Supplemental Information

Overcoming photovoltage deficit via phenylthiourea derivatives for efficient printed perovskite solar cells with enhanced stability

Jinlong Hu[a], Runxin Li[a], Qiongfeng Zhan[a], Jiajun Qin[b], Dadong Wen[a], Bing Yi[a], Huisheng Peng[b] and Zhihang Tang[a*]

[a]Academician Workstation for Smart Fiber Materials, Hunan Institute of Engineering, Xiangtan, 411104, P. R. China

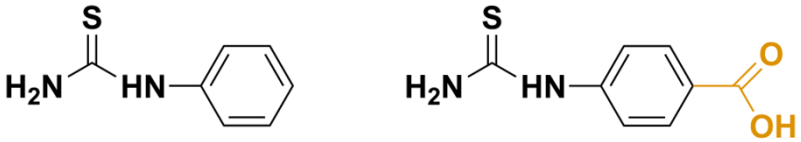
[b]State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University Shanghai 200438, P. R. China

*Correspondence: Zhihang Tang, zhtang@hnie.edu.cn

Experimental Section

Materials

Methylammonium iodide (MAI), Lead iodide (**(**PbI_2, 99.9985%), and Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA) were purchased from Xi'an p-OLED Co. (China). Bathocuproine (BCP) and $PC_{61}BM$ were purchased from Lumtec. Phenylthiourea and 1-(4-carboxyphenyl)-2-thiourea was purchased from Tokyo Chemical Industry (TCI), the corresponding molecular structures are shown in following picture. All the solvents including dimethylformamide, dimethyl sulfoxide, and isopropanol were purchased from Sigma-Aldrich.



PhTu PhTu-COOH

Blade Deposition of Perovskite Films

The $MAPbI_3$ precursor solution was prepared by dissolving 159 mg MAI and 461 mg PbI_2 in 1 mL mixed solvent of DMSO and DMF (volume ratio 1: 4). The additives with different amounts (0, 1, 2, 5, 10 mg) were directly added into the as-prepared precursor solution. After heated at 45 °C on a hotplate till completely dissolved, the precursor solution with different concentrations of additives was filtered and transferred into nitrogen-filled glovebox. The perovskite films were prepared at room temperature in nitrogen-filled glovebox by blade-coating, which performed on a commercial-blade coater (ZAA2300.H from ZEHNTNER) using a ZUA 2000.100 blade (from ZEHNTNER). For the fabrications of perovskite films, 20 µL precursor solution was used for blade deposition on a substrate area of 2.5 × 2.5 cm^2. The gap between the blade and substrate was 200 µm. Upon the precursor solution spread onto the substrate by blade-coating, the precursor films were transferred into a vacuum chamber and pumped to 1000 Pa and stayed at the pressure for 90 second. Then, the as-prepared films were immediately placed onto the hotplate and annealed at 100 °C for 10 min to fully crystallize the films.

Devices Fabrication

The pre-patterned indium tin oxide (ITO) coated glass (OPV Tech Co., Ltd.) was brushed by Hellmanex (TM) III detergent and then washed with deionized water. Subsequently, the ITO substrates were further cleaned by sonicating in acetone and isopropanol for 10 min each. A PTAA hole-transporting layer was spin-coated from 5 mg · mL^{-1} chlorobenzene solution on ITO substrate at 5000 rpm for 30 sec. The film was then annealed at 120 °C for 10 min in ambient air. The substrate was transferred to a nitrogen-filled glovebox after it cooled down to room temperature. On top of perovskite film, the electro-transporting layer $PC_{61}BM$ (20 mg mL^{-1} in chlorobenzene) and the interfacial layer BCP (saturated in isopropanol) was successively deposited by spin coating at 2000 rpm for 30 sec and 5000 rpm for 30 sec, respectively. Finally, 120 nm Ag layer was deposited by thermal evaporation. The active areas of the solar cells were 0.09 cm^2 for the small-size devices. All the devices for performance and stability evaluation were tested without encapsulation.

Materials Characterizations

X-ray diffraction (XRD, Bruker D8) with Cu Kα radiation (λ = 1.5418 Å) measurement was used to characterize the crystalline structure. Field emission scanning electron microscopy (SEM, FEI Apreo LoVac) was performed to investigate the morphology and microstructure of these thin films. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALab250Xi electron spectrometer (Thermo Fisher) using Al Kα radiation to analysis the elemental composition. Timeresolved PL experiments were performed with a spectrophotometer (Gilden Photonics) using a pulsed source at 480 nm (Ps diode lasers BDS-SM). The time-resolved signals were recorded by a time correlated single photon counting detection technique with a time resolution of 1 ns. The external quantum efficiency (EQE) was taken using a QE-R instrument from Enlitech. The current density-voltage (J-V) characteristics and steady-state output of the all solar cells were recorded using a Keithley 2400 source meter. The illumination was provided by a Newport Oriel 92192 solar simulator with an AM1.5G filter, operating at 100 mW · cm^{-2}, which was calibrated by a standard silicon solar cell from Newport.

Calculation Methodology

In this paper, the theoretical calculations were performed by density function (DFT) methods. DFT calculations were performed under exchange correlation function of generalized gradient approximation (GGA)[1] with Perdew, Burke, and Ernzerhof (PBE). The calculations for surface passivation were performed by VASP[2] code with the projector augmented wave method (PAW)[3]. The Kohn-Sham equation is solved by a plane wave basis set with a cutoff energy of 400 eV, and the Brillouin zone samples a 2 × 2 × 1 mesh centered at Γ point. Atoms are fully relaxed until the Hellmann-Feynman forces on them are within 0.05 eV · A^{-1}.

1. S. Grimme, S. Ehrlich and L. Goerigk, J Comput Chem, 2011, 32, 1456-1465.
2. G. Kresse and J. Furthmüller, Physical Review B, 1996, 54, 11169-11186.
3. G. Kresse and D. Joubert, Physical Review B, 1999, 59, 1758-1775.

Additional data and results.

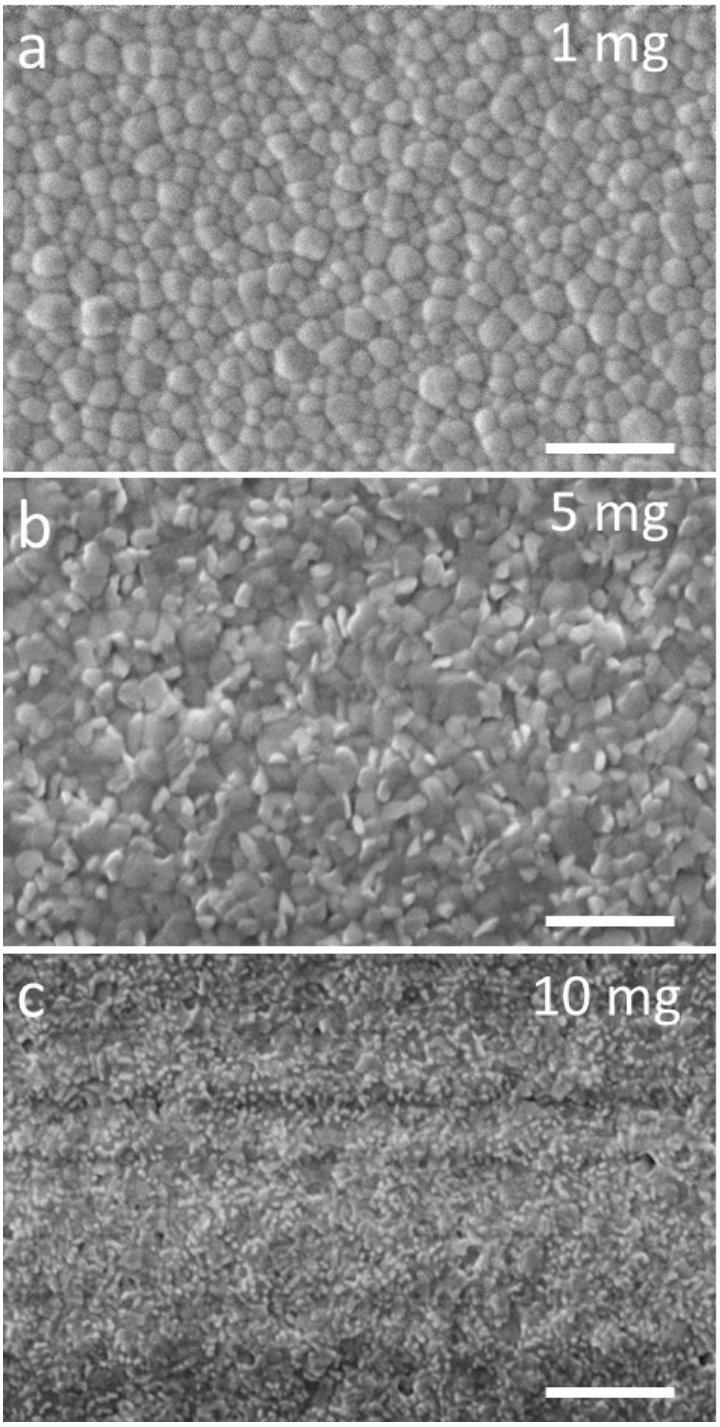


Figure S1. The SEM image of perovskite films processed with 1, 5 and 10 mg · mL^{-1} PhTu-COOH dopant. The scale bars are 1 μm.

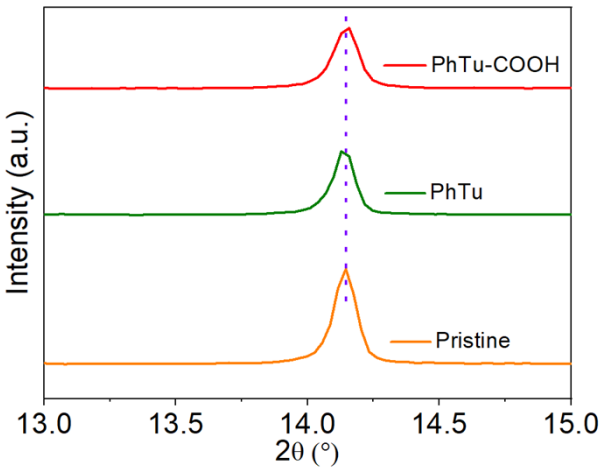


Figure S2. Zoom-in XRD spectra of the $MAPbI_3$ perovskite films processed without and with 2 mg · mL^{-1} PhTu and PhTu-COOH modification.

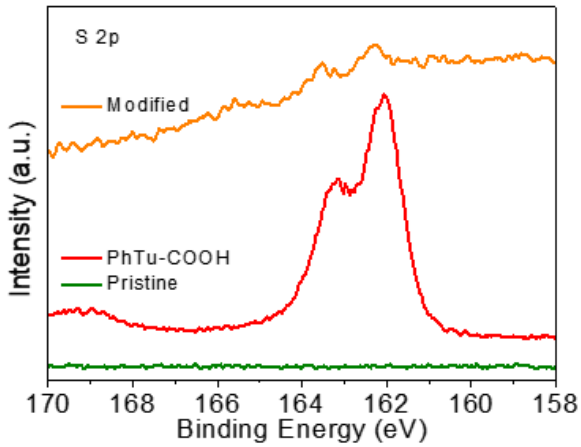


Figure S3. High-resolution S 2p spectrum of the pristine perovskite thin film, PhTu-COOH molecule and PhTu-COOH-modified thin films.

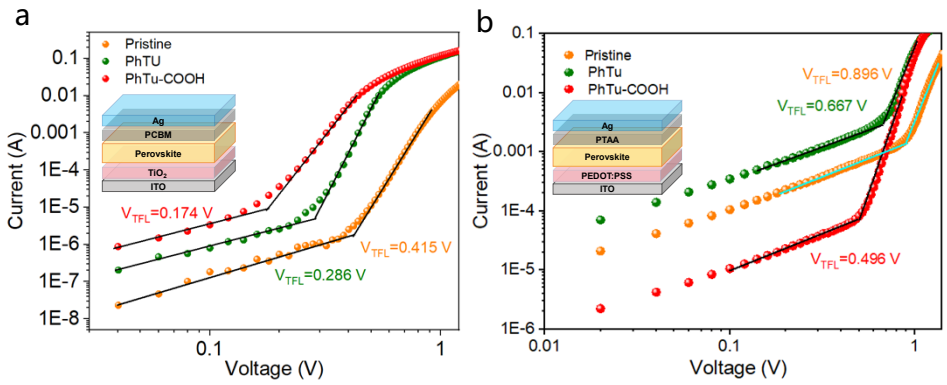


Figure S4. *I-V* logarithm curves in the dark for the pristine, PhTu- and PhTu-COOH-modified electron-only (a) and hole-only (b) devices.

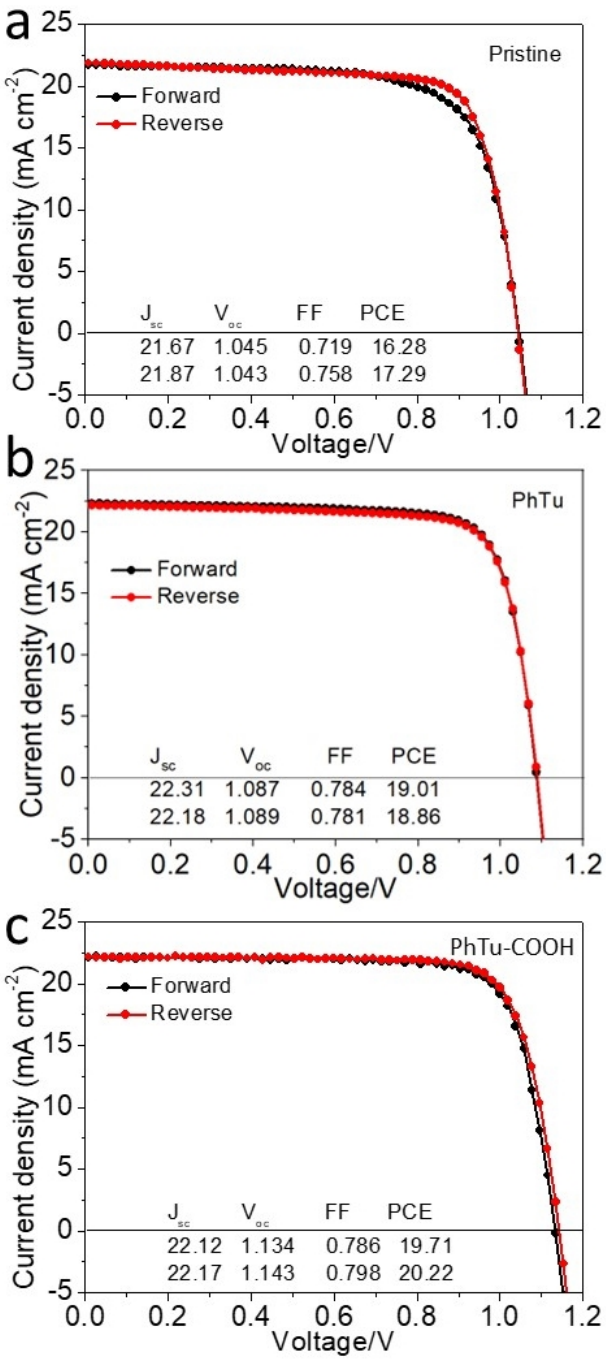


Figure S5. *J-V* curves of the perovskite solar devices measured in both forward and reverse scan directions: (a), (b), and (c) are the *J-V* curves of the pristine, PhTu and PhTu-COOH modified devices, respectively.

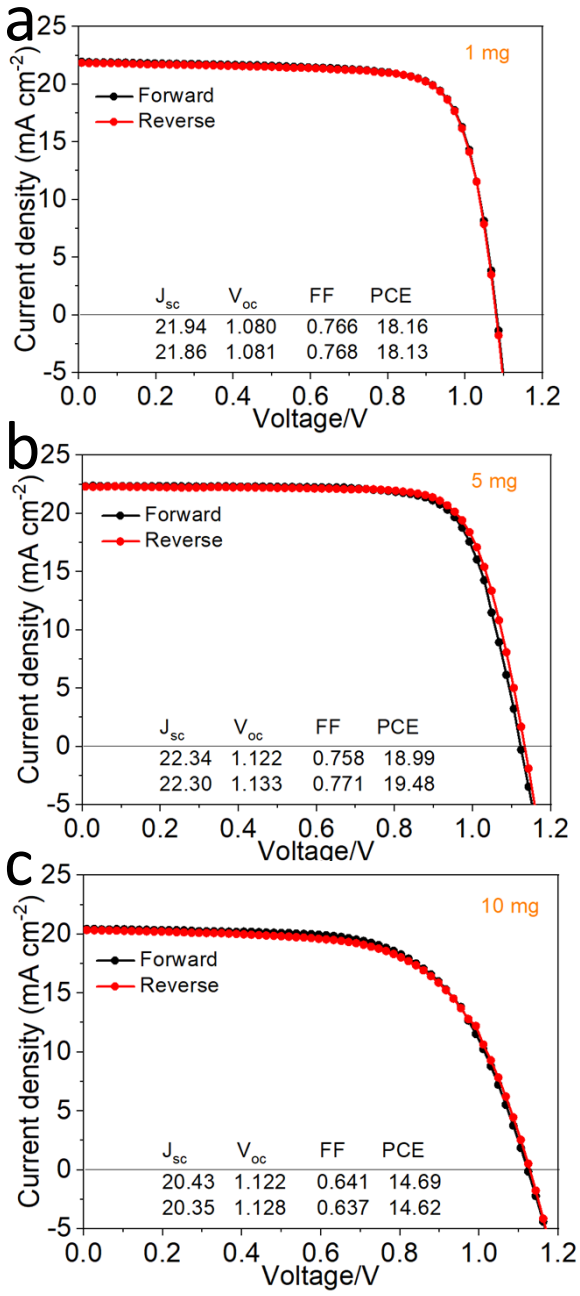


Figure S6. *J-V* curves of the perovskite solar devices measured in both forward and reverse scan directions: (a), (b), and (c) are the *J-V* curves of the devices with 1, 5, and 10 mg · mL^{-1} PhTu-COOH treatment, respectively.

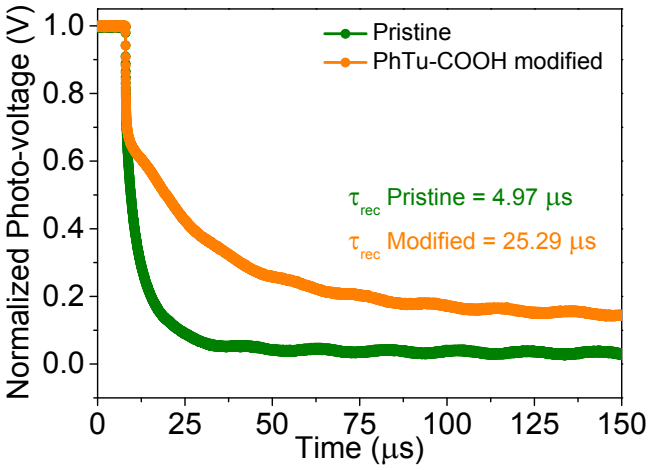


Figure S7. Transient photovoltage decay curves the pristine and PhTu-COOH-modified devices.

Table S1 Time-resolved PL values of perovskite films.

/	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{ave} (ns)
Pristine	17.9	34.8	41.6	74.7	31.02
PhTu	15.6	68.2	8.6	96.1	67.23
PhTu-COOH	128.4	130.6	48.7	39.3	129.04

Table S2. A comparison of the photovoltaic performance of the $MAPbI_3$ devices fabricated by our strategy with that of the devices prepared by the spin-coating method in the literature.

PCE	**Active area (cm^2)**	**V_{OC} (V)**	**J_{SC} (mA cm^{-2})**	**Note**	**Reference**
20.4%	0.06	1.14	23.48	Spin-coating	Adv. Mater. **2020,** 32, 1905661
20.31%	unreported	1.09	23.77	Spin-coating	Small **2024,** 20, 2311400
19.67%	0.0464	1.1	22.30	Spin-coating	Appl Surf Sci. **2022,** 575, 151740
20.78%	0.16	1.12	23.01	Spin-coating	Nano Energy **2020,** 67, 104229
20.27%	0.096	1.09	23.12	Spin-coating	J Energy Chem. **2022,** 65, 592
20.49%	unreported	1.13	23.17	Spin-coating	J Alloy Compd. **2025,** 1017, 179119
19.24%	unreported	1.052	23.90	Spin-coating	ACS Appl. Mater. Interfaces **2022,** 14, 35726
21.01%	0.0464	1.11	23.74	Spin-coating	Nano Energy **2020,** 71, 104639
20.38%	0.15	1.09	23.52	Spin-coating	ACS Appl. Mater. Interfaces **2024,** 16, 31218
20.85%	0.065	1.045	25.61	Spin-coating	J Power Sources **2025,** 629, 236058
20.22%	**0.09**	**1.143**	**22.17**	**Blade-coating**	**This work**