Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fluorine-substituted Benzothiadiazole-based Hole Transport Materials for Highly Efficient Planar Perovskite Solar Cells with *FF* exceeding 80 %

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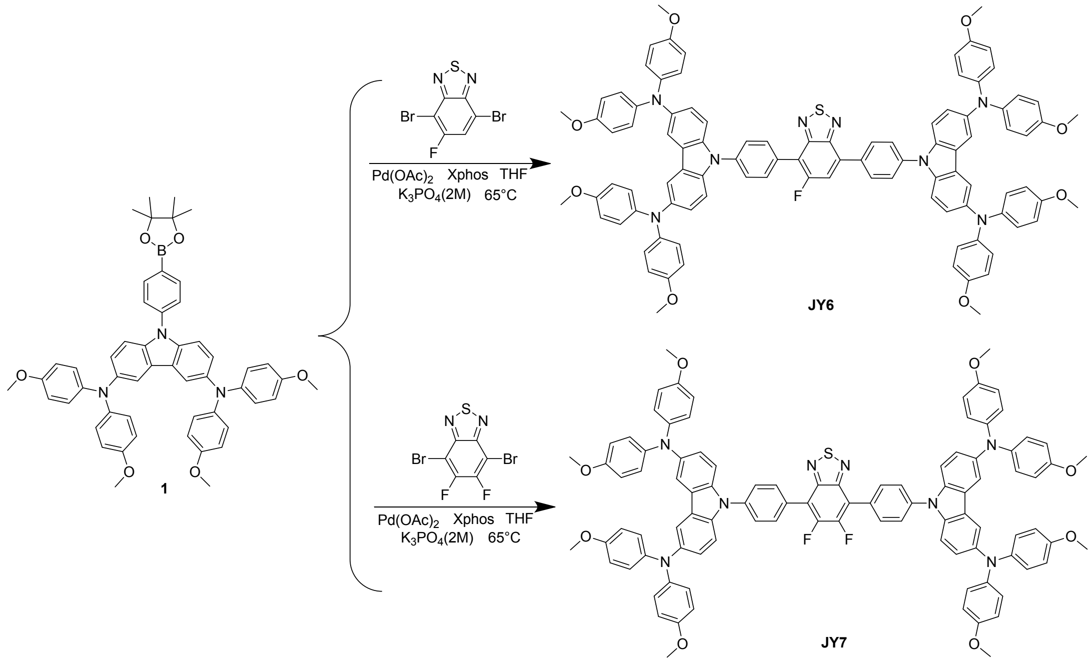
1. General information

Materials and Instruments

Unless otherwisely stated, all starting materials were purchased from commercial suppliers (Sigma-Aldrich, and the Energy Chemical) and used without further purification. Solvents for chemical synthesis such as tetrahydrofuran (THF) and toluene were freshly distilled over Na-K alloy under argon atmosphere prior to use. The nuclear magnetic resonance (NMR) spectra were obtained from a BRUKER AVANCE Ⅲ 600 MHz NMR Instrument (in d_8-THF). MALDI-TOF HRMS was performed on a Bruker Autoflex instrument, using 1,8,9-trihydroxyanthracene as a matrix. UV-vis absorption spectra were measured on a Shimadzu UV-2450 absorption spectrophotometer. PL spectra were measured on a Hitachi F-4600 FL Spectrophotometer. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. FE-SEM images were taken on JSM-7800F.

2. Synthetic procedures



Scheme S1. The synthesis routes for **JY6** and **JY7**.

The intermediate **1** was synthesized according to method reported in literature[1].

Synthesis of JY6 (9,9'-((5-fluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(4,1-phenylene))bis(N^3,N^3,N^6,N^6-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine)

Compound **1** (300 mg, 0.36 mmol), 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (47.33 mg, 0.15 mmol), $Pd(OAc)_2$ (2.72 mg, 0.003 mmol), Xphos (6.84 mg, 0.0036 mmol), K_3PO_4 solution (1 mL, 2 M in H_2O) were dissolved in distilled THF (10 mL). The reaction mixture was heated to 60 °C with stirring overnight. Then the mixture was cooling down to room temperature. The mixture was extracted with dichloromethane and washed several times with brine. The organic layer was dried with anhydrous magnesium sulfate. The filtrate was then evaporated under vacuum and purified by column chromatography (dichloromethane /petroleum ether =2/1) to give **JY6** as a red solid (155.9 mg, 67%); ^{1}H NMR (600 MHz, d_8-THF): δ(ppm): 8.47 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 7.8 Hz, 2H), 8.11&8.10 (d, J =12.0 Hz, 1H), 7.87-7.83 (m, 4H), 7.74 (s, 4H), 7.48-7.45 (m, 4H), 7.17 (d, J = 9.0 Hz, 4H), 6.98 (d, J = 8.4 Hz, 16H), 6.79 (d, J = 9.0 Hz, 16H), 3.75 (s, 24H); ^{13}C

NMR (150 MHz, d_8-THF). : δ(ppm): 160.62, 158.96, 155.13, 155.07, 151.07, 142.51, 142.21, 137.47, 137.39, 134.63, 133.19, 133.12, 132.22, 132.20, 130.81, 130.01, 126.42, 126.08, 124.48, 124.42, 124.30, 124.23, 119.49, 119.28, 116.75, 116.45, 116.43, 114.27, 110.47, 110.42, 54.59. MALDI-TOF m/z: $[M+H]^+$ calcd for $C_{98}H_{77}FN_8O_8S$: Cal 1544.5564; found 1544.5557.

Synthesis of JY7 (9,9'-((5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(4,1-phenylene))bis(*N*^{3},*N*^{3},*N*^{6},*N*^{6}-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine)

Compound **1** (300 mg, 0.36 mmol), 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (49.49 mg, 0.15 mmol), $Pd(OAc)_2$ (2.72 mg, 0.003 mmol), Xphos (6.84 mg, 0.0036 mmol), K_3PO_4 solution (1 mL, 2 M in H_2O) were dissolved in distilled THF (10 mL). The reaction mixture was heated to 60 °C with stirring overnight. Then the mixture was cooling down to room temperature. The mixture was extracted with dichloromethane and washed several times with brine. The organic layer was dried with anhydrous magnesium sulfate. The filtrate was then evaporated under vacuum and purified by column chromatography (dichloromethane /petroleum ether =2/1) to give **JY7** as a red solid (167.3 mg, 71%); ^{1}H NMR (600 MHz, d_8-THF): δ(ppm): 8.05 (d, J = 7.8 Hz, 4H), 7.73 (d, J = 8.4Hz, 4H), 7.59 (s, 4H),7.33 (d, J = 9.0 Hz, 4H), 7.03&7.01 (dd, J = 9 Hz, J = 1.8 Hz, 4H), 6.83 (d, J = 8.4 Hz, 16H), 6.64 (d, J = 8.4 Hz, 16H), 3.60 (s, 24H). ^{13}C NMR (150 MHz, d_8-THF): δ(ppm): 155.08, 150.41, 142.50, 142.24, 138.68, 137.33, 132.15, 128.86, 128.68, 127.92, 126.16, 124.49, 124.32, 124.23, 116.40, 114.28, 110.46, 54.61. MALDI-TOF m/z: $[M+H]^+$ calcd for $C_{98}H_{76}F_2N_8O_8S$: Cal: 1562.5469; found 1562.5479.

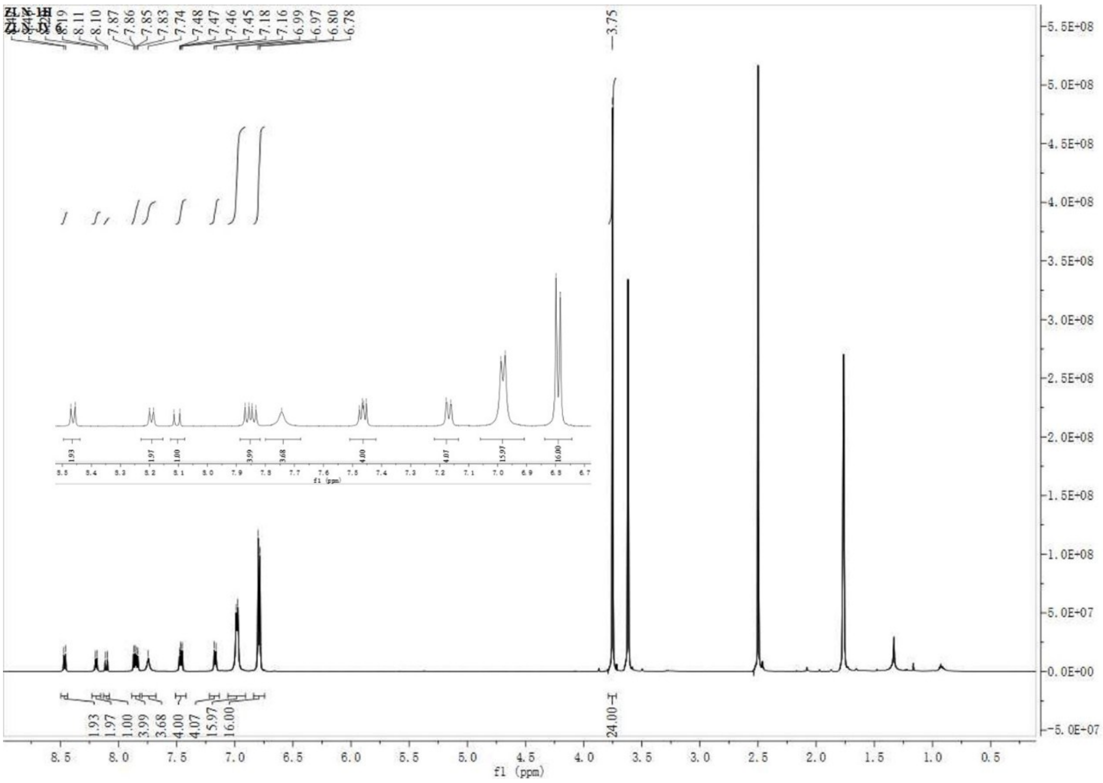


Figure S1. ^{1}H NMR spectrum of **JY6** in d_8-THF.

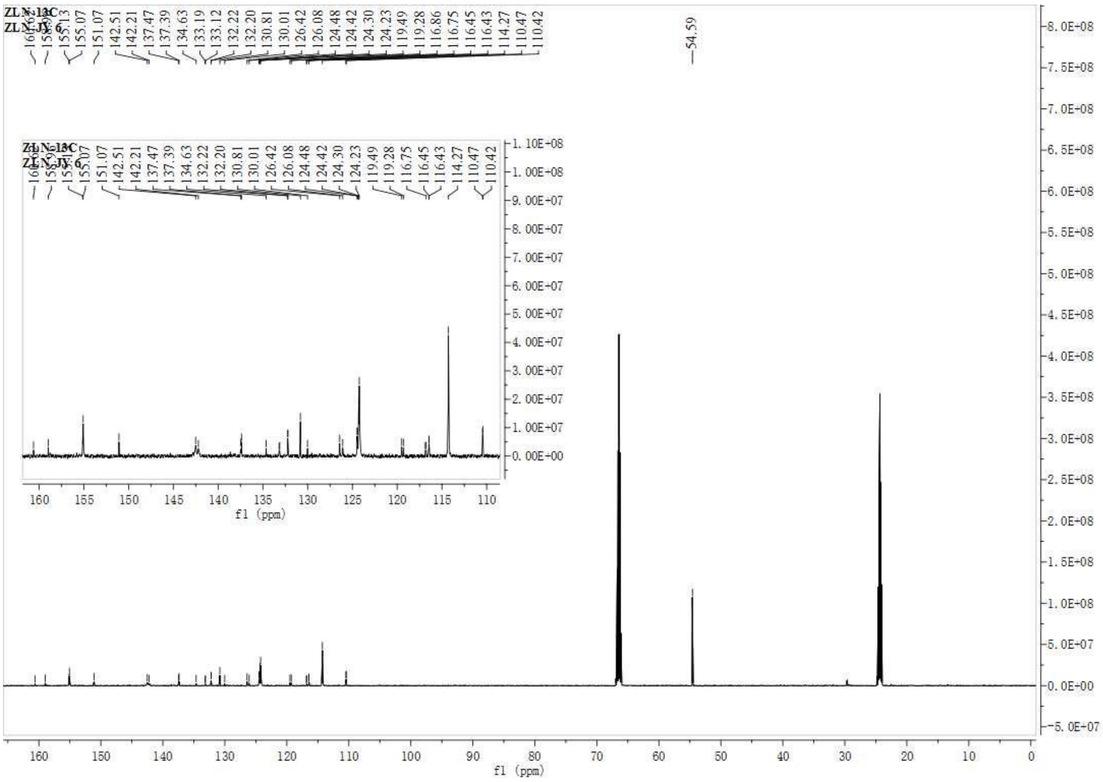


Figure S2. ^{13}C NMR spectrum of **JY6** in d_8-THF.

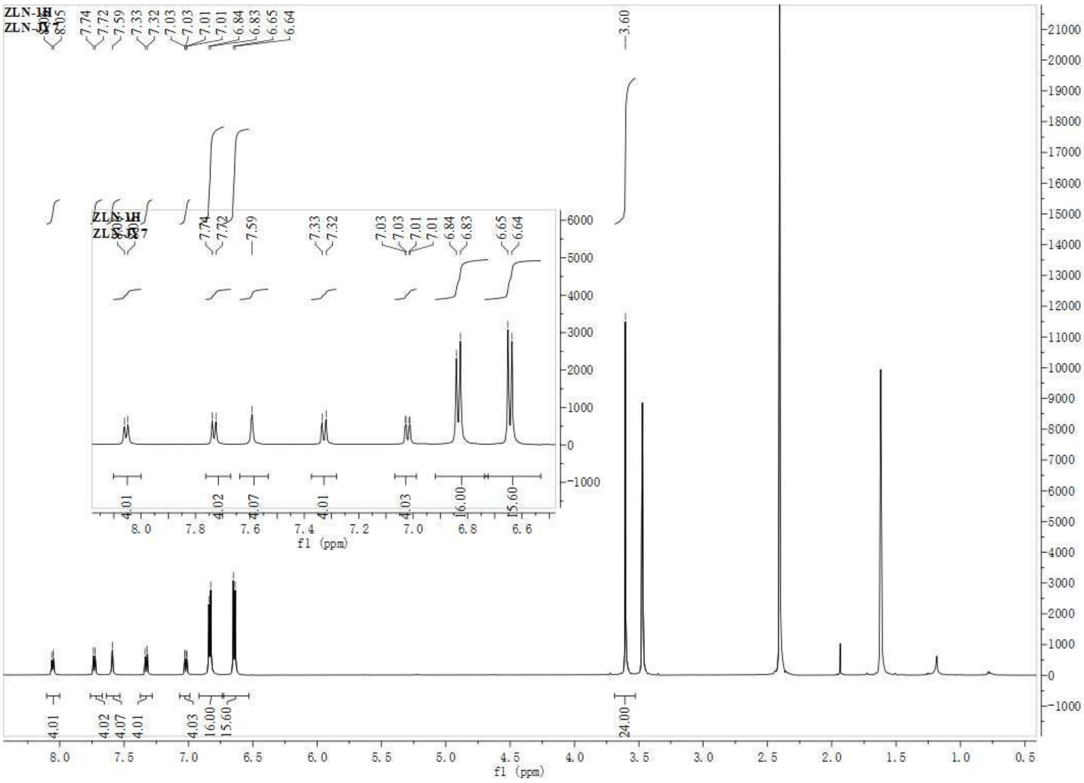


Figure S3. ^{1}H NMR spectrum of **JY7** in d_8-THF.

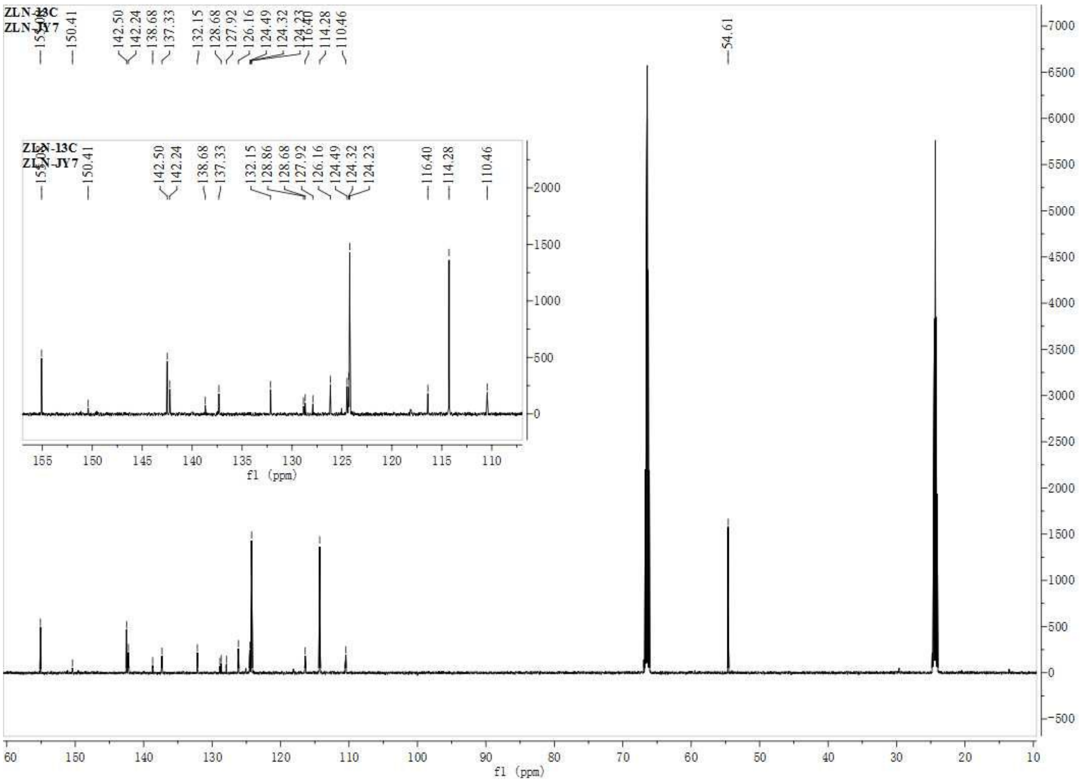
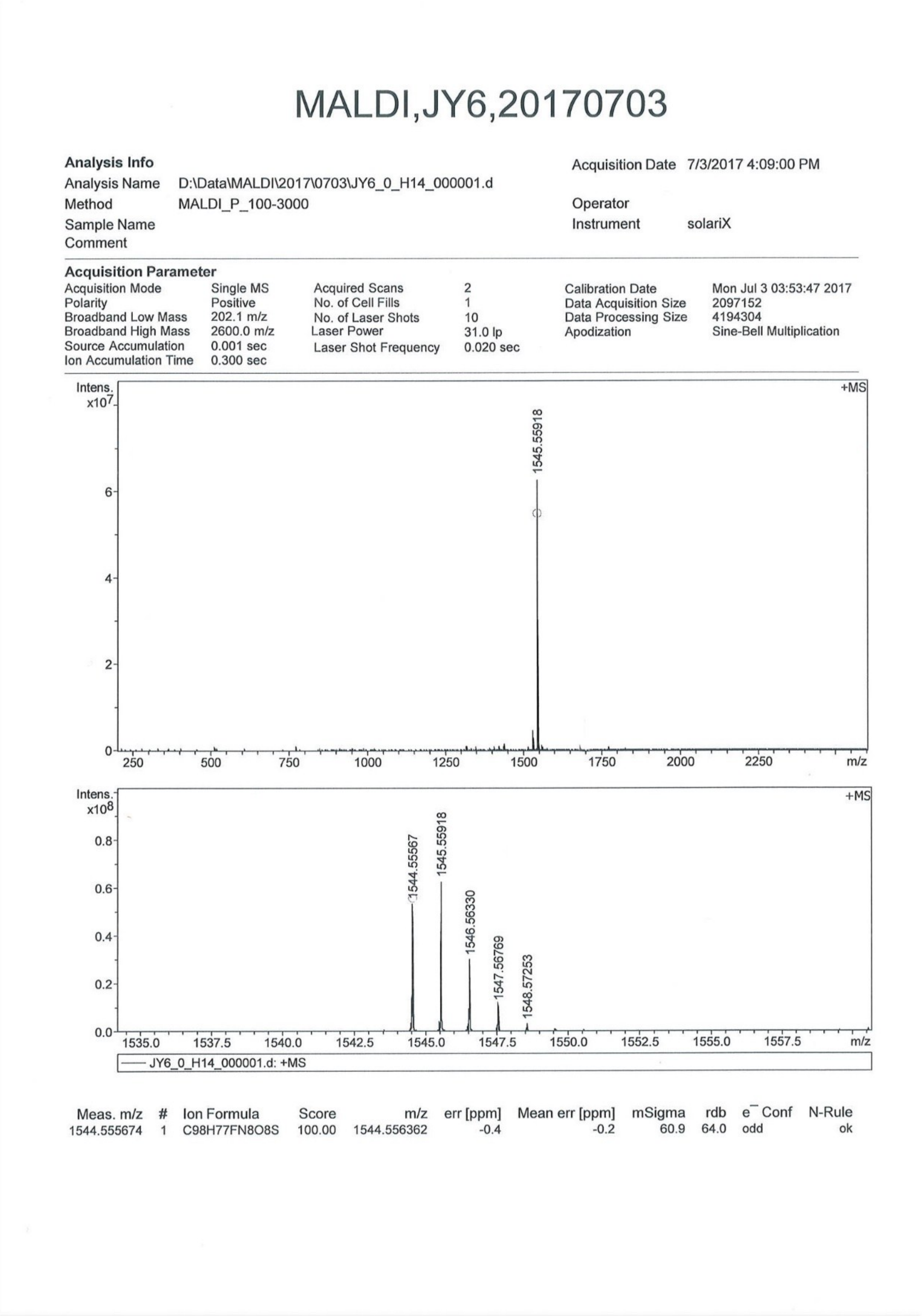


Figure S4. ^{13}C NMR spectrum of **JY7** in d_8-THF.



MALDI,JY6,20170703

Analysis Info

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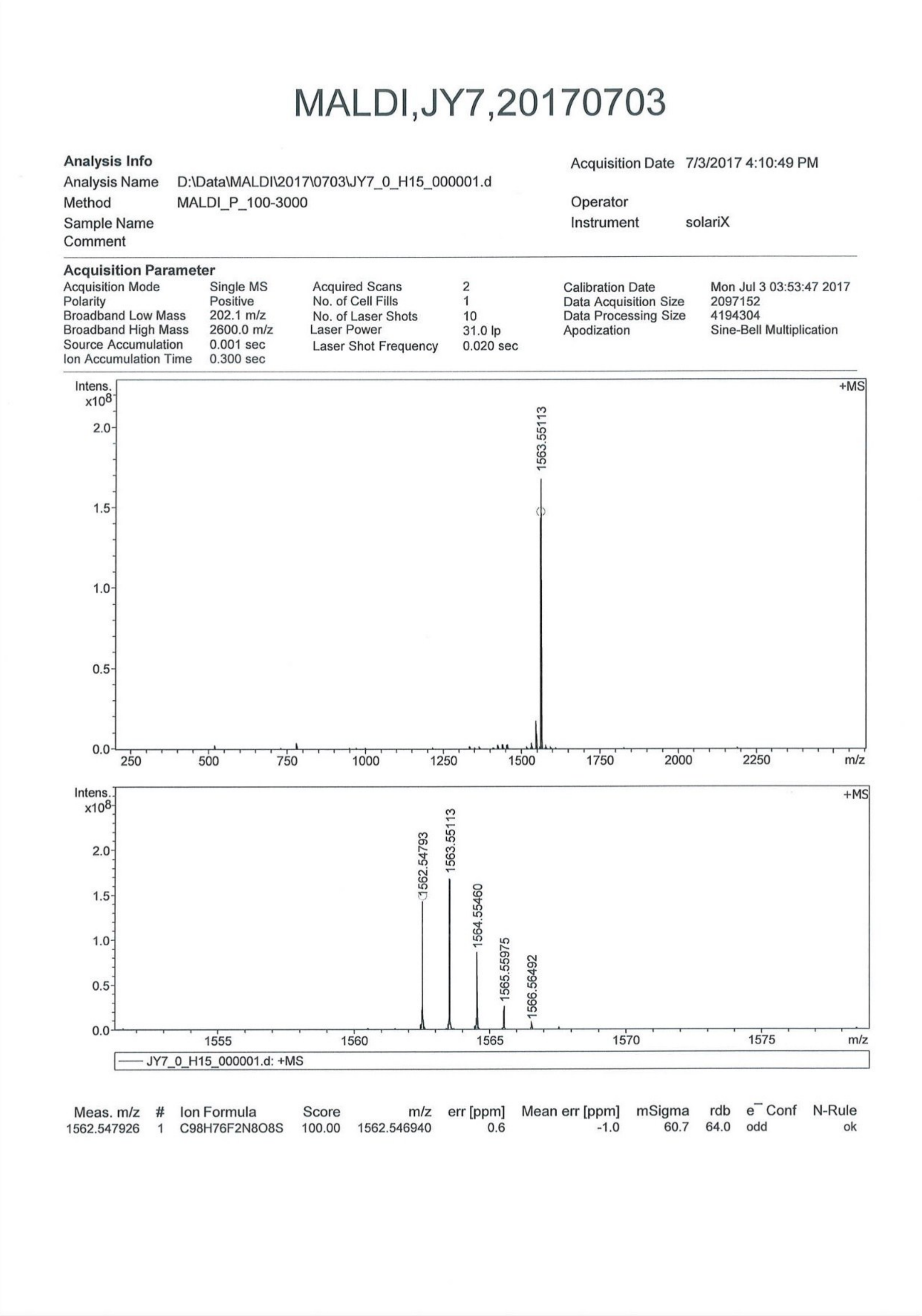
Method	MALDI_P_100-3000	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Mon Jul 3 03:53:47 2017
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	2600.0 m/z	Laser Power	31.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1544.555674	1	C98H77FN8O8S	100.00	1544.556362	-0.4	-0.2	60.9	64.0	odd	ok

Figure S5. MALDI-TOF mass spectrometry of **JY6.**



MALDI,JY7,20170703

Analysis Info

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Method	MALDI_P_100-3000	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Mon Jul 3 03:53:47 2017
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	2600.0 m/z	Laser Power	31.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1562.547926	1	$C_{98}H_{76}F_2N_8O_8S$	100.00	1562.546940	0.6	-1.0	60.7	64.0	odd	ok

Figure S6. High resolution mass spectrometry of **JY7.**

3. CV curves for JY6 and JY7

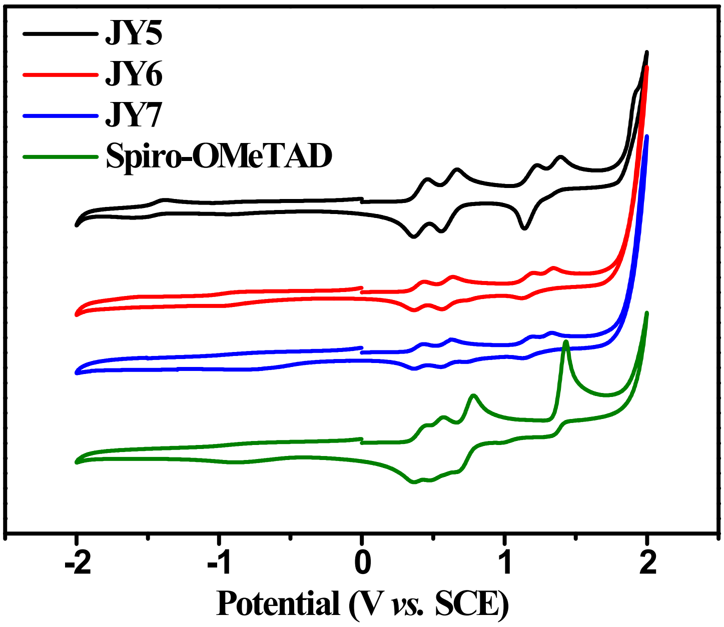
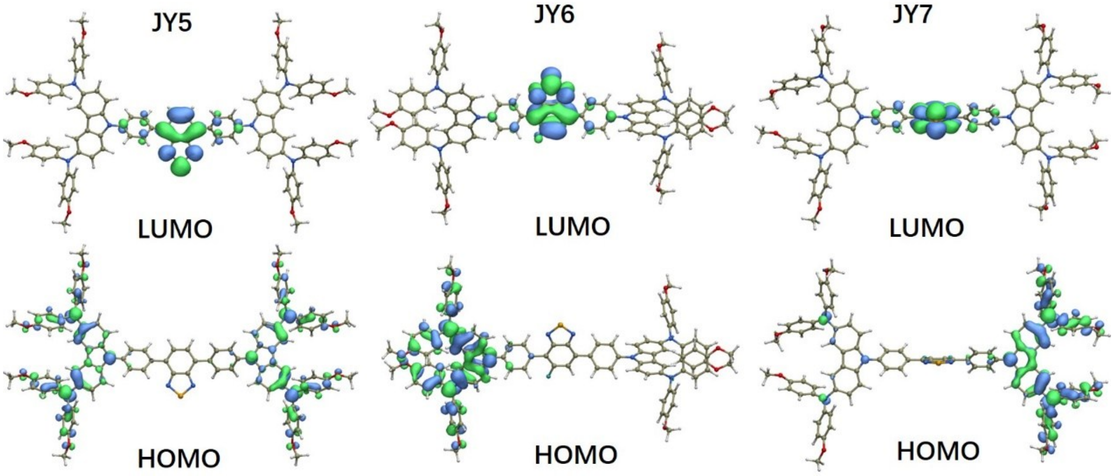


Figure S7. CV curves for JY6 and JY7, JY5 is for comparison and Spiro-OMeTAD as reference.



Scheme S2. Geometry-optimized structures and the frontier molecular orbital distributions of JY5, JY6 and JY7 based on DFT calculations.

Table S1. Photophysical and electronic properties of the new HTMs.

HTM	λ_{abs}/nm	^{exp}HOMO/LUMO /eV[a]	^{cal}HOMO/LUMO /eV[b]	E_g/eV[c]	Hole mobility (10^{-4}cm^{2}V^{-1}s^{-1})[d]
JY5	285,310	-5.21/-2.93	-4.23/-2.47	2.28	3.53
JY6	285,310	-5.21/-2.87	--4.21/-2.55	2.34	8.84
JY7	285,310	-5.23/-2.92	-4.28/-2.62	2.31	4.28

[a]E_{HOMO} was obtained from the first oxidation curve from CV; E_{LUMO} was obtained by $E_{LUMO}=E_{HOMO}+E_g$; [b]E_{HOMO} and E_{LUMO} determined from theoretical calculations; [c]E_g was calculated from the onset of the absorption spectra; [d]Hole mobility was measured by the SCLC method, and the HTMs are all doped. *exp* refers to the experimental results, and *cal* refers to results from theoretical calculations.

4. Thermal properties

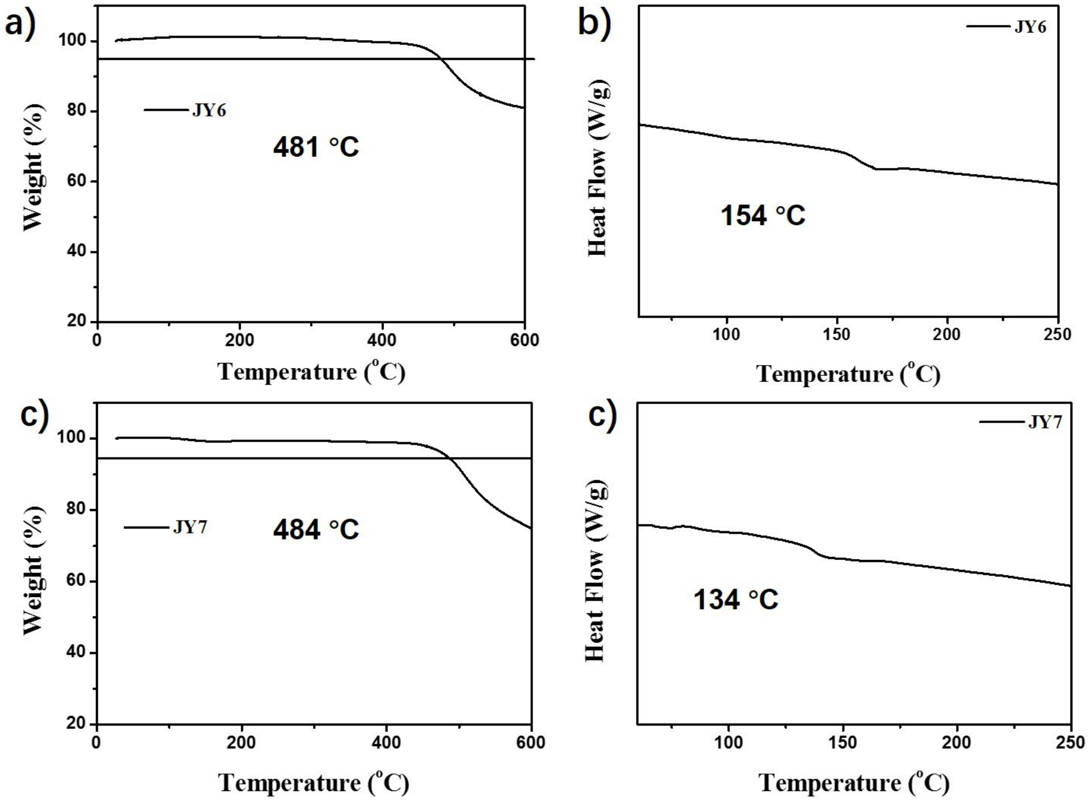


Figure S8. a,c) Thermogravimetric analysis (TGA) and b,d) Differential scanning calorimetry (DSC) of JY6 and JY7 under N_2 atmosphere.

5. The Space-charge-limited current (SCLC) hole mobility measurements[2]

Hole mobility tests were conducted using a diode configuration of ITO/PEDOT:PSS/HTM/MoO_3/Ag by taking current-voltage current in the range of 0-6 V and fitting the results to a space charge limited form, based on the following equation $J = 9\varepsilon_{\theta}\varepsilon_{\gamma}\mu_{h}V^2/8L^3$. J is the current density, L is the film thickness of the active layer, μ_h is the hole mobility, ε_γ is the relative dielectric constant of the transport medium, ε_θ is the permittivity of free space ($8.85*10^{-12}$ F m^{-1}), V is the internal voltage of the device. The thickness (measured by step profiler) of doped JY5, doped JY6, doped JY7 layers were 127, 103 and 132 nm, respectively.

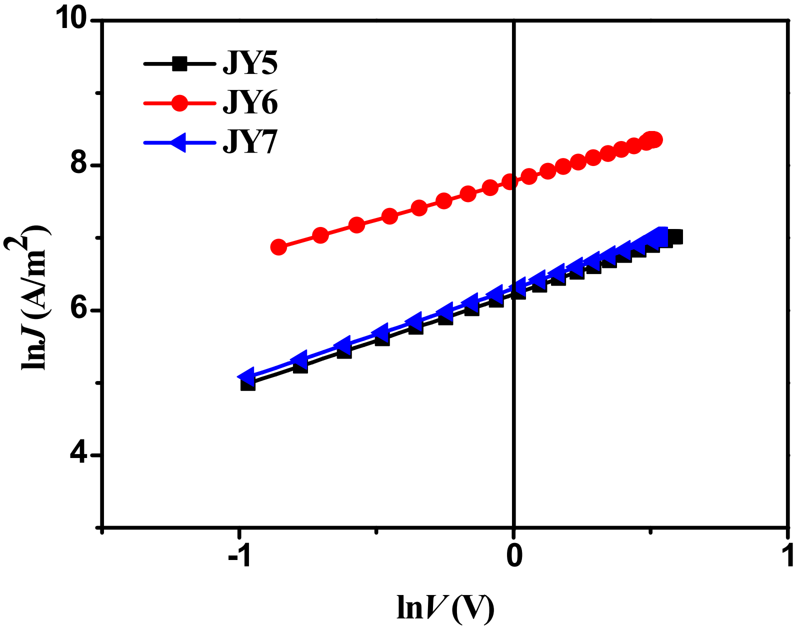


Figure S9. The hole mobility measurement of HTMs from the space charge limitation of current (SCLC) *J–V* characteristics obtained in the dark for hole-only devices.

6. Device fabrication and testing

Preparation of HTM Solutions

As for the reference, the **s**piro-OMeTAD solution (72.5 mg sprio-OMeTAD, 28.5 μL *4-tert-butylpyridine (tBP)* and 17.5 μL lithium-bis(trifluoromethanesulfonyl)imide (Li-TSFI) stock solution (520 mg mL^{-1} in acetonitrile) in 1 mL chlorobenzene) was prepared according to literature[3]. Different HTMs (**JY5**, **JY6** and **JY7**) were all dissolved in CB in a concentration of 50 mg mL^{-1}. In order to improve the conductivity of the HTMs, 19.6 μL *t*BP and 12.0 μL Li-TSFI stock solution were added in 1 mL of HTMs solution.

Device fabrication

FTO-coated glass with sheet resistance of 14 Ω sq^{-1} was washed by sonication with deionized water, ethanol and acetone and then treated with oxygen plasma for two minutes. All the devices were fabricated based on conventional structure (FTO/compact TiO_2/Perovskite/HTM/Ag electrode) and in conventional methods. A compact layer of TiO_2 was deposited on the FTO substrate by spin-coating the titanium precursor (350 μL titanium isopropoxide and 25 μL HCl in 5 mL isopropanol) at 5000 rpm for 60 s following by calcination on a hotplate at 500 ^{o}C for 60 min (275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, and 500 °C for 60 min). Subsequently, mixed-lead-halide perovskite precursor (The mole ratio of PbI_2:$PbCl_2$:MAI is 1:1:4, 202.8 mg PbI_2, 122.7 mg $PbCl_2$ and 279.8 mg MAI in 1 mL DMF) was spin-coated on the substrate in sequence at 2000 rpm for 60 s, followed by annealing at 95 ºC for 40 min in a nitrogen-filled glovebox. Then, the HTM solution was spin-coated on the perovskite layer at 5000 rpm for 60 s. After oxidizing the HTM layer in air for 15 h, the device was pumped to lower than 10^{-5} torr and an approximately 100 nm thick Ag counter electrode was deposited on top.

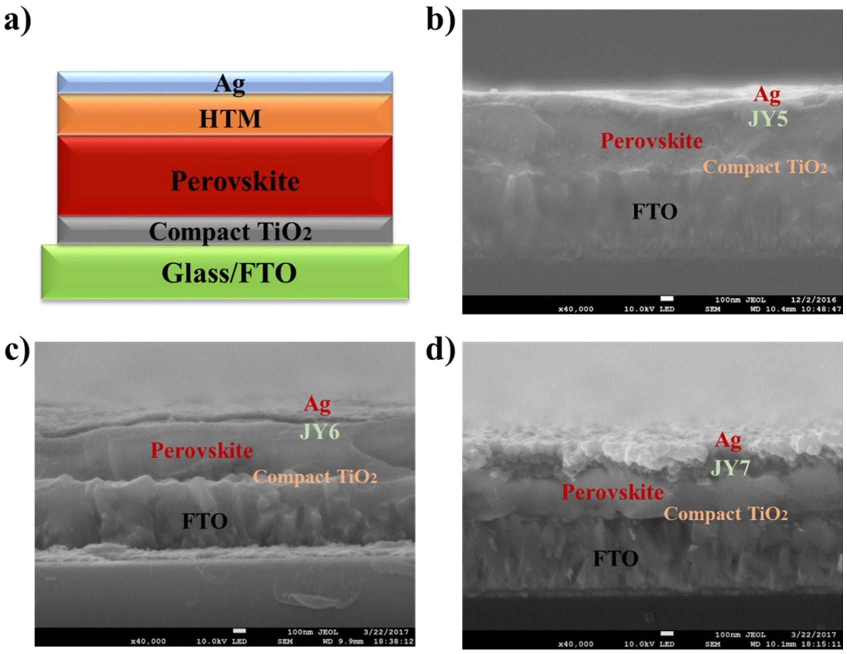


Figure S10. a) Device architecture, and b-d) Cross-section SEM images of the devices with **JY5, JY6 and JY7** as HTMs, respectively.

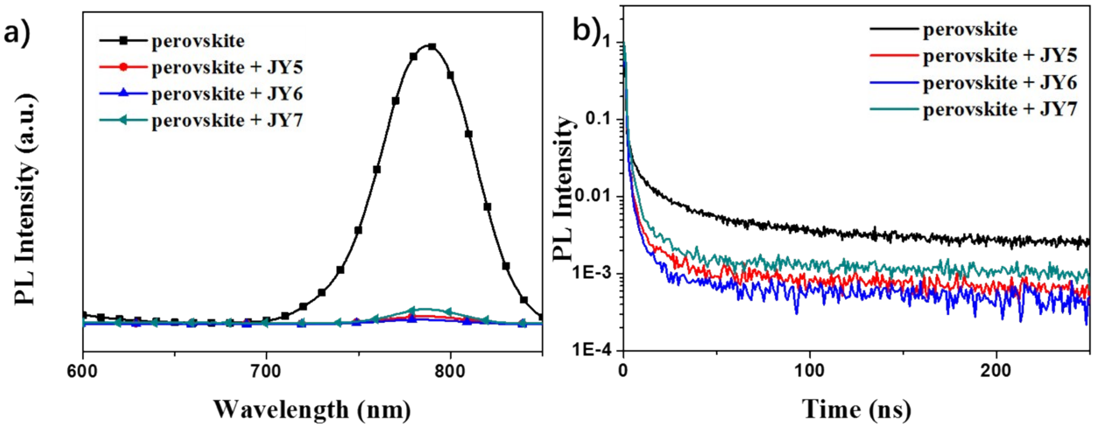


Figure S11. a) Steady state PL spectra and b) time-resolved PL decay curves of perovskite solar cells with different HTMs on top.

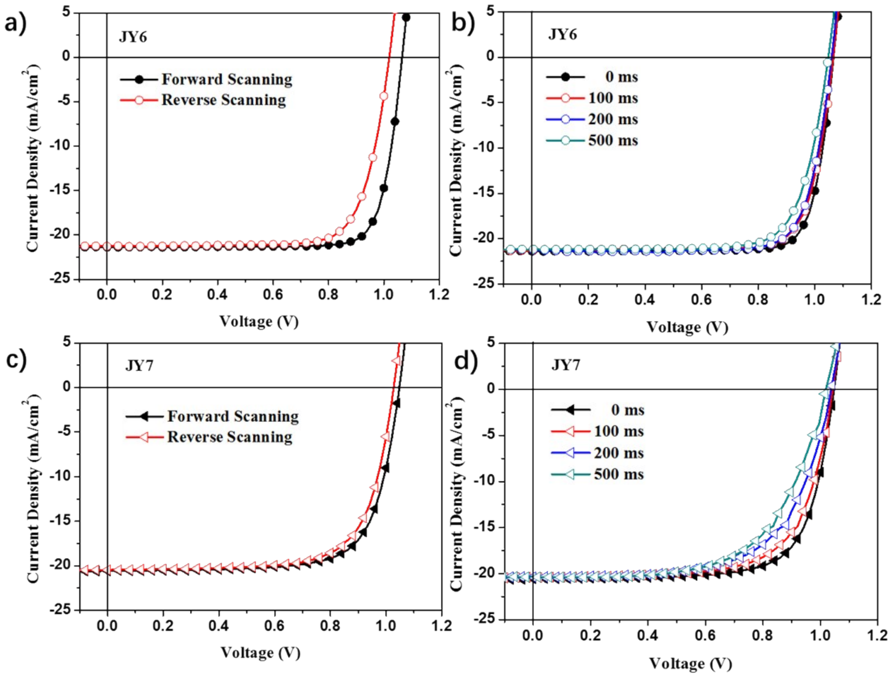


Figure S12. a,c) *J-V* curves measured from forward scanning and reverse scanning; b,d) *J-V* curves measured at different scanning time: 0, 100, 200 and 500 ms.

Table S2. Parameters for hysteresis measurement of JY6.

JY6	**V_{oc} (mV)**	**J_{sc}(mA/cm^2)**	***FF***	**PCE (%)**
Forward	1066	21.39	81 %	18.54
Reverse	1020	21.28	76 %	16.47
100 ms	1065	21.31	78 %	17.79
200 ms	1059	21.25	78 %	17.72
500 ms	1047	21.18	76 %	16.81

Table S3. Parameters for hysteresis measurement of JY7.

F33	**V_{oc} (mV)**	**J_{sc}(mA/cm^2)**	***FF***	**PCE (%)**
Forward	1047	20.58	73 %	15.71
Reverse	1027	20.45	71 %	14.95
100 ms	1043	20.44	69 %	14.64
200 ms	1037	20.37	64 %	13.48
500 ms	1019	20.34	62 %	12.81

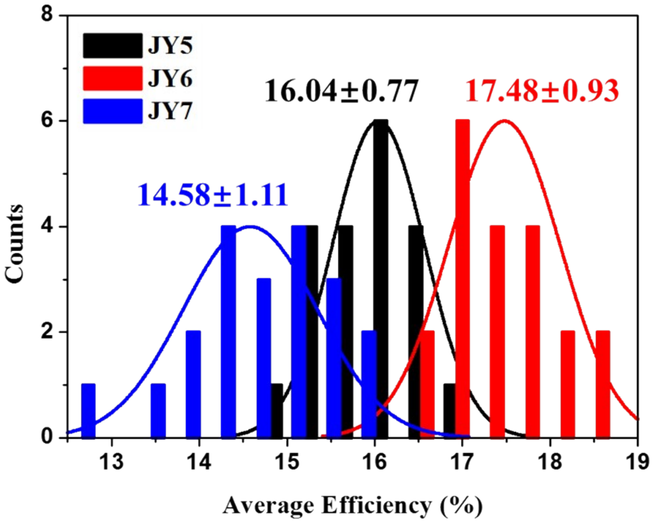


Figure S13. Histograms of PCE statistics by using **JY6**, **JY7** as HTMs, respectively. **JY5** was for comparison.

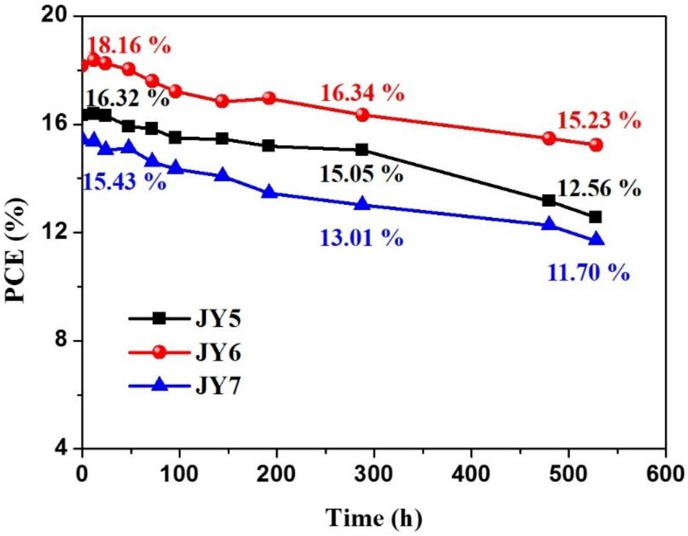


Figure S14. Stability of PSCs containing JY6 and JY7 as HTMs (PCEs measured in a glove box without encapsulation).

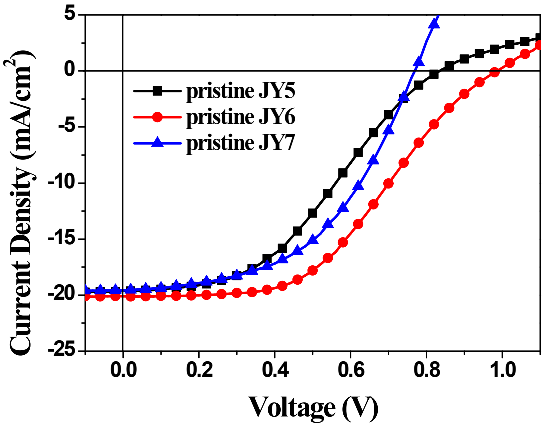


Figure S15. *J-V* curves measured using dopant-free JY5, JY6 and JY7-based PSCs.

Table S4. Photovoltaic parameters of pristine JY5, JY6 and JY7-based perovskite solar cells.

Undoped HTMs	**V_{oc} (mV)**	**J_{sc}(mA/cm^2)**	***FF***	**PCE (%)**
JY5	835	19.64	41 %	6.65
JY6	987	20.11	46 %	9.06
JY7	769	19.58	50 %	7.56

Reference

[1] S. Hirata, Y. Sakai, K. Masui, H. Tanaka, S. Y. Lee, H. Nomura, N. Nakamura, M. Yasumatsu, H. Nakanotani, Q. Zhang, K. Shizu, H. Miyazaki and C. Adachi, *Nature Materials*, 2015, **14**, 330.

[2] S. S. Reddy, K. Gunasekar, J. H. Heo, S. H. Im, C. S. Kim, D.-H. Kim, J. H. Moon, J. Y. Lee, M. Song and S.-H. Jin, *Adv. Mater*. 2016, **28**, 686.

[3] Y.-K. Wang, Z.-C. Yuan, G.-Z. Shi, Y.-X. Li, Q. Li, F. Hui, B.-Q. Sun, Z.-Q. Jiang and L.-S. Liao, *Advanced Functional Materials*, 2016, **26**, 1375.