Electronic Supplementary Information

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

Jian Liu,a Yongzhen Wu,a Chuanjiang Qin,a Xudong Yang,*a Takeshi Yasuda,a Ashraful Islam,a Kun Zhang,a Wenqin Peng,a Wei Chena and Liyuan Hanab1

a Photovoltaic Materials Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan, Fax: (+)81-29-859-2301, E-mail: HAN.Liyuan@nims.go.jp; Yang.Xudong@nims.go.jp.

b State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dong Chuan RD. Minhang District, Shanghai 200240, China

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 CH2Cl2 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 CH2Cl2 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/AgNO3 in saturated KNO3(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 CuKα 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 CH3NH3I

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 CH3NH3I was recrystallized from a mixed solvent of diethyl ether and ethanol to afford the desired pure CH3NH3I 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 $\Omega$ 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 °C for 15 min and sintering at 500 °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 : $\alpha$-terpilenol = 1 : 1.5 : 3 (w/w/w) ) at 3000 rpm for 30 s, followed by drying at 125 °C for 15 min and then warm up to 500 °C by a speed of 25 °C/min, sintering at 500 °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 °C for 30 min. After cooling to room temperature, dipping the resulted TiO$_2$/PbI$_2$ composite film into a solution of CH$_3$NH$_3$I 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 °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 $\mu$L Li-TFSI)/acetonitrile (170 mg/1 mL) and 17.5 $\mu$L TBP were spin-coated on CH$_3$NH$_3$PbI$_3$/mp-TiO$_2$/bl-TiO$_2$/FTO substrate at 4,500 r.p.m. for 40 s, respectively. P3HT were coated on CH$_3$NH$_3$PbI$_3$/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 $\mu$L Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (28.3 mg/1 mL) and 3.4 $\mu$L TBP as additives, respectively. TTF-1 were coated on CH$_3$NH$_3$PbI$_3$/mp-TiO$_2$/bl-TiO$_2$/FTO substrate around 50 °C using TTF-1/chlorobenzene/dichlorobenzene (15 mg/0.6 mL/0.4 mL) solutions with or without 6.8 $\mu$L Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (28.3 mg/1 mL) and 3.4 $\mu$L TBP 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$_2$Cl$_2$.

**Fig. S3** Cyclic voltammograms of TTF-1 and P3HT in CH$_2$Cl$_2$/TBAHFP (0.1 M), [c] = 1 × 10$^{-3}$ mol L$^{-1}$, 293 K, scan rate = 100 mV s$^{-1}$, vs. Ag/AgNO$_3$. 
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).

Fig. S6 Differential scanning calorimetry curve of TTF-I 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).

Fig. S11 $^1$H NMR spectrum of TTF-1.