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Electronic Supplementary Information (ESI)

Novel one-step synthesized and dopant-free hole transport material for efficient and stable perovskite solar cells

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+ X.M.Z. and F.Z. have the equivalent contribution

Experimental Section

Materials: All chemicals were obtained from Sigma Aldrich, Angene Chemical, Acros or Aladdin and were used without any further treatment. CH_3NH_3I was synthesized following our previous report. [1]

Synthesis and characterization of ST1: Synthetic route is shown in **Figure 1.**

4-(4-(bis(4-(4-(dibutylamino)styryl)phenyl)amino)styryl)-N,N-dibutylaniline (ST1): ST1 was synthesized by a one-step Heck reaction: To a Schlenk tube equipped with a Teflon valve was added tris(4-bromophenyl)amine (0.481 g, 1 mmol), 4-N,N-dibutylaminostyrene (0.836 g, 3.6 mmol), $Pd(OAc)_2$ (20 mg, 0.089 mmol), tri-otolylphosphine (65.1 mg, 0.217 mmol), Et_3N (5 mL, 36 mmol) and anhydrous DMF (8 mL). Nitrogen was bubbled through the solution for 15 minutes. The tube was sealed and heated at 100 °C for 72h. The reaction mixture was then poured into 300 mL water and extracted using 500 mL ethylacetate. The crude product was purified by column chromatography (silica gel, hexane: ethylacetate = 1:30) to give pure product ST1 (0.802 g, yield 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 12H), 7.15 (m, 6H), 7.00 (d, *J* = 19.0 Hz, 6H), 6.67 (m, 6H), 3.33 (t, *J* = 7.7 Hz, 12H), 1.64 (dd, *J* = 15.2, 7.7 Hz, 12H), 1.41 (m, 12H), 1.01 (t, *J* = 7.3 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.73, 127.62, 127.25, 126.81, 124.47, 111.69, 77.36, 77.24, 77.04, 76.72, 76.72, 50.83, 29.53, 20.38, 14.04. Measured mass (933.2104), calculated mass for $C_{66}H_{84}N_4$ (933.43).

Instruments and measurements: Nuclear magnetic resonance (NMR) spectra were recorded on a INOVA 500 MHz spectrometer. Mass spectra were recorded on a FINNIGAN LCQ Advantage mass spectrometer. UV-vis spectra were collected on a Thermo Evolution 300 UV-visible spectrometer in the 10^{-5} mol L^{-1} THF solution. Decomposition temperature (T_d) and glass transition temperature (T_g) of the synthesized compounds were determined by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a TA Q500 thermo gravimetric analyzer and TA Q20 thermal analyzer. Cyclic Voltammetry (CV) was carried out on an IM6e electrochemistry workstation in the 10^{-3} mol L^{-1} THF solution with 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, Pt electrode as working electrode and counter electrode, saturated calomel electrode as reference electrode, with a scanning rate of 30 mV s^{-1} at room temperature. Surface morphology of the $TiO_2/CH_3NH_3PbI_3$/HTM/Au film was obtained by using a XL30S-FEG, FEI scanning electron microscope (SEM).

Mobility measurements: The time-of-flight (TOF) measurements were conducted on TOF401 (Sumitomo Heavy Ltd., Japan). Hole-only devices were prepared using a structure of ITO/HTM (~1 µm) /Al (120 nm) with an active area of 3 mm × 10 mm. Indium-tin-oxide (ITO) coated substrates were cleaned with following sequence: in acetone, methanol, and diluted water, then annealed at 120 °C for 20 min followed by O_2 plasma treatment. The chlorobenzene solutions of ST1 (25 mg mL^{-1}) were spin-coated on a cleaned ITO-coated glass substrate several times at a spinning rate of 2000 rpm to achieve the hole transport layers with the thickness of ~1µm, and then the films were baked at 50 ℃ for 25 min in nitrogen atmosphere to evaporate any residual solvent. Then, a 120 nm Al were evaporated as the cathode. **Figure S2** displays typical room-temperature TOF transient of holes for ST1 under an applied field of $\sim 2.5\times10^5$ V cm^{-1}. The transit time (t_T) was obtained from the intersection point of two asymptotes in the double-logarithmic representations (insets of **Figure S2**).

Device fabrication: To fabricate the devices, the conductive fluorine-doped tin oxide (FTO) substrates were cleaned with following sequence: in deionized water, acetone and isopropanol. A compact titanium dioxide (TiO_2) layer of about 50 nm was deposited by spray pyrolysis of 10 ml 2-propanol solution containing 0.6 g titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) and 0.4 g acetylacetone at 450 ℃ in air. The preparation of TiO_2 organic solution following our previous literature.[1] A 200 nm mesoporous TiO_2 was coated on the substrate by spin coating with a speed of 5000 rpm for 20 s with a ramp of 2000 rpm, from a diluted 30 nm particle paste (Dyesol) in Ethanol, the weight ratio of TiO_2 and Ethanol is 6:1. After that, the substrates were sintered at 500°C for 30 min. The $CH_3NH_3PbI_3$ film was fabricated by anti-solvent method using a similar method as developed by our recent paper.[2] The perovskite film was deposited by spin coating onto the TiO_2 substrate. The precursor solution was prepared in a glovebox of 1.30 M PbI_2 in DMSO, where the molar ratio for PbI_2/CH_3NH_3I is 1.05:1. The spin-coating procedure was performed by 2000 rpm for 10 s followed with 6000 rpm for 30 s. Chlorobenzene (100 µl) was dropped on the spinning substrate during the second spin-coating step 15 s before the end of the procedure. The substrate was then heated at 100 °C for 90 min on a hotplate. Then, the HTMs were deposited on the top of perovskite by spin coating at 4000 rpm for 20 s. The Spiro-OMeTAD solutions were prepared dissolving the Spiro-OMeTAD in 1 ml chlorobenzene at concentration of 60 mM with the addition of 30 µl t-BP, 18 µl of 520 mg ml^{-1} LiTSFI acetonitrile solution. ST1 was dissolved in chlorobenzene at 25 mg mL^{-1} and devices were finalized by thermal evaporation of 80 nm gold.

Device characterization: Current-voltage characteristics of the devices were measured with a solar simulator employing a light source and a digital source meter (Keithley Model 2400). The light source was a 450 W xenon lamp (Oriel) equipped with a Schott K113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectrum of the lamp with the AM1.5G standard in the region of 350-750 nm. The setting time was 0.01 s and the delay time was 0 s. IPCE spectra were recorded by focusing light from the 300W Xenon lamp (ILC Technology, USA) through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK). The monochromatic light WAS chopped at 3 Hz before impinging onto the photovoltaic cell. The monochromator was incremented through the visible spectrum to generate the IPCE dependence on wavelength. All measurements were conducted using a non-reflective metal aperture of 0.16 cm^2 to define the active area of the device and avoid light piping through the sides and the cover glass.

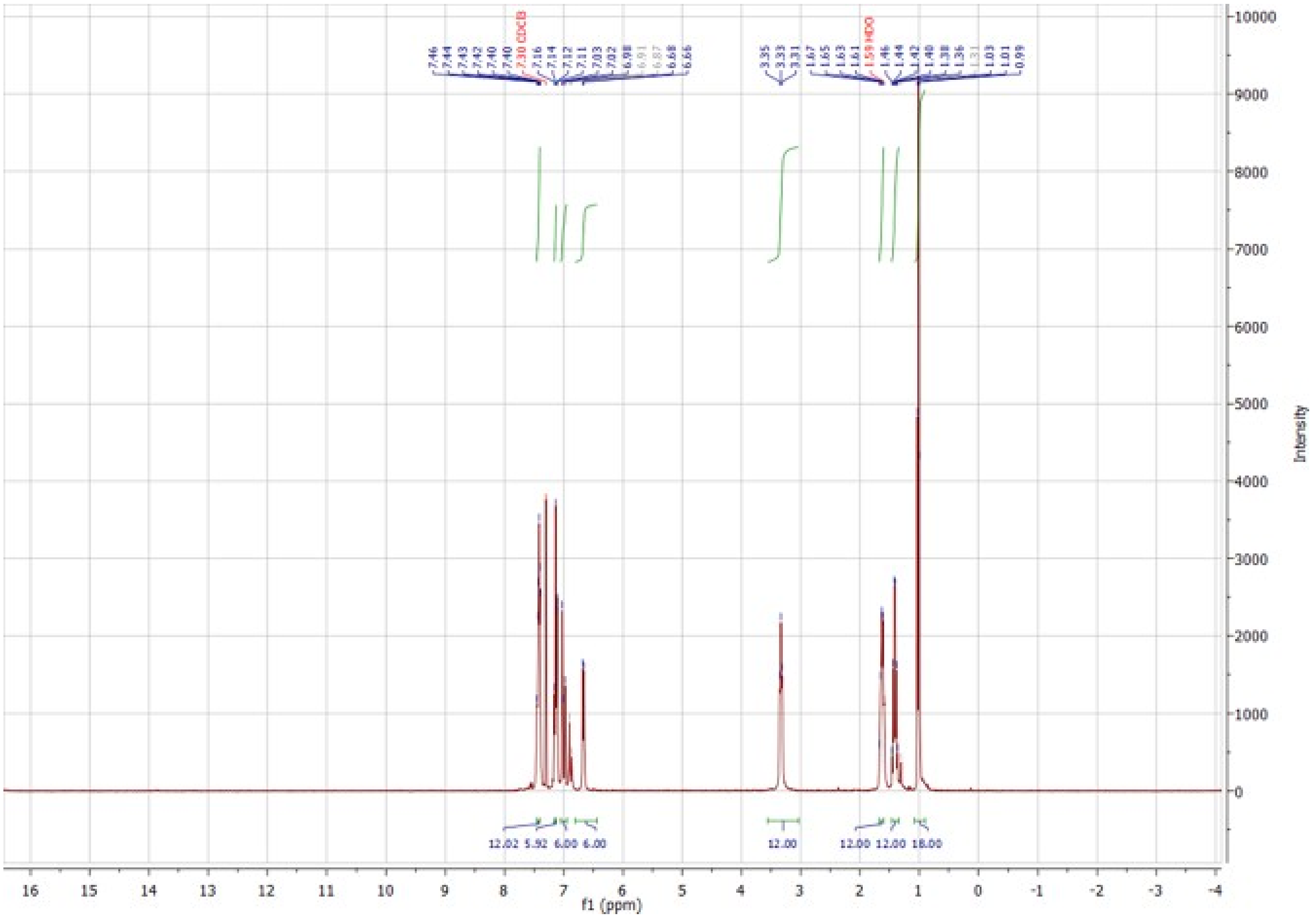


Figure S1. ^{1}H NMR spectrum of ST1

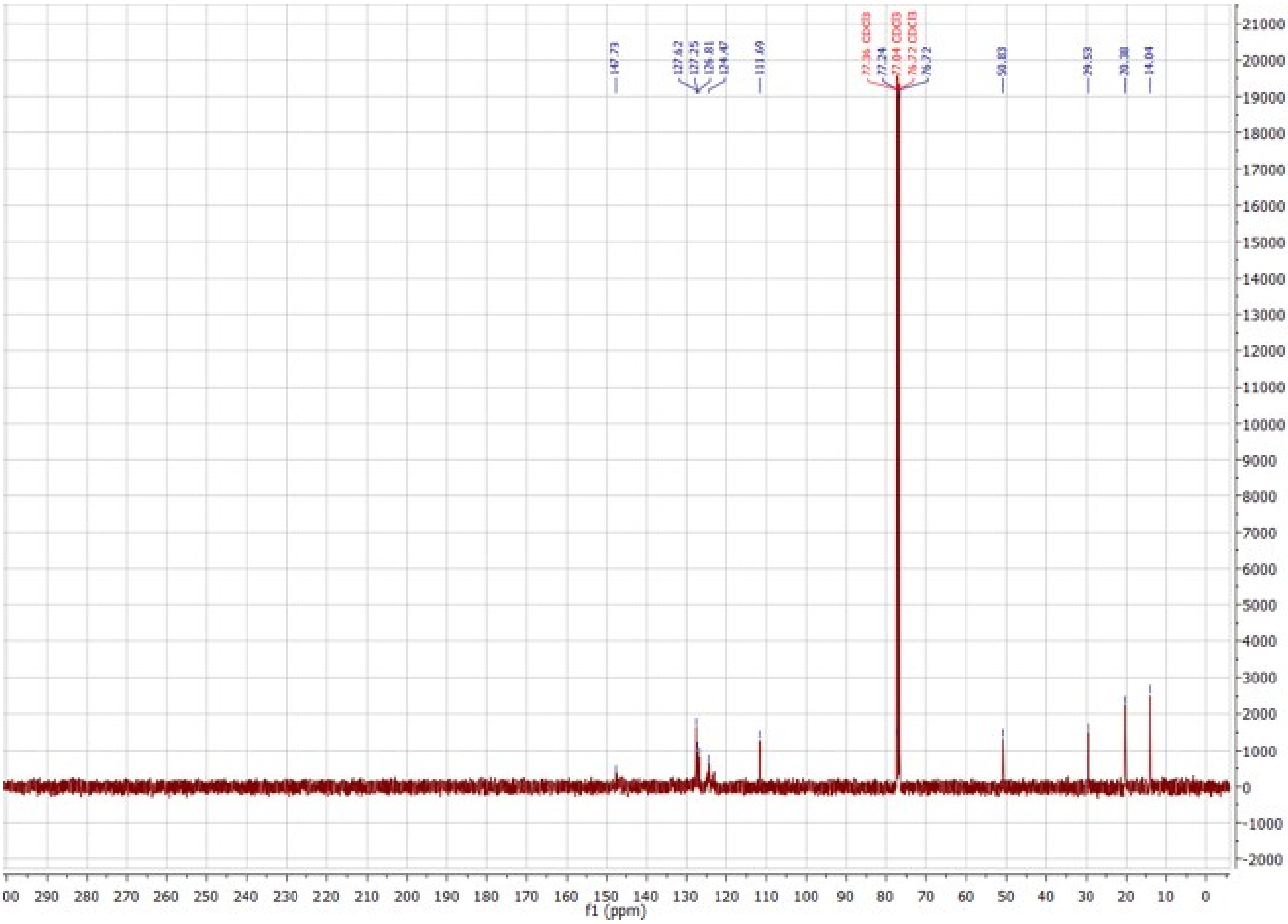


Figure S2. ^{13}C NMR spectrum of ST1

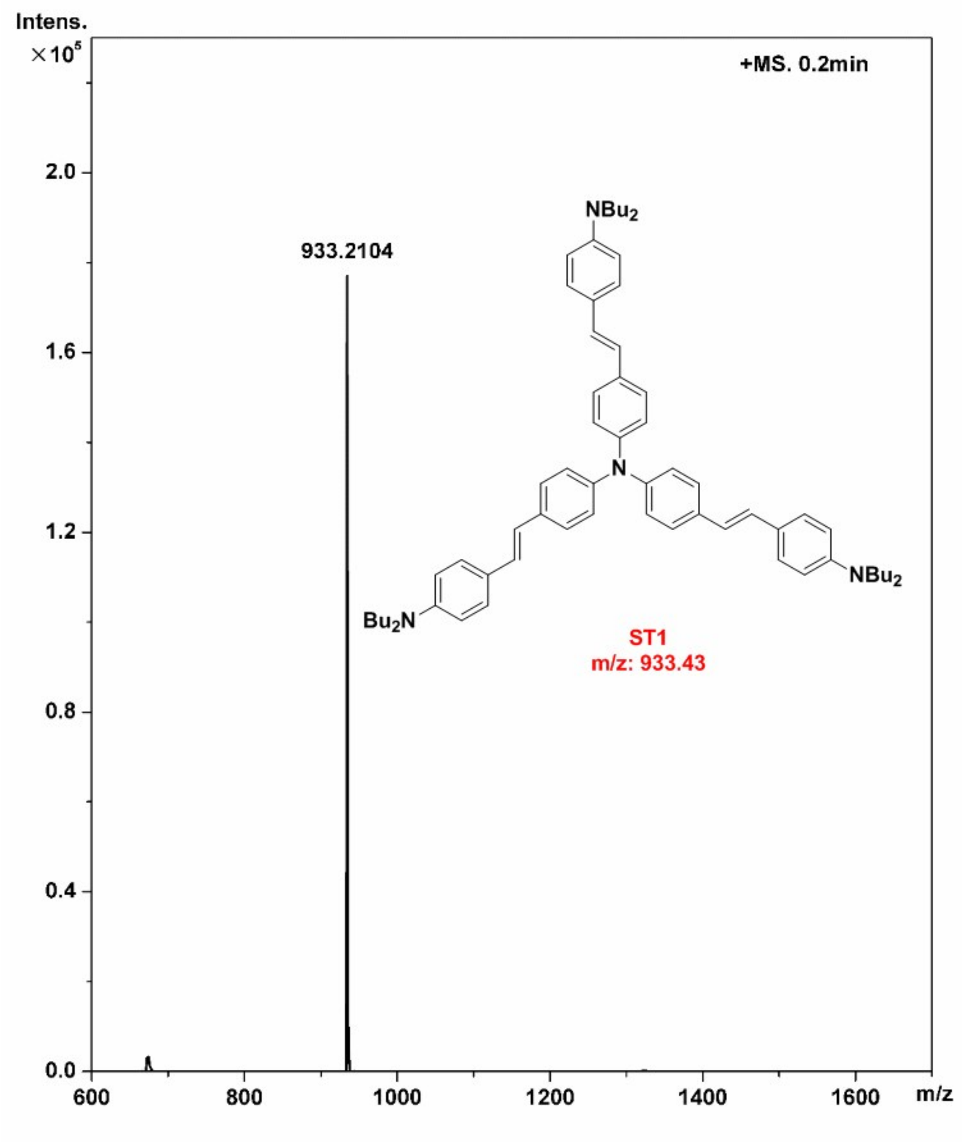


Figure S3. Mass spectrum of ST1

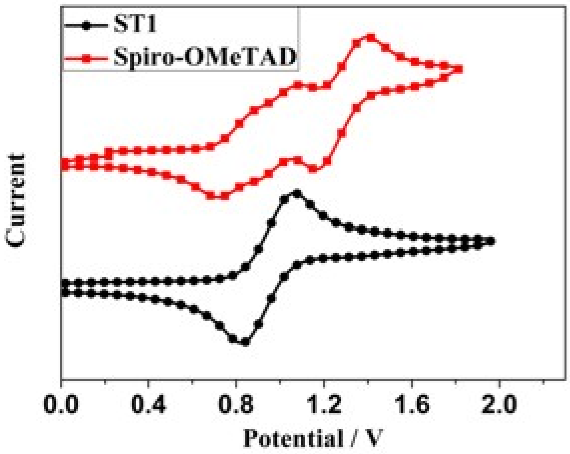


Figure S4. Cyclic voltammograms of ST1 and Spiro-OMeTAD

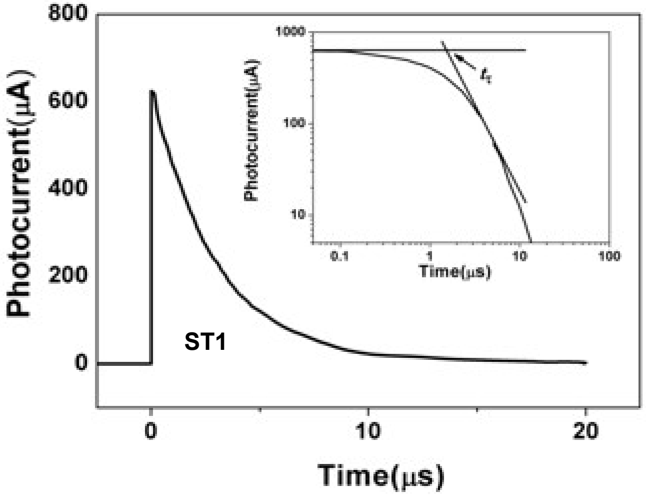


Figure S5. TOF transient for ST1 at room temperature

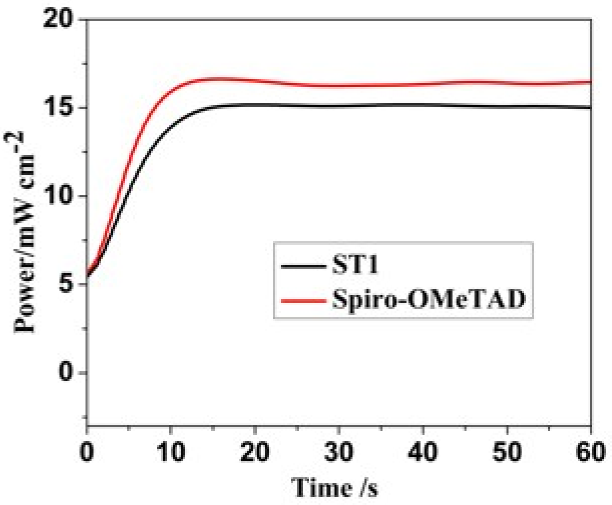


Figure S6. The stabilized power output for PSCs fabricated with ST1 and Spiro-OMeTAD

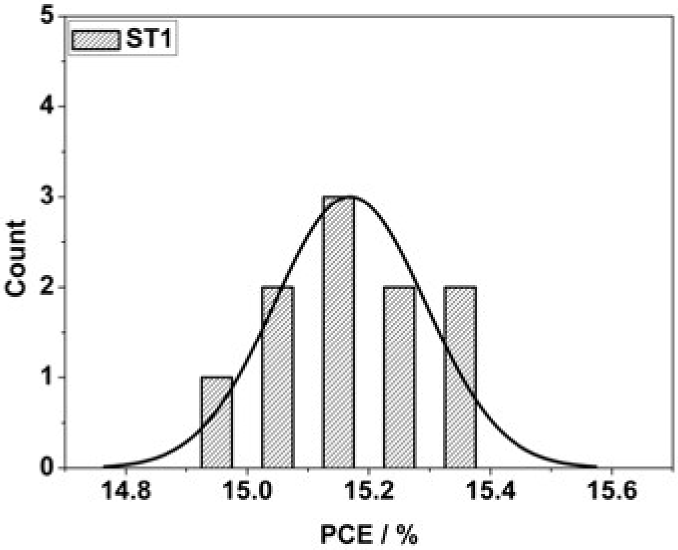


Figure S7. The reproducibility of perovskite solar cells based on dopant-free ST1

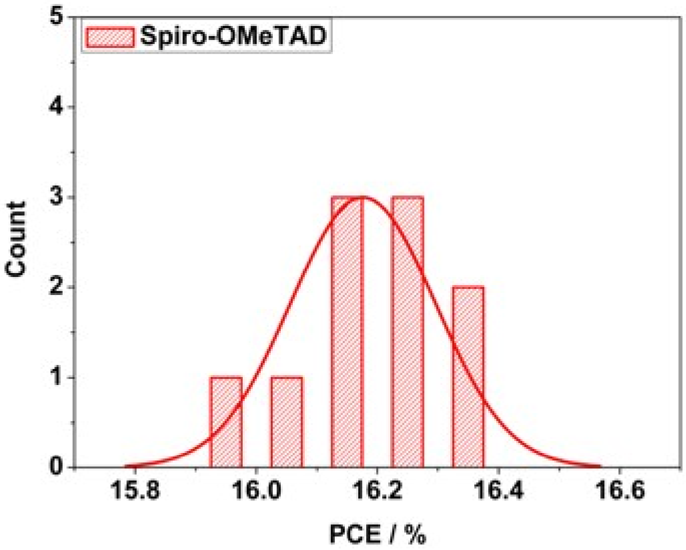
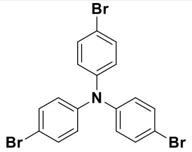
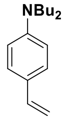


Figure S8. The reproducibility of perovskite solar cells based on doped Spiro-OMeTAD

Table S1 The quantities and prices of commercial reagents, solvents and materials for the production of 1 gram of ST1

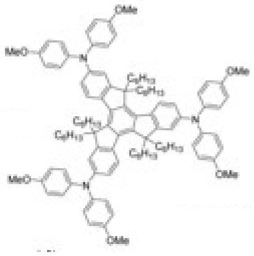
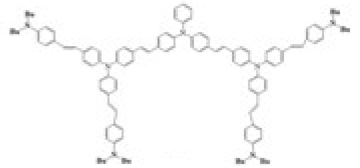
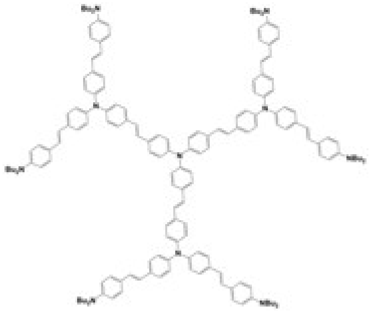
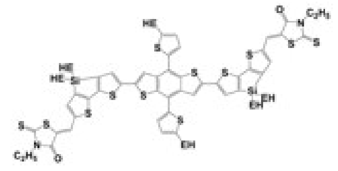
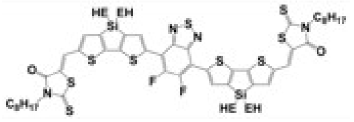
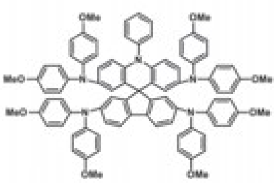
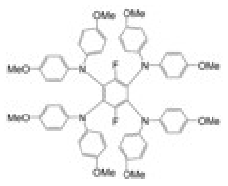
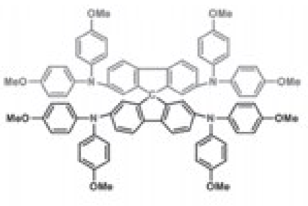
Materials	quantity	Unit-price[a)]	Total price (USD)
	0.600g	15.4 USD/1g	9.733
	1.042g	10 USD/1g	10.420
$Pd(OAc)_2$	0.025g	80.2 USD/1g	2.005
Tri-o-tolyphosphine	0.081g	22.7 USD/ 1g	1.839
DMF	6.235ml	19.5 USD/ 500ml	0.243
Et_3N	10ml	24.7 USD/ 1L	0.247
60 μm silica gel	263g	19.9 USD/ 1kg	5.234
Deionized Water	400ml	29.0 USD/ 25L	0.464
Ethyl acetate	987ml	57.1 USD/ 10L	5.636
Hexane	13ml	59.0 USD/ 1L	0.767
Total cost to obtain 1 gram of ST1			36.588

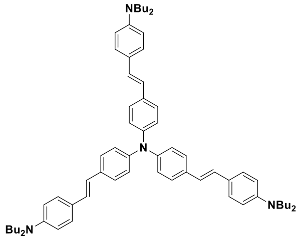
[a)] All data about prices in this table are respectively from Sigma-Aldrich, Aladdin and Angene Chemical website on July 31, 2016.

Table S2 Photovoltaic parameters of perovskite solar cells at room temperature in ambient air under dark of 30 % relative humidity (fresh and after 4 weeks)

sample	J_{sc}(mA cm^{-2})	V_{oc}(V)	FF	PCE(%)
Fresh ST1	21.07	1.059	0.66	15.4
ST1 after 2 weeks	20.77	1.042	0.64	14.9
ST1 after 4 weeks	20.25	1.036	0.60	13.2
Fresh Spiro-OMeTAD	21.41	1.034	0.71	16.3
Spiro-OMeTAD after 2 weeks	20.10	1.017	0.65	13.8
Spiro-OMeTAD after 4 weeks	18.98	1.002	0.52	10.3

Table S3 Synthetic steps of reported dopant-free HTMs and doped Spiro-OMeTAD and the corresponding parameters for PSCs based on them

HTMs	**Structure**	**MW**	**T_g(°C)**	**PCE(%)**	**Long-term stability**	**Synthetic steps**	**Reference**
Trux-OMeTAD		**1529.20**	**n/a**	**18.6**	**n/a**	**4**	**4**
Z1011		**1701.46**	**149.4**	**16.5**	**PCE increased by 9% after 1008h in dry air without encapsulation**	**8**	**1**
Z1013		**2428.9**	**171.8**	**15.4**	**The device showed a slight increase of the PCE after 4 weeks storing at room temperature under ambient air condition.**	**8**	**7**
DERDTS-TBDT		**1752.59**	**n/a**	**16.2**	**PCE drooped by 5% after 220 hours without encapsulation in the N_2 glove box**	**6**	**3**
DORDTS-DFBT		**1514.55**	**n/a**	**6.2**	**PCE drooped by 80% after 220 hours without encapsulation in the N_2 glove box**	**4**	**3**
SAF-OMe		**1316.57**	**126.0**	**12.4**	**PCE drooped by 39% after 240 hours in ambient condition at a relative humidity of 30% without any encapsulation.**	**3**	**5**
DFTAB		**1023.41**	**n/a**	**7.2**	**n/a**	**1**	**6**
Doped Spiro-OMeTAD		**1225.43**	**125.0**	**16.3**	**PCE drooped by 37% after 672 hours at room temperature without encapsulation in ambient air in the dark at 30 % relative humidity**	**5**	**Studied in this paper**

ST1		**933.21**	**100.3**	**15.4**	**PCE drooped by 14% after 672 hours at room temperature without encapsulation in ambient air in the dark at 30 % relative humidity**	**1**	**Reported in this paper**

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