Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information

A dopant-free hole-transporting material for efficient and stable perovskite solar cells

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General

All chemicals and reagents were used as received from chemical companies. Anhydrous solvents were degassed by Argon bubbling for 20 min before use. UV-VIS-NIR spectra were measured in CH_2Cl_2 solution or thin-film state using UV-3600 UV-VIS-NIR Spectrophotometer (SHIMADZU). Cyclic voltammetry (CV) was performed on a CH Instruments 624D potentiostat/galvanostat system. All CV measurements were carried out in anhydrous CH_2Cl_2 containing 0.1 M TBAHFP as a supporting electrolyte, purging with argon prior to conduct the experiment. Platinum electrode was used as a working electrode, $Ag/AgNO_3$ in saturated KNO_3(aq.) as a reference electrode, and a platinum wire as a counter electrode.. Differential scanning calorimetry (DSC) analyses were performed on a NETZSCH DSC 200 F3 Low-Temperature Difference Scanning Calorimeter, the sample was heated (5 °C/min) from 0 °C to 150 °C, then cooled to 0 °C for one cycle. XRD patterns were recorded by using an X-ray diffractometer (Rigaku, RINT-2500) with a CuKa radiation source. The surface morphology of were analyzed by using a JEM-6500F field-emission scanning electron microscope (SEM). Incident photon-to-current conversion efficiency spectra were measured by a CEP-200BX spectrometer (Bunko Keiki). The current-voltage (*I-V*) curves were obtained by a WXS-90S-L2 Super solar simulator (WACOM).

Preparation of corresponding materials in perovskite solar cells

Synthesis of CH_3NH_3I

To a stirred solution of methylamine in methanol (40 wt %, 20 mL) was added aqueous hydroiodic acid (57 wt%, 21.5 mL) dropwise at 0 °C during 10 min. The reaction mixture was stirred at the same temperature for 2 h. Evaporation of the solvent under reduced pressure below 50 °C. The residue was treated with diethyl ether, and the precipitate was collected by filter, washed with diethyl ether three times. The crude product CH_3NH_3I was recrystallized from a mixed solvent of diethyl ether and ethanol to afford the desired pure CH_3NH_3I as white crystals.

Purification of PbI2

The commercial PbI_2 was purified by recrystallization from water.

Cell Fabrication

Perovskite thin film and solar cells were fabricated on FTO-glass substrate with a sheet resistance of 14 Ω sq^{-1}. To make a dense TiO_2 blocking layer, the cleaned FTO glasses were coated with 1.0 M Titanium tetraisopropanolate in n-butanol solution (containing 1.0 M HCl) by spin-coating at 2000 rpm for 60 s. Drying at 125 ^{o}C for 15 min and sintering at 500 ^{o}C for 60 min. After cooling to room temperature, a ~400 nm thick mesoporous TiO_2 film was then deposited by spin coating of diluted TiO_2 paste (CCIC 18NRT : EtOH : α-terpilenol = 1 : 1.5 : 3 (w/w/w)) at 3000 rpm for 30 s, followed by drying at 125 ^{o}C for 15 min and then warm up to 500 ^{o}C by a speed of 25 ^{o}C/min, sintering at 500 ^{o}C for 60 min, and then cooling to room temperature slowly. The prepared mesoporous TiO_2 films were infiltrated with a hot solution of PbI_2 in *N*,*N*-dimethylformamide (460 mg/ 1 mL) by spin coating at 3000 r.p.m. for 30 s and dried at 70 ^{o}C for 30 min. After cooling to room temperature, dipping the resulted TiO_2/PbI_2 composite film into a solution of CH_3NH_3I in 2-propanol (10 mg/mL) for 30 min. The resulting perovskite film was washed with dry 2-propanol and N_2 flow, dried at 70 ^{o}C for 30min. The HTMs were coating via solution process by following details. Spiro-OMeTAD/chlorobenzene (180 mg/1 mL) solutions with or without additives containing 37.5 μL Li-TFSI)/acetonitrile (170 mg/1 mL) and 17.5 μl TBP were spin-coated on $CH_3NH_3PbI_3$/mp-TiO_2/bl-TiO_2/FTO substrate at 4,500 r.p.m. for 40 s, respectively. P3HT were coated on $CH_3NH_3PbI_3$/mp-TiO_2/bl-TiO_2/FTO substrate at 3,000 r.p.m. for 30 s using P3HT/chlorobenzene (15 mg/1 mL) solutions with or without 6.8 μL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (28.3 mg/1 mL) and 3.4 μLTBP as additives, respectively. TTF-1 were coated on $CH_3NH_3PbI_3$/mp-TiO_2/bl-TiO_2/FTO substrate around 50 ^{o}C using TTF-1/chlorobenzene/dichlorobenzene (15 mg/0.6 mL/0.4 mL) solutions with or without 6.8 μL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (28.3 mg/1 mL) and 3.4 μLTBP as additives, respectively. The thickness of HTM layer in the optimized device was estimated by subtracting the perovskite capping thickness from the total thickness of perovskite capping layer and HTM layer. The thickness was estimated from the average value of 4 samples for each measured by surface profiler. The thickness of HTM layers in their corresponding devices were 230 nm for TTF-1, 265 nm for P3HT and 320 nm for spiro-OMeTAD, respectively. Finally, a ~140 nm thick Ag layer was deposited by thermal evaporation under reduced pressure of 2×10^{-6} mbar.

Fig. S1 Deliquescence characterization of lithium salt Li-TFSI under a humidity around 40% at 25.2 °C for 2 min.

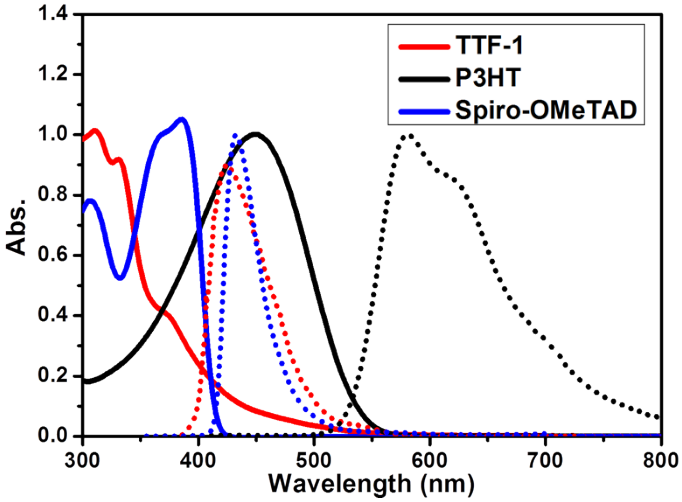


Fig. S2 Normalized UV-vis and emission spectra of **TTF-1**, **P3HT** and **spiro-OMeTAD** in CH_2Cl_2.

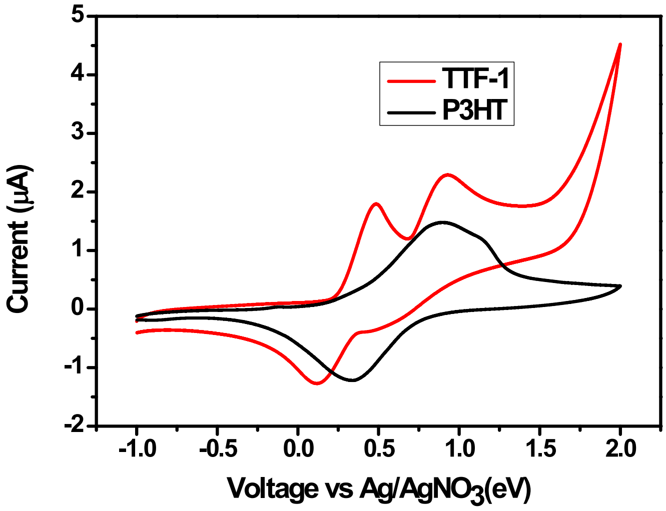
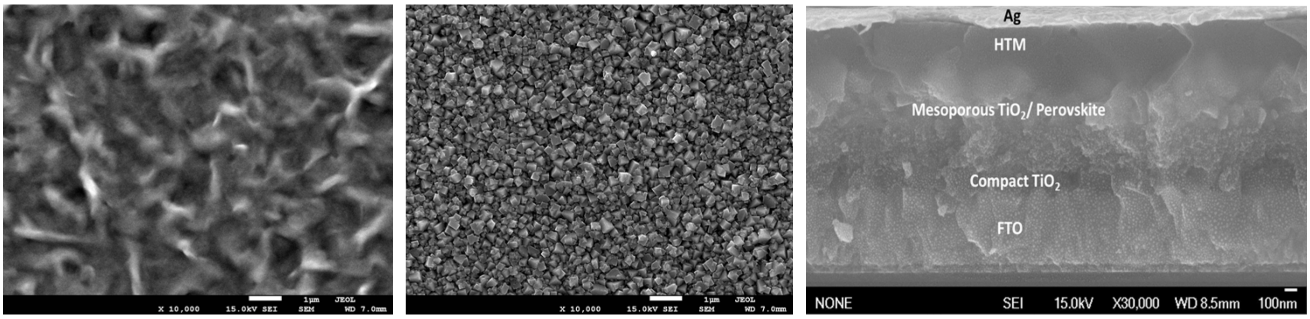


Fig. S3 Cyclic voltammograms of **TTF-1** and **P3HT** in CH_2Cl_2/TBAHFP (0.1 M), [c] = 1 × 10^{-3} mol L^{-1}, 293 K, scan rate = 100 mV s^{-1}, vs. Ag/$AgNO_3$.



(a) (b) (c)

Fig. S4 (a) SEM image of PbI_2 on the mesoporous TiO_2 surface; (b) SEM image of perovskite on the mesoporous TiO_2 surface; (c) Cross-sectional structure of a representative device.

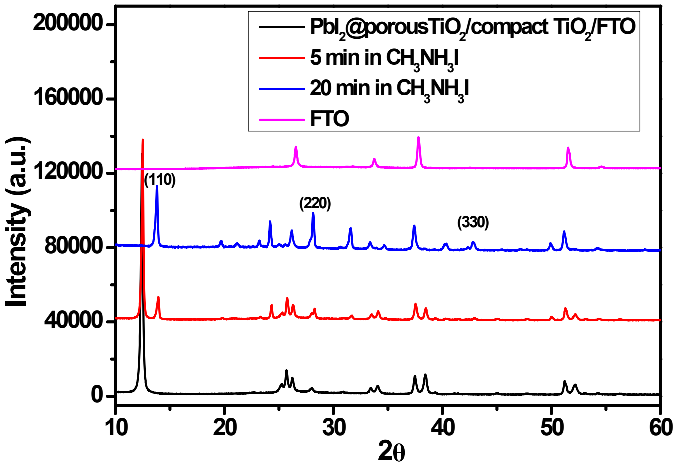
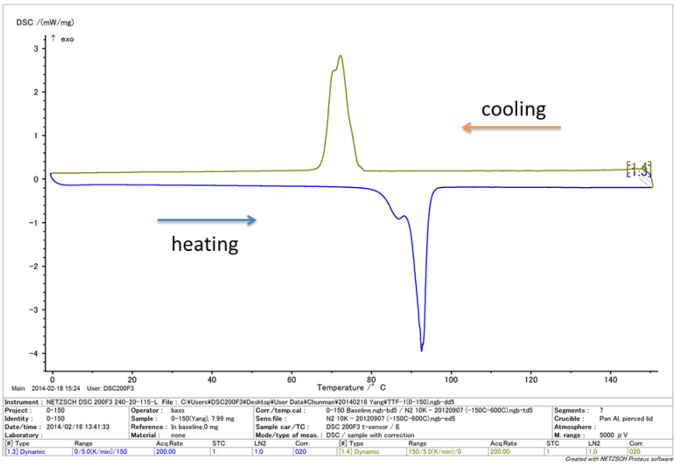


Fig. S5 X-ray diffraction spectra of PbI_2 on porous TiO_2/compact TiO_2/FTO glass before and after the transformation. The plot shows the X-ray intensity as a function of 2θ (twice the diffraction angle).



Instrument : NETZSCH DSC 200F3 240-20-115-L File : C:¥Users¥DSC200F3¥Desktop¥User Data¥Chunman¥20140218 Yang¥TTF-1(0-150).ngb-dd5

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Identity : 0-150
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Laboratory :
Operator : baxs
Sample : 0-150(Yang), 7.99 mg
Reference : In baseline,0 mg
Material : none
Corr./temp.cal : 0-150 Baseline.ngb-bd5 / N2 10K - 20120907 (-150C-600C).ngb-td5
Sens.file : N2 10K - 20120907 (-150C-600C).ngb-ed5
Sample car./TC : DSC 200F3 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 7
Crucible : Pan Al, pierced lid
Atmosphere :
M. range : 5000 μV

[#] Type	Range	Acq.Rate	STC	LN2	Corr.	[#] Type	Range	Acq.Rate	STC	LN2	Corr.
[1.3] Dynamic	0/5.0(K/min)/150	200.00	1	1.0	020	[1.4] Dynamic	150/5.0(K/min)/0	200.00	1	1.0	020

Fig. S6 Differential scanning calorimetry curve of **TTF-1** at a heating (cooling) rate of 5 °C/min during 0 °C -150 °C.

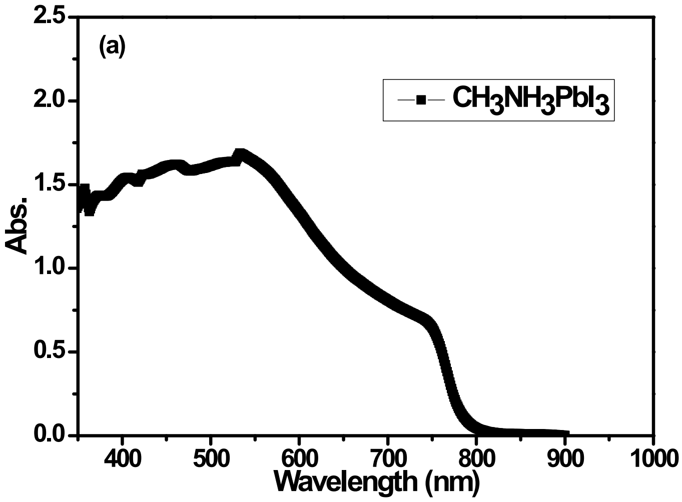


Fig. S7 Absorption spectrum of FTO/compact-TiO_2/mesoporous-TiO_2/Perovskite film for cells

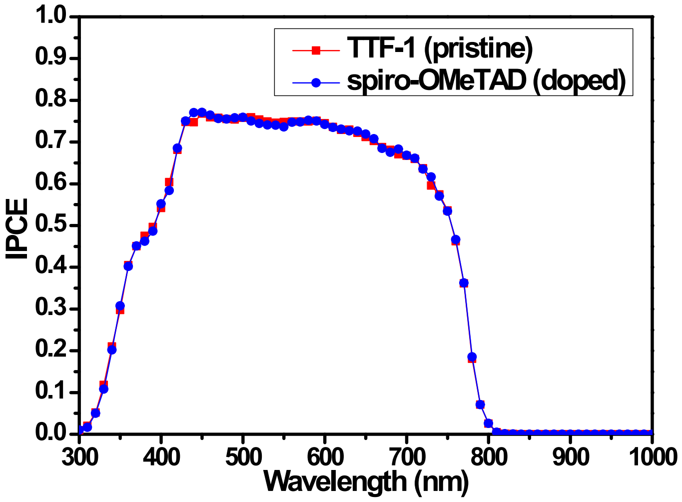


Fig. S8 IPCE spectra of typical small area perovskite solar cells (0.09 cm^2) based on dopant-free **TTF-1** (pristine) and p-type doping **spiro-OMeTAD** (doped).

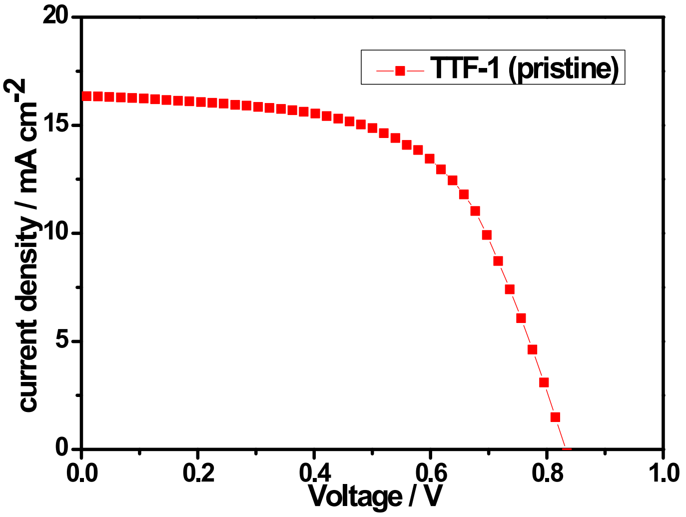


Fig. S9 Current–voltage curve of the large area perovskite solar cells (1 cm^2) based on dopant-free **TTF-1** (pristine).

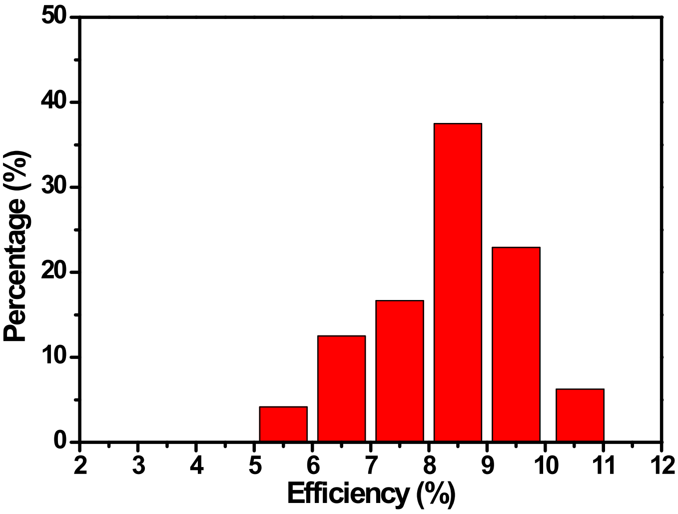
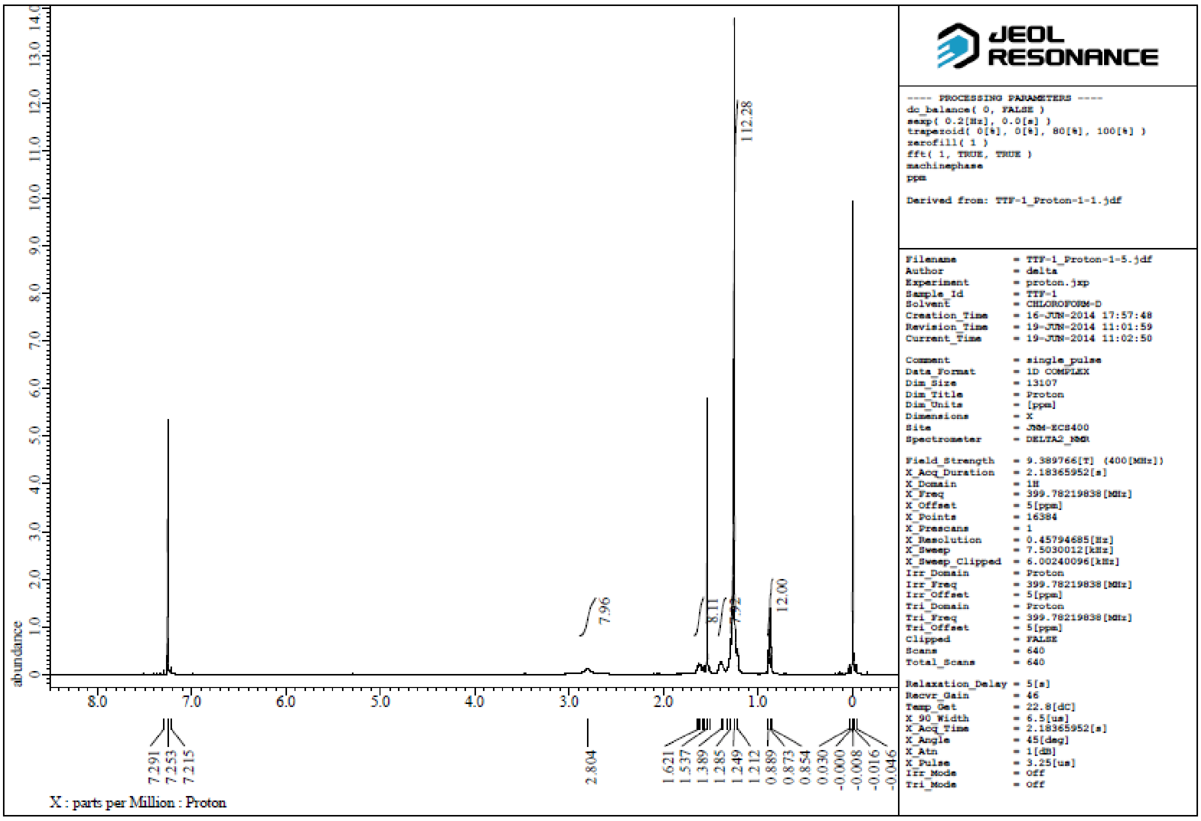


Fig. S10 Device performance statistics from perovskite solar cells based on dopant-free **TTF-1** (48 cells).



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fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TTF-1_Proton-1-1.jdf
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Experiment        = proton.jxp
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Solvent           = CHLOROFORM-D
Creation_Time     = 16-JUN-2014 17:57:48
Revision_Time     = 19-JUN-2014 11:01:59
Current_Time      = 19-JUN-2014 11:02:50

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Dimensions        = X
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Spectrometer      = DELTA2_NMR

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Fig. S11 ^{1}H NMR spectrum of **TTF-1**.