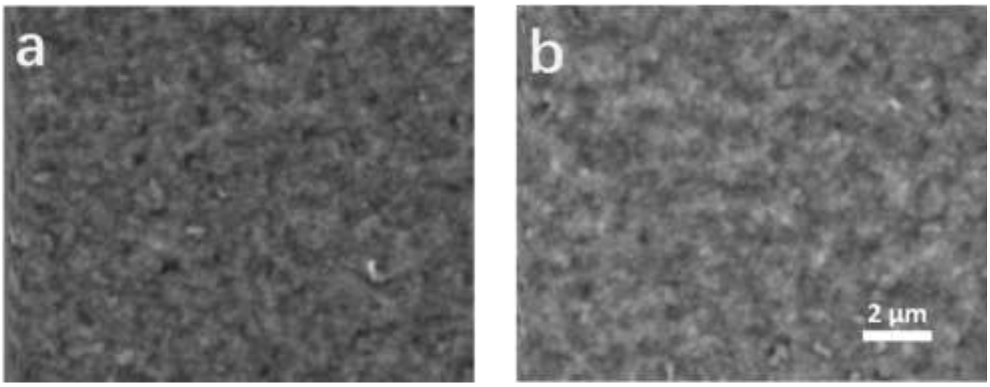


Fig. S1 SEM images (top view) of the perovskite layers covered by **LD29** and spiro-OMeTAD.

Table S1 Detailed device parameters of perovskite solar cells with different HTMs.

HTM	Concentration (mg mL^{-1})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
pristine LD29	60	0.99	18.43	70	12.78
pristine LD29	60	1.03	18.62	68	13.06
pristine LD29	60	1.02	19.01	68	13.20
pristine LD29	60	1.02	18.57	66	12.49
pristine LD29	40	1.01	19.44	69	13.56
pristine LD29	40	0.98	18.63	63	11.49
pristine LD29	40	0.99	19.29	65	12.43
pristine LD29	40	1.01	19.38	68	13.32
pristine LD29	20	1.02	19.60	71	14.29
pristine LD29	20	1.03	19.23	68	13.51
pristine LD29	20	1.03	18.60	70	13.39
pristine LD29	20	0.99	19.06	67	12.66
doped LD29	60	1.07	21.37	75	17.12
doped LD29	60	1.10	21.61	76	18.04
doped LD29	60	1.09	21.65	74	17.49
doped LD29	60	1.07	20.98	75	16.84
doped LD29	40	1.07	20.49	76	16.67
doped LD29	40	1.03	21.04	75	16.24
doped LD29	40	1.02	19.87	74	15.00
doped LD29	40	1.03	21.66	75	16.74
doped LD29	20	1.04	21.36	72	15.98
doped LD29	20	1.05	20.71	74	16.10
doped LD29	20	1.04	20.27	75	15.83
doped LD29	20	1.06	19.29	75	15.33
doped spiro-OMeTAD	73	1.08	21.84	76	17.96
doped spiro-OMeTAD	73	1.07	21.59	75	17.34
doped spiro-OMeTAD	73	1.11	22.02	75	18.25
doped spiro-OMeTAD	73	1.08	22.17	74	17.73

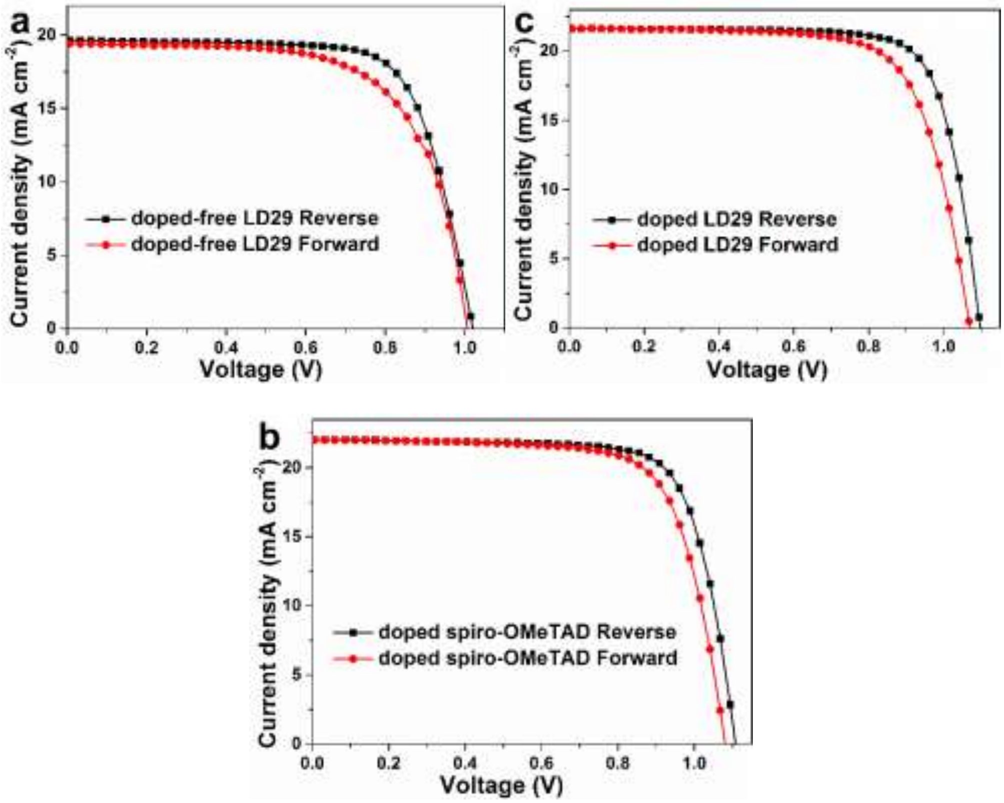


Fig. S2 *J*-*V* curves measured by forward scan (from short circuit to open circuit) and reverse scan (from open circuit to short circuit) of the PSCs with different HTMs under AM 1.5 illumination.

Table S2 Photovoltaic parameters of best-performing PSCs with different HTMs and measured through forward and reverse scans.

HTM		V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
pristine **LD29**	Reverse	1.02	19.60	71	14.29
	Forward	1.00	19.42	66	12.90
doped **LD29**	Reverse	1.10	21.61	76	18.04
	Forward	1.07	21.63	71	16.45
doped spiro-OMeTAD	Reverse	1.11	22.02	75	18.25
	Forward	1.08	22.02	72	17.11

Table S3 Photovoltaic data for pristine **LD29**-hased device with light soaking effect under one sun conditions.

Time (min)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	1.00	19.45	50	9.75
1	1.00	19.50	62	12.14
2	1.01	19.56	66	13.08
3	1.02	19.57	69	13.76
4	1.02	19.59	70	14.02
5	1.02	19.59	70	14.25
6	1.02	19.60	71	14.29

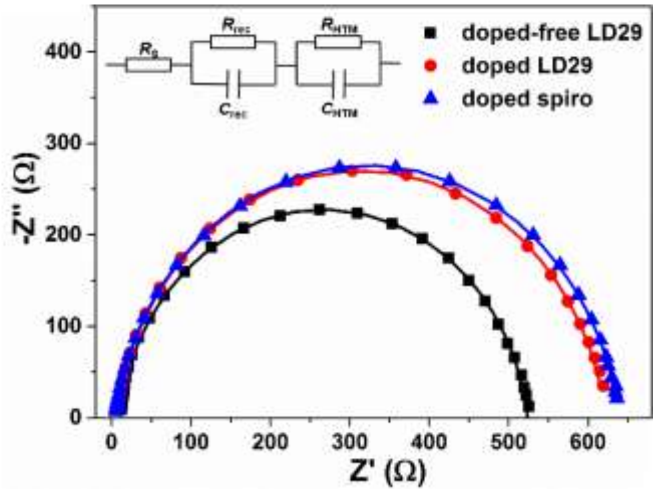


Fig. S3 Nyquist plots of PSCs based on pristine **LD29**, doped **LD29** and doped spiro-OMeTAD measured at 1.0 V forward bias in the dark.

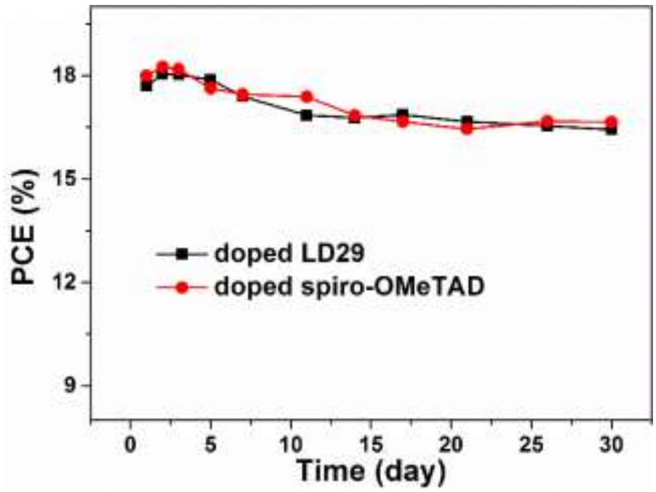


Fig. S4 Stability test for the devices with different HTMs at room temperature without encapsulation in a dark drying oven.

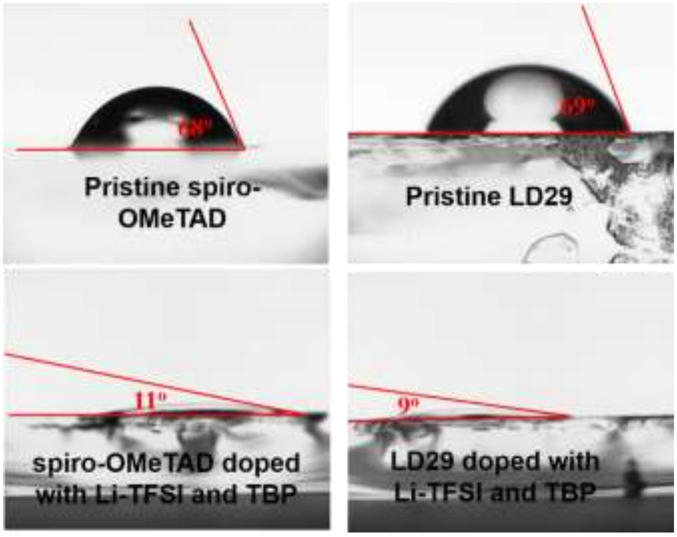


Fig. S5 Water contact angle of pristine or doped **LD29** and spiro-OMeTAD.

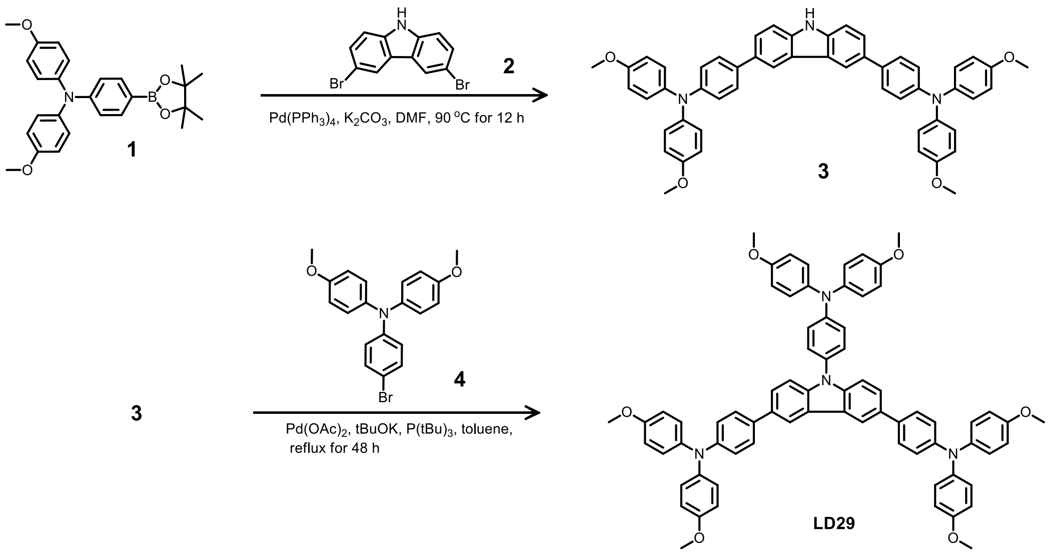


Fig. S6 Synthetic routes for **LD29**.

Compound **1** and compound **4** are developed in our lab, the synthesis routine is shown in our previous report.[1] The structure of target product (**LD29**) is confirmed by NMR, elemental analysis and HRMS (MALDI-TOF) measurements.

Compound 3

Compound **2** (0.20 g, 0.6 mmol), compound **1** (0.56 g, 1.3 mmol), 2M solution of K_2CO_3 (8 mmol, 1.1 g) in H_2O, [Pd(PPh_3)$_4$] (0.05 mmol, 60 mg) , DMF (20 mL) were added into a 50 mL Ar-protected flask. The reaction solution was kept with stirring at 90 ^{o}C for 12 h. After cooling to R.T., the reaction mixture was poured into cold Na_2SO_4 aqueous solution, then the crude product precipitates out as solid. The crude product was purified by column chromatography (CH_2Cl_2/PE = 2:1) to obtain compound **3** as light green solid (0.38 g, 81%). ^{1}H NMR (400 MHz, DMSO) δ 11.28 (s, 1H), 8.44 (s, 2H), 7.60 (d, *J* = 8.1 Hz, 6H), 7.50 (d, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 5.6 Hz, 2H), 6.92 (d, *J* = 6.6 Hz, 2H), 3.75 (s, 12H). Anal. Calcd. for $C_{52}H_{43}N_3O_4$(%): C, 80.70; H, 5.60; N, 5.43. Found: C, 80.69; H, 5.61; N, 5.42.

LD29

Compound **3** (0.23 g, 0.3 mmol), compound **4** (0.15 g, 0.4 mmol), tBuONa (0.58 g, 6 mmol), $P(tBu)_3$ (0.1 M in toluene, 0.3 mL), $Pd(OAc)_2$ (45 mg, 0.2 mmol) were added into a 50 mL flask. Then 15 mL dry toluene was injected in to the flask and degassed using Ar. The reaction solution was kept with stirring at reflux for 48 h. After cooling to R.T., the mixture was diluted by 30 mL CH_2Cl_2 and washed with 50 mL deionized water for 3 times. The organic phase was dried by Na_2SO_4, and removed solvent using rotary evaporator. The crude product was purified by column chromatography (CH_2Cl_2/PE = 2:1) to obtain white **LD29** (0.26 g, 82%). ^{1}H NMR (400 MHz, DMSO) δ 8.56 (d, 2H), 7.67 (m, 6H), 7.40 (d, *J* = 6.2 Hz, 4H), 7.06-6.93 (m, 28H), 3.76 (s, 18H). Anal. Calcd. for $C_{72}H_{60}N_4O_6$(%) C, 80.27; H, 5.61; N, 5.20. Found: C, 80.25; H, 5.59; N, 5.21. MS (MALDI-TOF) *m/z*: [M^+] calcd, 1076.45; found 1076.44.

A simple analysis of relative costs of spiro-OMeTAD and LD29

The lab synthesis cost of **LD29** are estimated on a model originally proposed by Osedach *et al.*[2] Recently, Pertrus and Malinauskas *et al.*[3-5] has used the model to estimate the cost of hole transporting materials. For every synthetic step the required amounts of reactants, catalysts, reagents and solvents are calculated to obtain 1 gram of **LD29** are reported (Table S6).

Table S4 Materials, quantities and cost for the synthesis of **compound 3**.

Chemical	Weight Reagent or solvent (g/g)	Price of chemical (RMB/g)	Cost of chemical (RMB/g product)	Total cost (RMB/g)
4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline [1]	1.47	70	103	
3,6-Dibromocarbazole	0.53	2.73 (ark)	1.44	
DMF	50	0.03	1.5	
$Pd(PPh_3)_4$	0.16	72	11.52	
K_2CO_3	2.89	0.04	0.032	
Na_2SO_4	5	0.02	0.1	
CH_2Cl_2	450	0.03	13.5	
Petroleum ether	260	0.02	5.2	
compound 3				136

Table S5 Materials, quantities and cost for the synthesis of **LD29**.

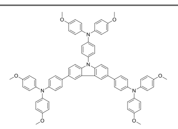
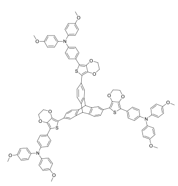
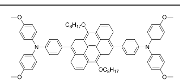
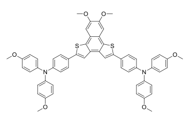
Chemical	Weight Reagent or solvent (g/g)	Price of chemical (RMB/g)	Cost of chemical (RMB/g product)	Total cost (RMB/g)
Compound 3	0.89	136	121	
Compounds 4 [1]	0.58	50	29	
tBuONa	2.23	0.64	1.42	
$P(tBu)_3$	0.1	55	5.5	
Pd(OAc)2	0.17	172	29	
toluene	50	0.04	2	
CH_2Cl_2	450	0.03	13.5	
Petroleum ether	260	0.02	5.2	
LD29				207

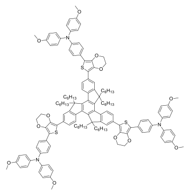
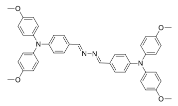
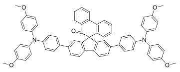
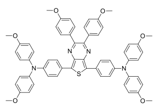
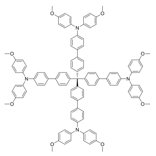
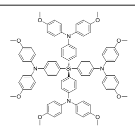
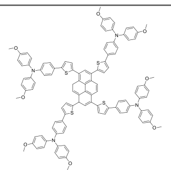
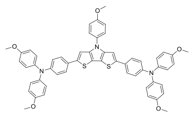
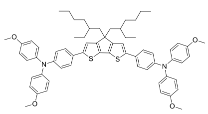
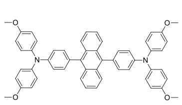
207 RMB/g ≈ 30.3 $/g

Table S6 Survey of the estimated chemical synthesis cost for different HTMs.

compound	**Material cost ($/g)**	**Commercial price ($/g)**
LD29	30.2	-
Spiro-OMeTAD	91.67[3-5]	170-500[3-5]

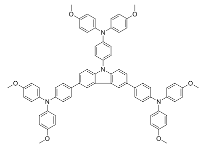
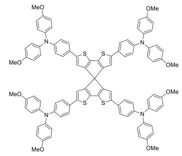
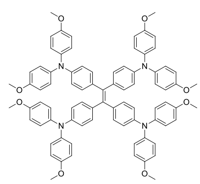
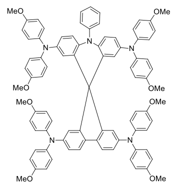
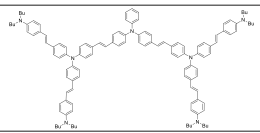
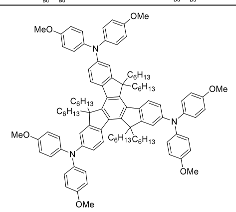
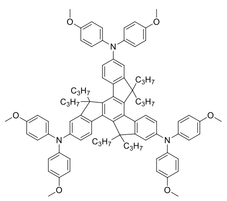
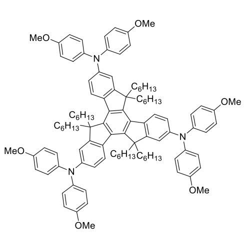
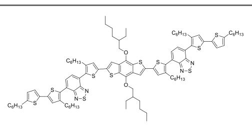
Table S7 The comparison of some reported doped HTMs and **LD29** with cost analysis.

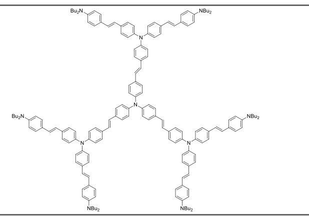
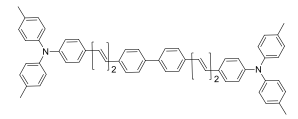
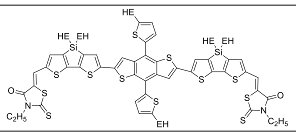
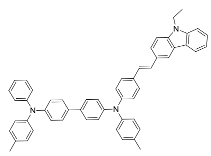
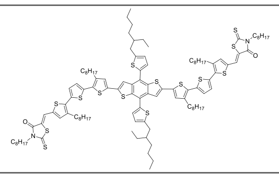
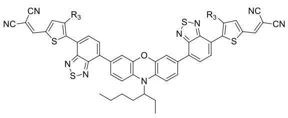
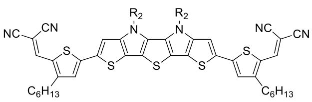
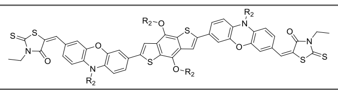
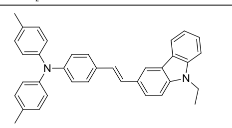
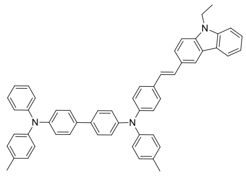
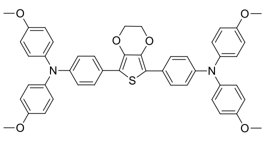
sample	Molecular structures	Device structures	PCE (%)[a]	Ref. PCE[b]	cost ($/g)[c]	Ref.
LD29		$FTO/TiO_2/(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}/HTM$	18.09	18.25	30.2	This work
TET		$FTO/SnO_2/C_{60}$-SAM/$MA_{0.7}FA_{0.3}PbI_3$/HTM	18.6	19.0	123	6
TPA-ANT-TPA		$FTO/TiO_2/MAPbI_3$/HTM	17.5	16.8	67	7
NDT		$FTO/SnO_2/MAPbI_3$/HTM	18.78	18.05	78.8	8

TRUX-E-T		FTO/SnO_2/C_{60}-SAM/$MA_{0.7}FA_{0.3}PbI_3$/HTM	18.36	19.13	38.9	9
Diazo-OMeTPA		FTO/TiO_2/$MAPbI_3$/HTM/Au	14.4	15.1	54	10
Yih-1		FTO/TiO_2/$MAPbI_3$/HTM	16.06	16.08	29.14	11
YN2		FTO/TiO_2/$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$/HTM	19.27	17.80	35.5	12
TPA-TPM		FTO/TiO_2/$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$/HTM	16.76	17.42	52.3	13
Si-OMeTPA		p-i-n ITO/HTM/$MAPbI_3$/PCBM	19.06	-	29.57	14
OMe-TATPyr		ITO/SnO_2/$MAPbI_3$/HTM	20.0	17.3	50.5	15
H16		FTO/TiO_2/ mixed-ion perovskite/HTM	18.16	18.27	30	16
CDTh-EtHex 2		FTO/TiO_2/$MAPbI_3$/HTM	15.51	16.19	179.05 (€/g)	17
A102		FTO/TiO_2/$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$/HTM	17.56	12.27	34.6	18

[a] The best PCE of developed HTMs; [b] The best PCE of standard doped Spiro-OMeTAD; [c] Synthesis cost of developed HTMs in their reports.

Table S8 The comparison of some reported doped-free HTMs and **LD29**.

sample	Molecular structures	Device structure	PCE (%)[a]	Ref.
LD29		FTO/TiO_2/ $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$/HTM	14.29	This work
Spiro-CPDT		FTO/TiO_2/$MAPbI_3$/HTM	13.4	19
TAE-1		FTO/TiO_2/$MAPbI_3$/HTM	11.02	20
SAF-OMe		ITO/TiO_2/$MAPbI_{3-x}Cl_x$/HTM	12.39	21
Z1011		FTO/TiO_2/$MAPbI_3$/HTM	16.3	22
Trux 1		ITO/HTM/$MAPbI_3$/PCBM/ZnO/ Al	10.2	23
1		FTO/TiO_2/$MAPbI_3$/HTM	3.18	24
Trux-OMeTAD		ITO/HTM/$MAPbI_3$/PCBM/ZnO/ Al	18.6	25
BDT-C1		FTO/TiO_2/$MAPbI_3$/HTM	13.9	26

Z1013		FTO/TiO_2/$MAPbI_3$/HTM	15.4	[27]
2TPA-2-DP		FTO/TiO_2/$MAPbI_3$/HTM	12.96	[28]
DERDTS-TBDT		ITO/TiO_2/$MAPbI_{3-x}Cl_x$/HTM/MoO_3	16.2	[29]
TPBC		FTO/TiO_2/$MAPbI_3$/HTM	13.1	[30]
DOR3T-TBDT		ITO/TiO_2/$MAPbI_{3-x}Cl_x$/HTM/MoO_3	14.9	[31]
POZ2		FTO/TiO_2/$MAPbI_3$/HTM	12.8	[32]
oligothiophene 1		FTO/TiO_2/$MAPbI_3$/HTM	10.5	[33]
M1		ITO/ZnO/$PC_{70}BM$/ $MAPbI_3$/HTM	13.2	[34]
apv-EC		FTO/TiO_2/$MAPbI_3$/HTM	12.0	[35]
TPBC		FTO/TiO_2/$MAPbI_3$/HTM	13.3	[36]
H101		FTO/TiO_2/$MAPbI_3$/HTM	11.03	[37]

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