Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Self-Assembled Atomically Thin Hybrid Conjugated Polymer Perovskites with Two-Dimensional Structure

Furkan H. Isikgor, Chilla Damodara Reddy, Mengsha Li, Hikmet Coskun, Bichen Li, Yong-Wei Zhang, Stephen J. Pennycook, Jianyong Ouyang.

Materials and Methods

Materials and chemicals

Polyaniline (emeraldine base, average M_w ~50,000), lead(II) iodide (PbI_2, 99.999% purity), hydroiodic acid (HI, 55wt%, in H_2O), *N,N*-dimethylformamide (DMF, anhydrous, 99.8% purity) and *N*-methyl-2-pyrrolidone (NMP, anhydrous, ≥ 99.5% purity) were purchased from Sigma-Aldrich. Methylammonium iodide (CH_3NH_3I) was received from Dyesol Ltd. All materials were used as received without further purification.

Fabrication of PANI-based perovskite films

PANI-based perovskite films were fabricated on pre-cleaned glass substrates of 1.5×1.5 cm^2. The glass substrates were cleaned by sonication successively in detergent, deionized water, acetone and isopropanol. The sonication time was 15 min for each cleaning. They were then dried with N_2 flow and followed by a UV-ozone treatment for 10 min. At first, 100 μl of PbI_2 solution in anhydrous DMF was dripped on a glass substrate. It was dried at 110°C. Then, 100 μl of PANI dispersion in NMP and HI aqueous solution are consecutively dripped on the dried PbI_2 film. NMP immediately dissolves the dried PbI_2 layer and leads to the formation of a dark green solution on glass substrate. Drying this solution at 110°C gives rise to PANI-perovskite thin films (Figure S1). Various concentrations of PbI_2 were used to prepare different PANI-perovskite thin films (Table S1). The same procedure was used for the preparation of PANI-PbI_2 samples but without the HI dripping.

Molecular Dynamic Simulations

The inorganic two dimensional PbI_4^{2-} sheets are constructed with lead and iodine atomic distance of 3.35 Å. The Buckingham potential parameters are considered for the interaction between the lead and iodide ions.[1] The organic chain of protonated emaraldine salt is constructed with appropriate distance between the different atoms. The hybrid potential (the combination of AIREBO,[2] 12-6 Lennard-Jones, two body and three body potentials[1]) is used for organic chain interactions with appropriated charges taken into consideration. The open source large scale molecular dynamics LAMMPS package is used for thermal equilibration at room temperature with NVT thermostat.[3]

Stability measurements

PANI-perovskite-2.0's stability was monitored by XRD under Singapore's very high humidity condition (the mean annual relative humidity=84%).[4] For the stability measurement, the PANI-perovskite-2.0 thin film was kept in open air at room temperature under ambient light soaking condition. For comparison purpose, $CH_3NH_3PbI_3$ thin film was also aged at the same time under identical conditions. $CH_3NH_3PbI_3$ film is prepared according to the described procedure in our previous study,[5] except an equimolar of CH_3NH_3I and PbI_2 was used in this study. Stabilities of PANI-perovskite-2.0 and $CH_3NH_3PbI_3$ against humidity are compared by taking ratio of the integrated perovskite XRD peaks with respect to the all other peaks. Their relative stabilities are then depicted in Fig. S13. Half decomposition of the materials is obtained by linear fitting of the decomposition curves.

Characterization of materials

UV-Visible absorption spectra were obtained using a Shimadzu UV-1800 spectrophotometer. X-Ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance XRD Instrument. Fourier transform infrared (FTIR) spectrums were acquired with an Agilent 660 FTIR spectrometer. The FTIR samples were prepared by dispersing the materials in KBr pellets. X-ray photoelectron spectroscopy (XPS) spectra were collected using an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al K α X-ray source (1486.6 eV). The CasaXPS program (2.3.14 version) was employed to subtract the Shirley background, compositional analysis, and deconvolution of the XPS peaks. Optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were acquired with Nikon Eclipse LV100, VeecoNanoScope IV Multi-Mode AFM operated in the tapping mode, Zeiss Supra-40 SEM and JEOL-2010F-200 kV TEM equipments, respectively. The van der Pauw four-point probe technique with a Keithley 2400 source/meter was employed to measure the electrical conductivities. Seebeck effect of samples was measured in ambient using two Peltier devices (TEC1-19906, Beijing Geshang Electronic Pte.Ltd.) affixed on an alumina heat sink. The thermal voltage output (ΔV) was measured with a Keithley 2000 multimeter. Water contact angles were measured with a VCA Optima Contact Angle Measurement system.

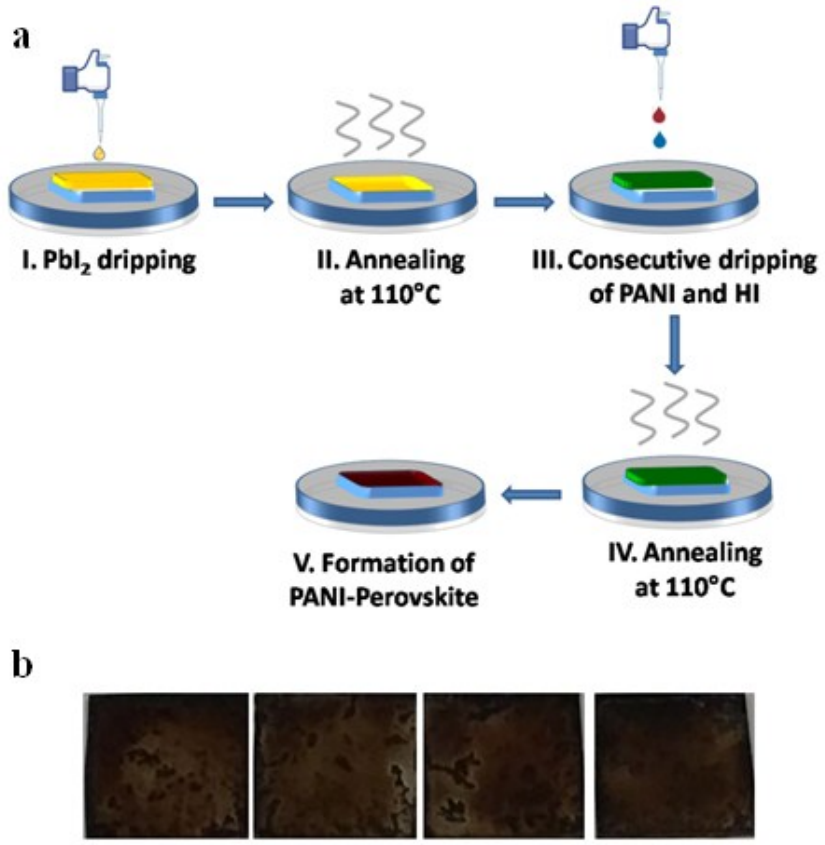

Figure S1. (a) Schematic procedure for the preparation of PANI-perovskite thin films, **(b)** images of the PANI-perovskite-0.5, -0.8, -1.0, and -2.0 thin films (from left to right).

Table S1. Optimized conditions for preparation of PANI-perovskite, PANI-PbI_2, PANI-HI and PANI thin films.

Sample	**PbI_2 (M)**	**PANI-nitrogen (M)**	**HI (M)**	**Annealing time (min)**	**PbI_2/PANI-nitrogen molar ratio**
PANI-perovskite-0.5, -0.8, -1.0, -2.0	1.10×10^{-2}, 1.76×10^{-2}, 2.20×10^{-2}, 4.40×10^{-2}, respectively	2.20×10^{-2}	0.43	30, 24, 20, 18, 15, respectively	0.5, 0.8, 1.0, 2.0, respectively
PANI-PbI_2-0.5, -0.8, -1.0, -2.0	1.10×10^{-2}, 1.76×10^{-2}, 2.20×10^{-2}, 4.40×10^{-2}, respectively	2.20×10^{-2}	-	15	0.5, 0.8, 1.0, 2.0, respectively
PANI	-	2.20×10^{-2}	-	15	-
PANI-HI	-	2.20×10^{-2}	0.43	35	-

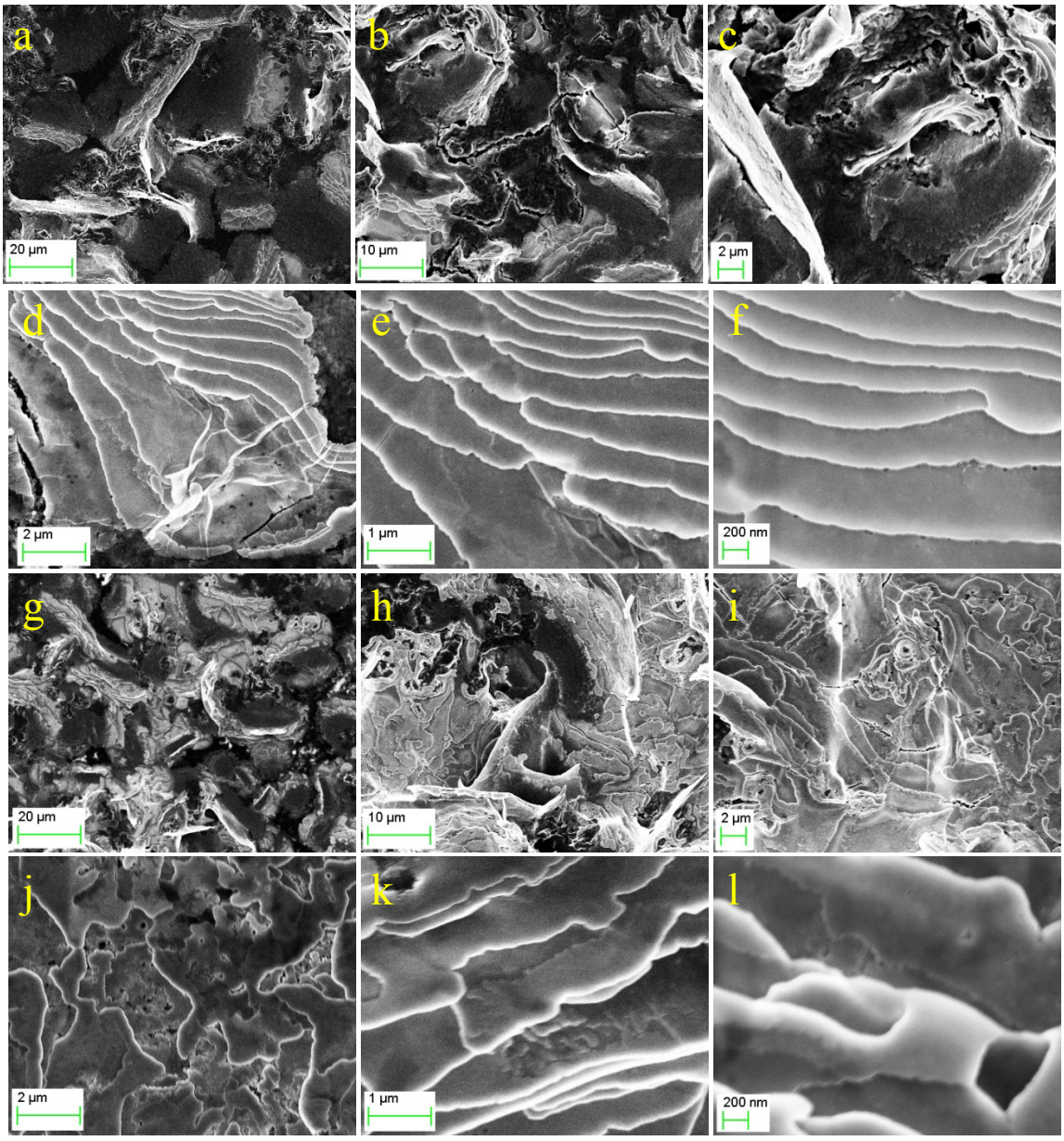

Figure S2. SEM images of **(a-f)** PANI-perovskite-1.0 and **(g-l)** PANI-perovskite-2.0. The scale bars are **(a, g)** 20 µm, **(b, h)** 10 µm, **(c, d, i, j)** 2µm, **(e, k)** 1 µm, and **(f, l)** 200 nm.

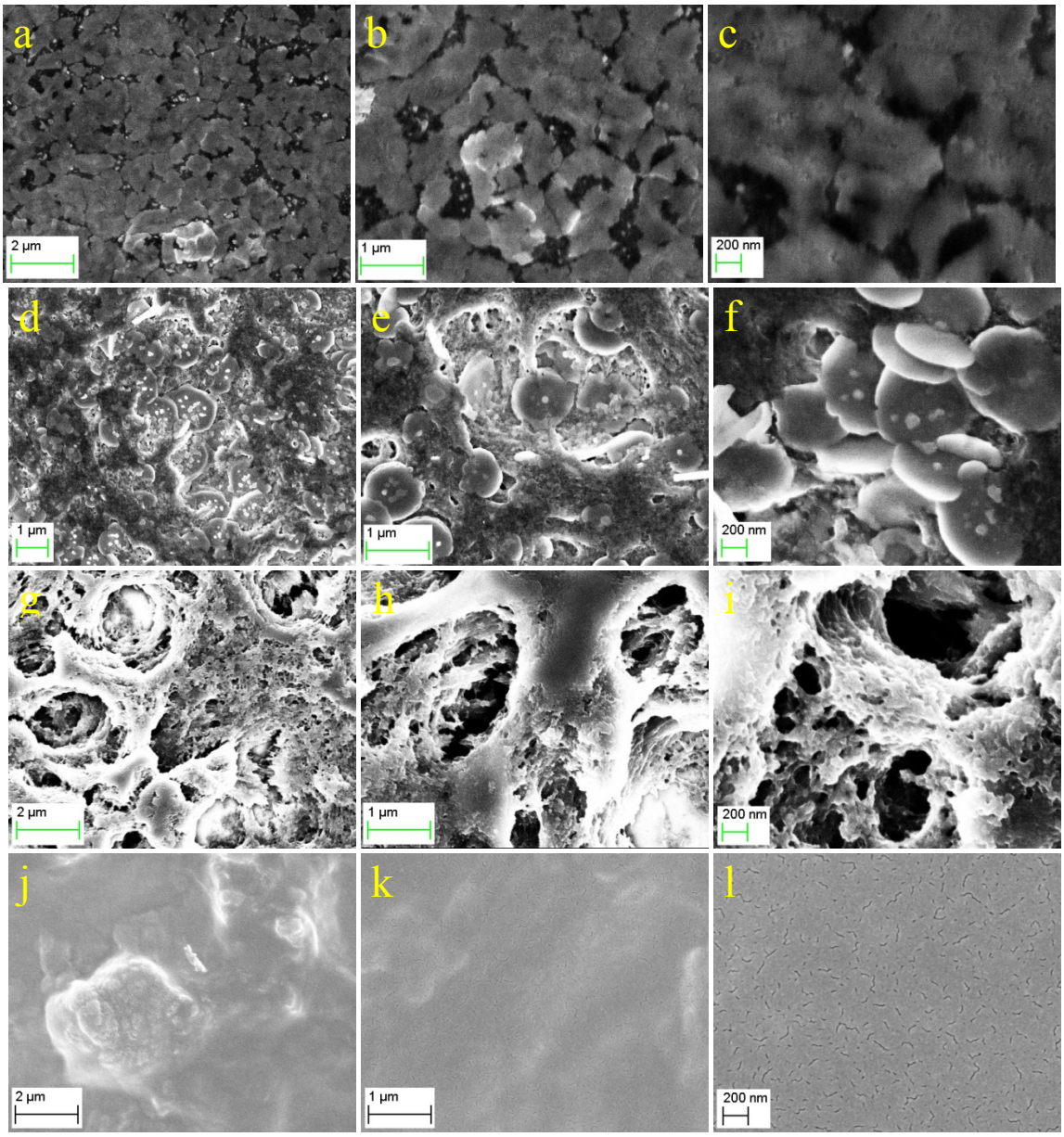

Figure S3. SEM images of **(a-c)** PANI-PbI_2-1.0, (d-f) PANI-PbI_2-2.0, **(g-i)** PANI-HI and **(j-l)** PANI. The scale bars are **(a, g, j)** 2 µm, **(b, d, e, h, k)** 1 µm and **(c, f, i, l)** 200 nm.

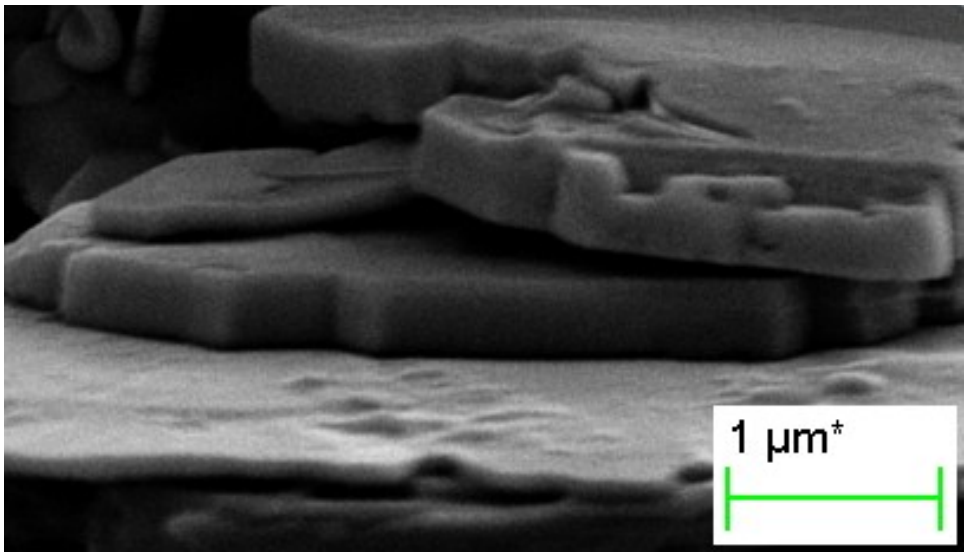

Figure S4. Cross-sectional SEM image of PANI-perovskite-2.0.

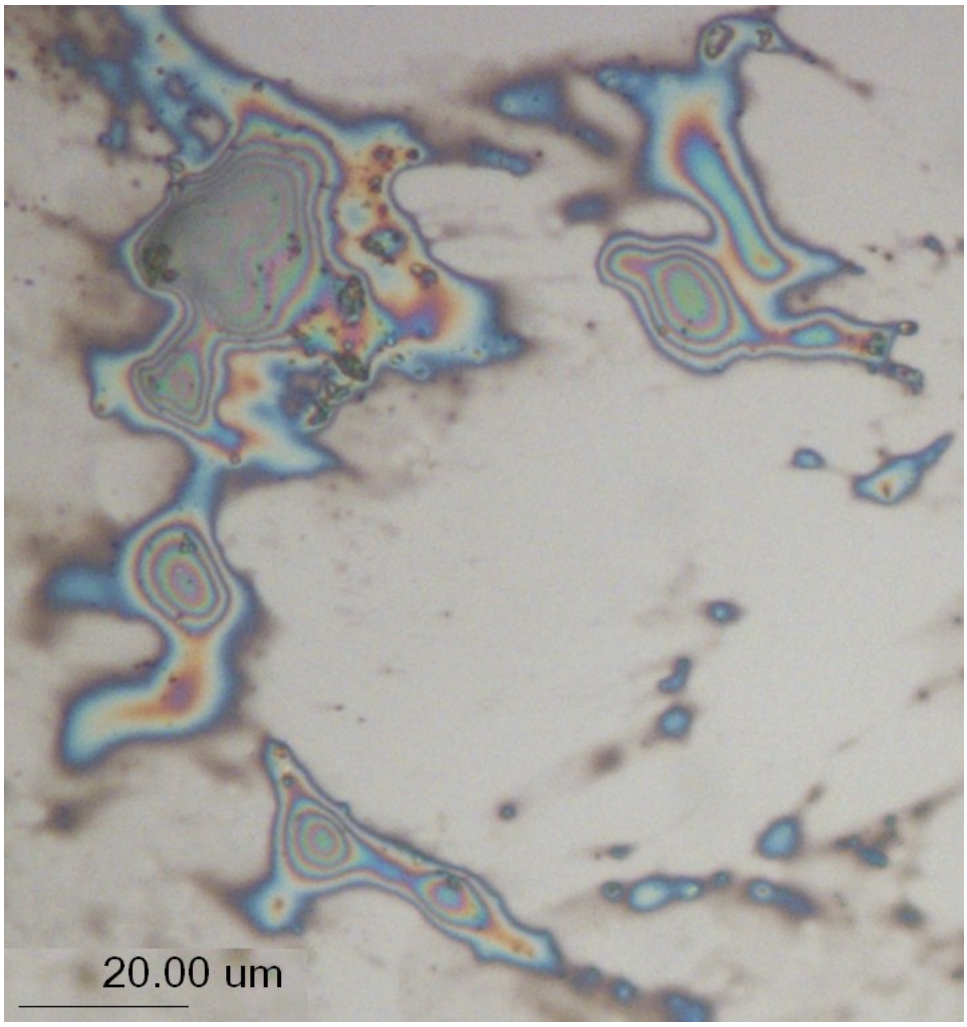

Figure S5. Optical microscopy image of PANI-perovskite-2.0. The scale bar is 20 μm.

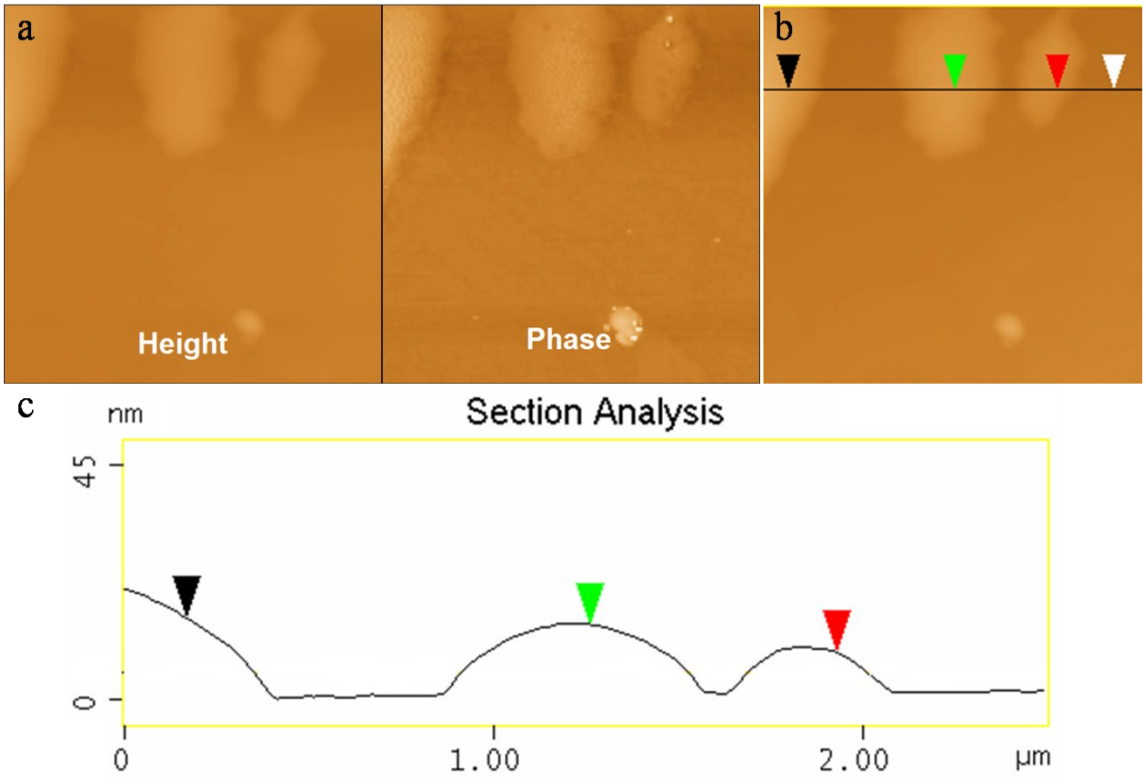

Figure S6. AFM images of mechanically exfoliated PANI-perovskite-2.0 on a silicon wafer. **(a)** Height-phase image (scale: 2.5 µm), **(b)** section analysis image, and **(c)** section analysis graph.

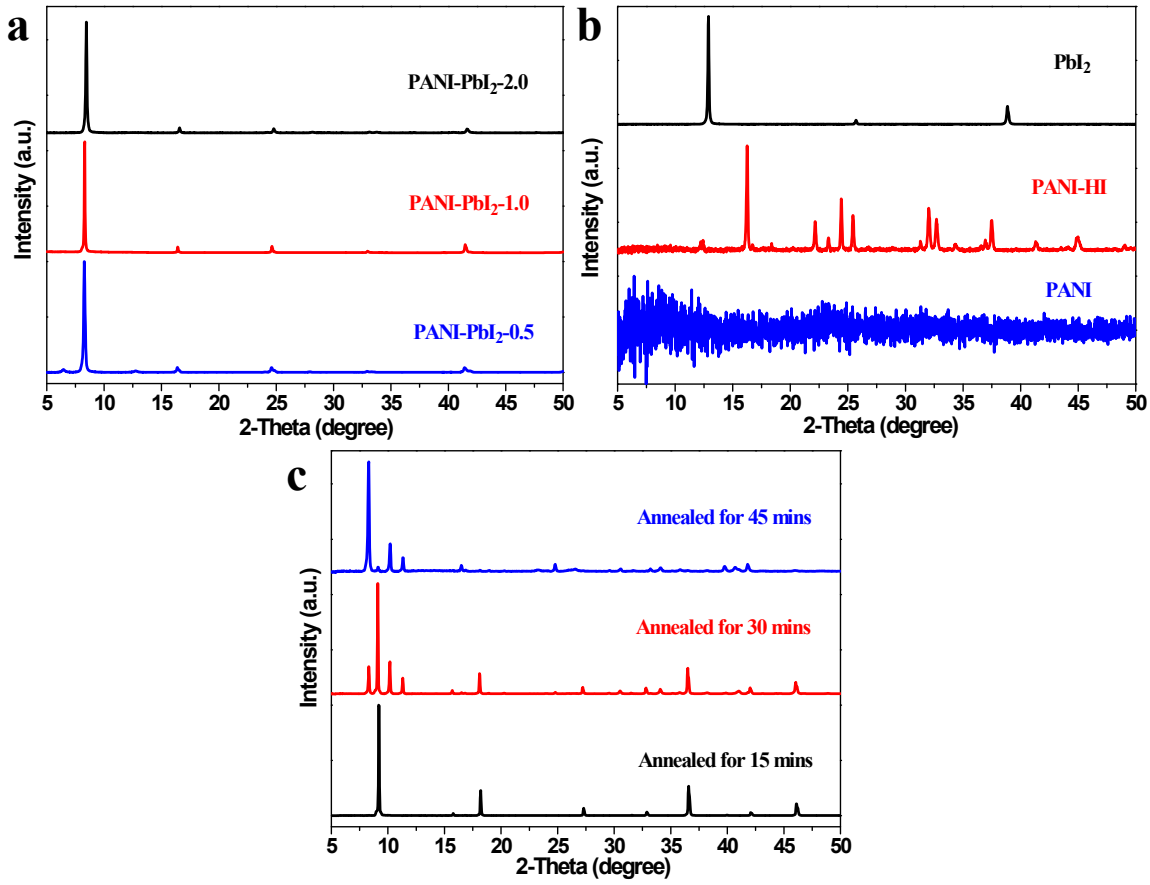

Figure S7. XRD patterns of **(a)** PANI-PbI_2, and **(b)** PANI, PANI-HI and PbI_2 thin films. **(c)** XRD patterns of PANI-perovskite-2.0 thin film annealed at 110 °C for 15, 30 and 45 minutes.

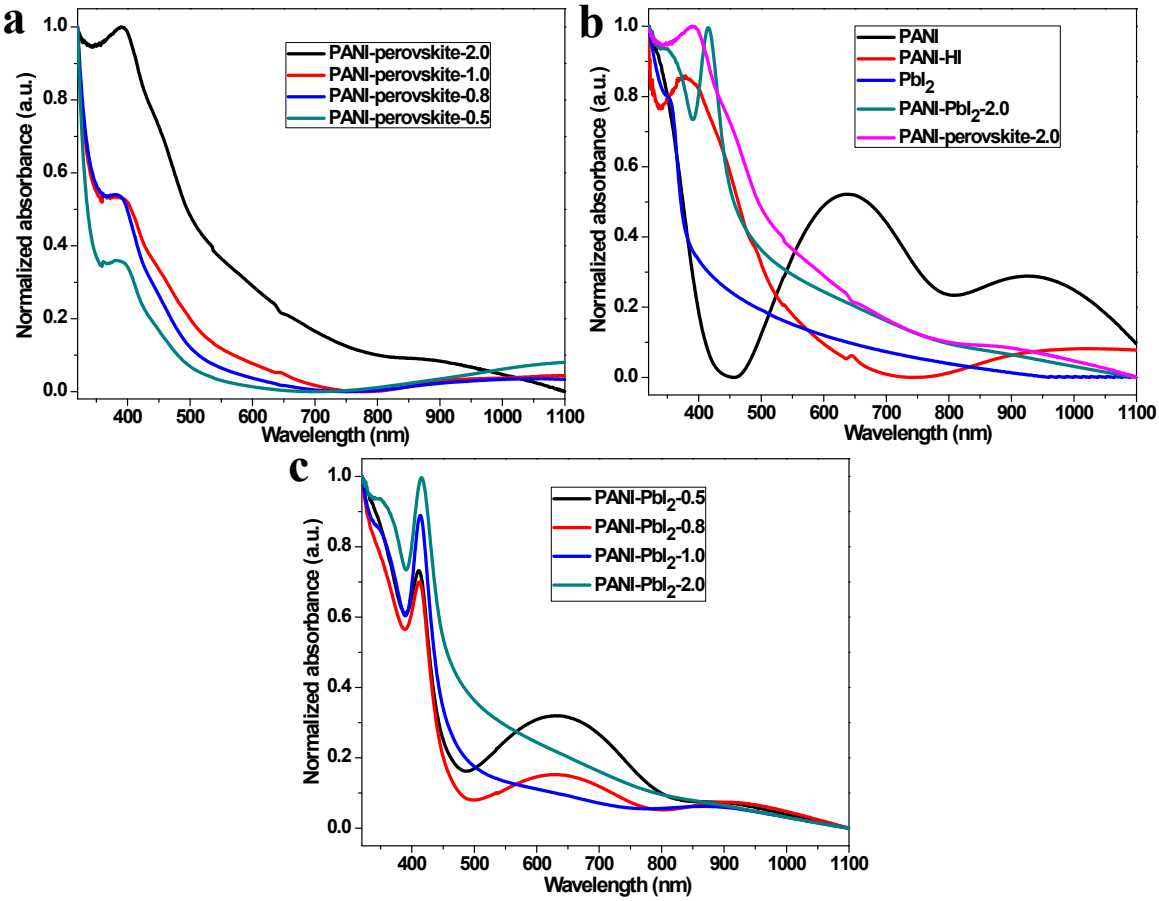

Figure S8. UV-Vis absorption spectra of the **(a)** PANI-perovskite, **(b)** PANI, PANI-HI, PbI_2, PANI-PbI_2-2.0, and PANI-perovskite-2.0, and **(c)** PANI-PbI_2 thin films.

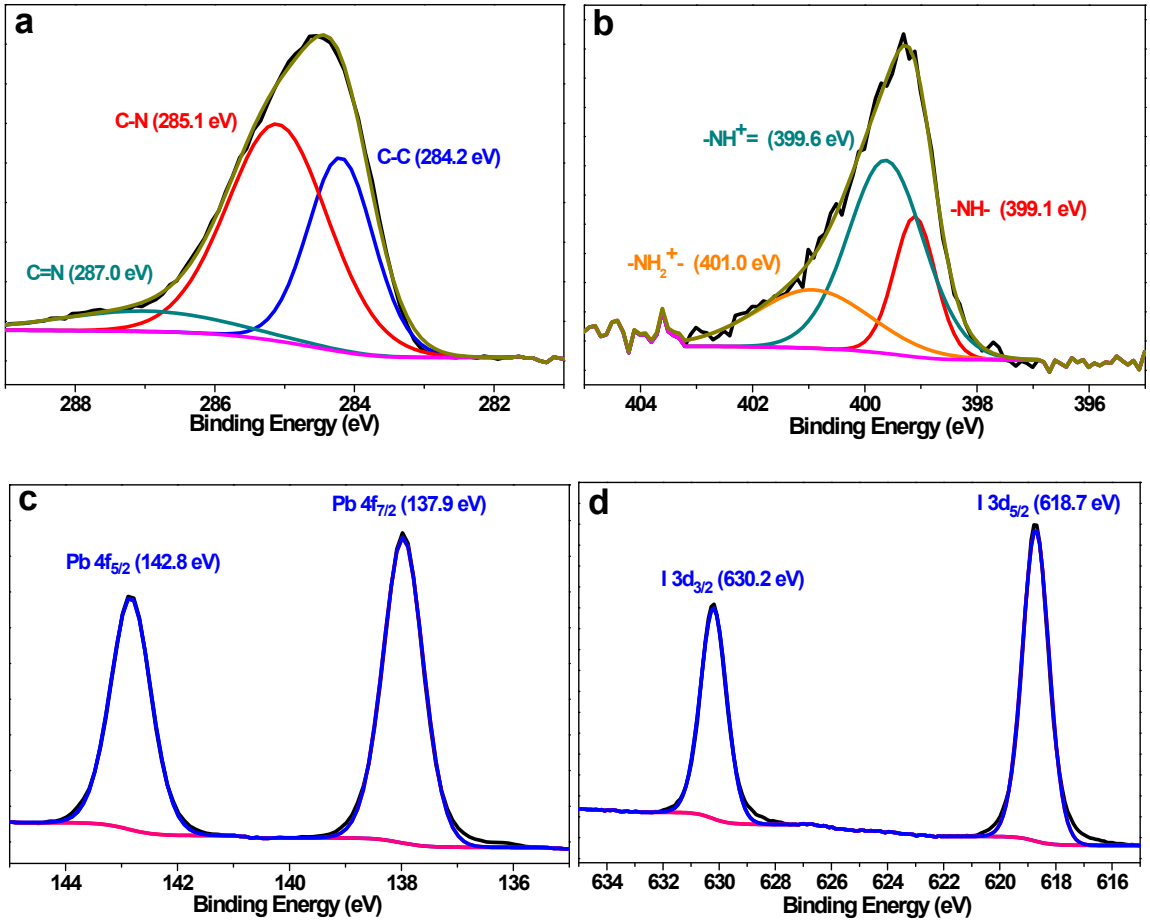

Figure S9. (**a**) C 1s, (**b**) N 1s, (**c**) Pb 4f and (**d**) I 3d XPS spectra of PANI-perovskite-2.0.

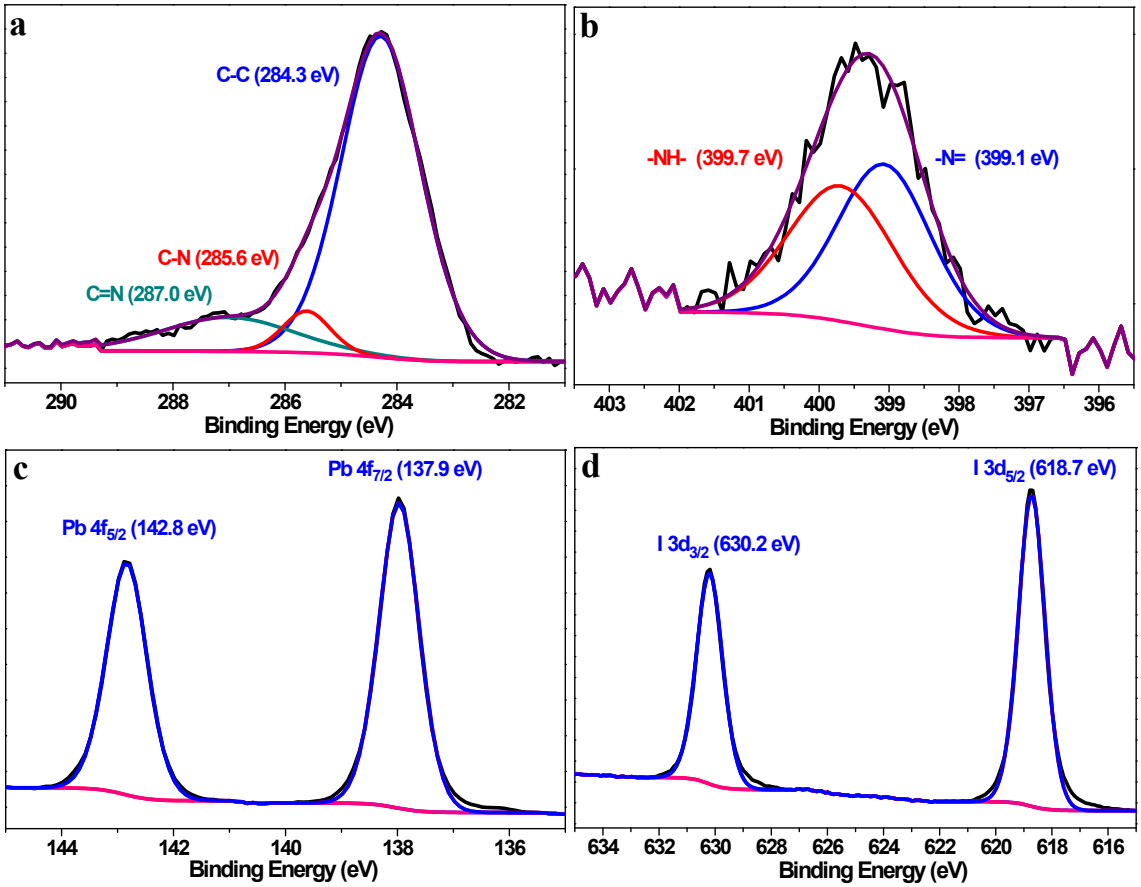

Figure S10. (a) C 1s, **(b)** N 1s, **(c)** Pb 4f and **(d)** I 3d XPS spectra of PANI-PbI_2-2.0.

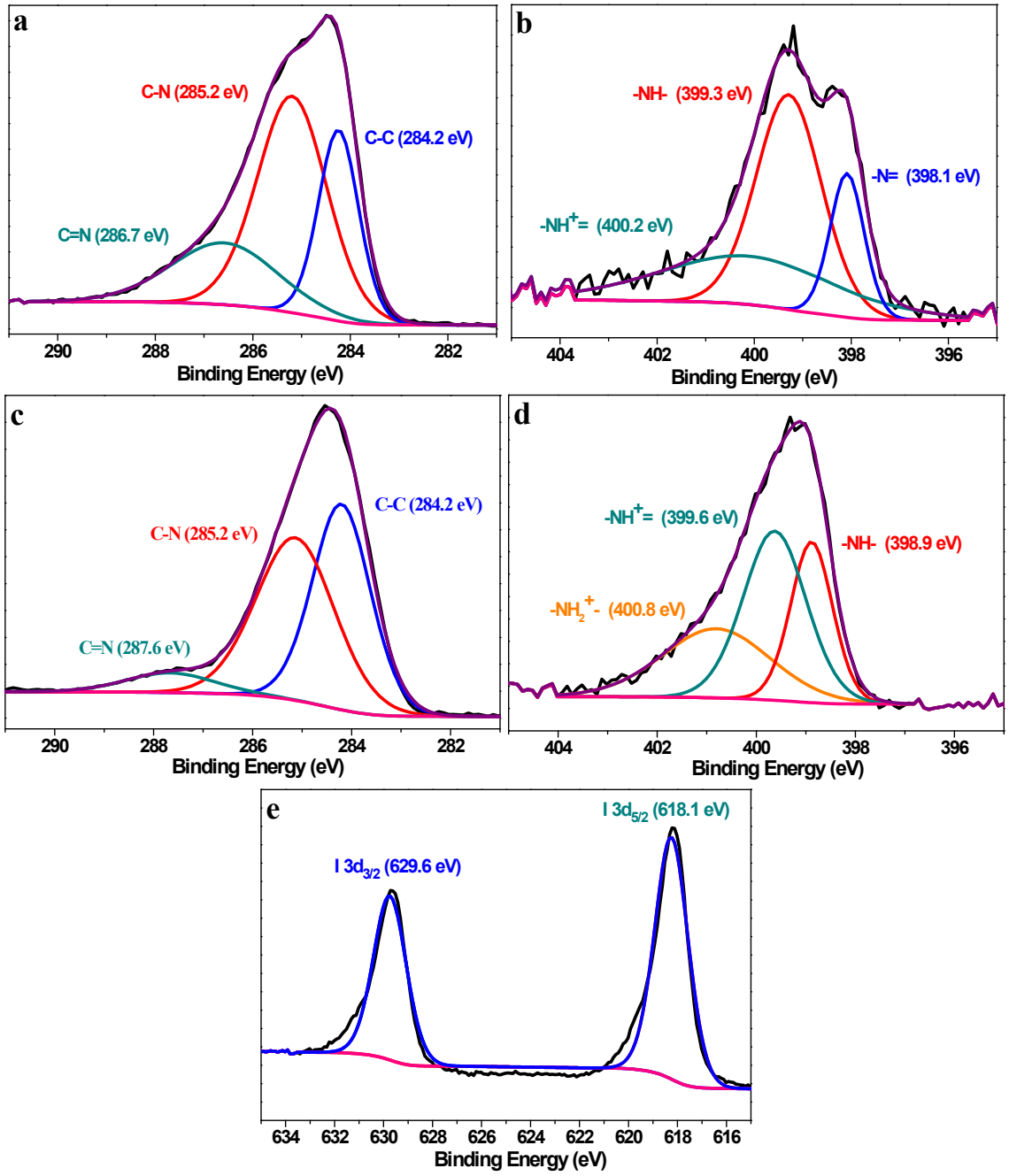

Figure S11. (a) C 1s, **(b)** N 1s XPS spectra of PANI, and **(c)** C 1s, **(d)** N 1s, **(e)** I 3d XPS spectra of PANI-HI.

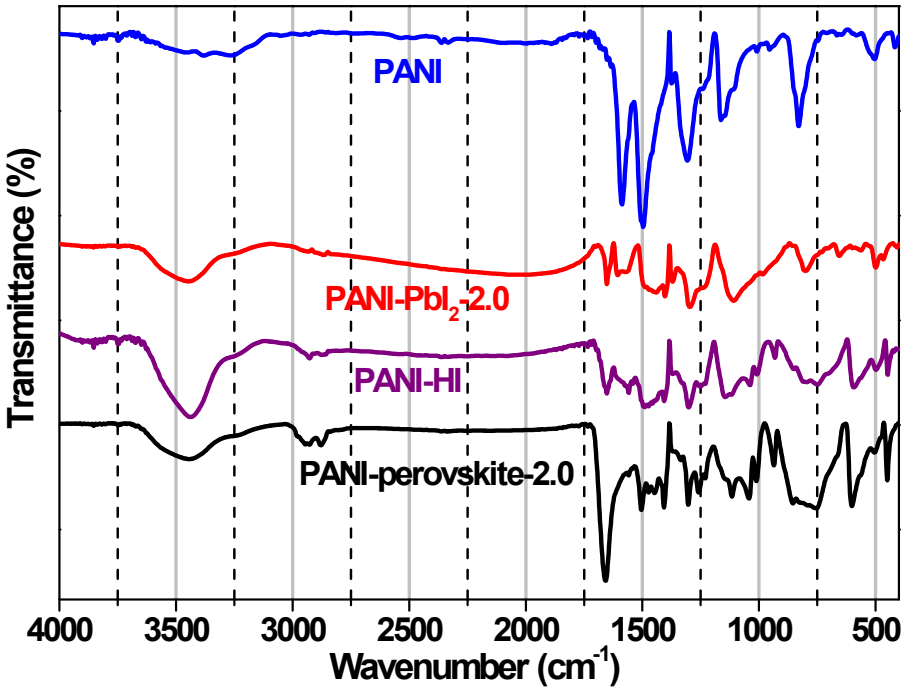

Figure S12. FTIR spectra of PANI, PANI-HI, PANI-PbI_2-2.0 and PANI-perovskite-2.0 pellets.

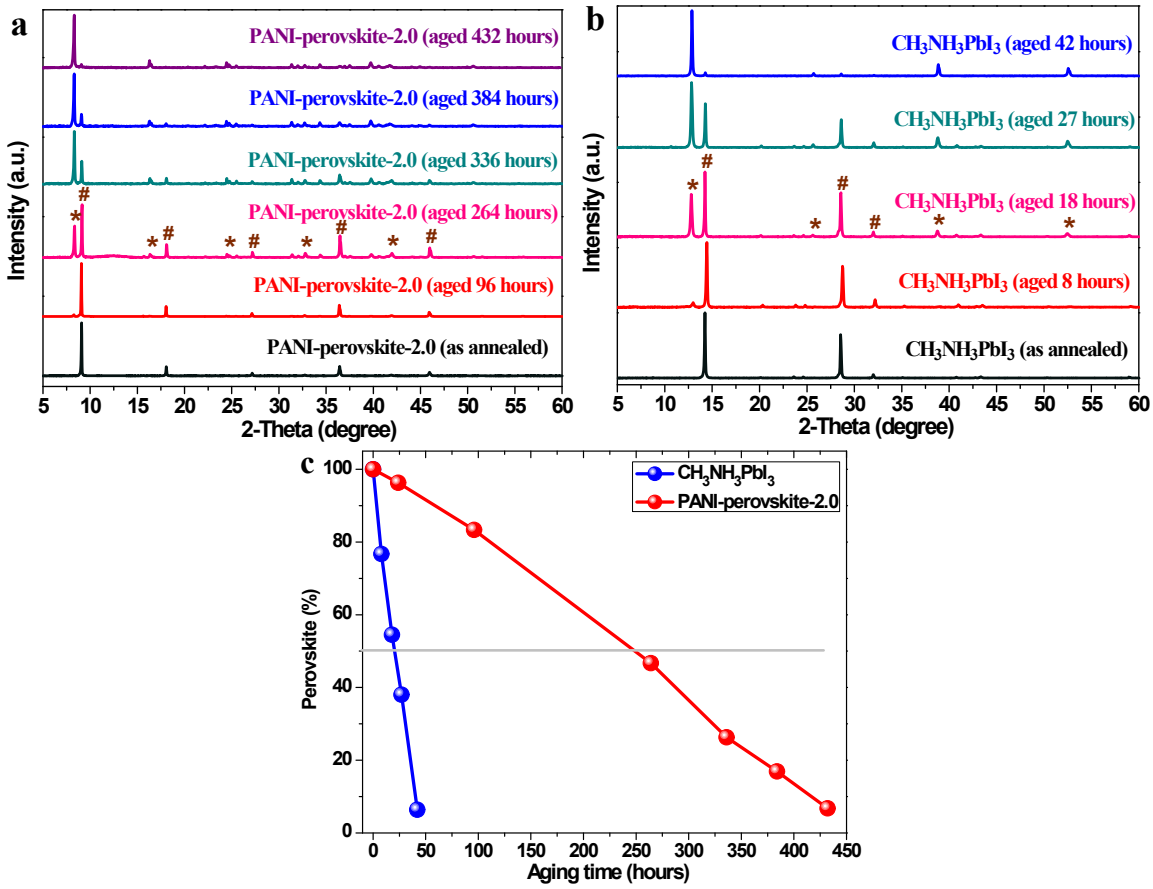

Figure S13. (a) XRD patterns of as annealed and aged PANI-perovskite-2.0 thin film under high humidity condition. The patterns indicated with # are from PANI-perovskite and the ones with * are due to PANI-PbI_2. **(b)** XRD patterns of as annealed and aged $CH_3NH_3PbI_3$ thin film under high humidity condition. The patterns indicated with # are from $CH_3NH_3PbI_3$ and the ones with * are due to PbI_2. **(c)** Relative stabilities of PANI-perovskite-2.0 and $CH_3NH_3PbI_3$ under intense humidity (~84%).

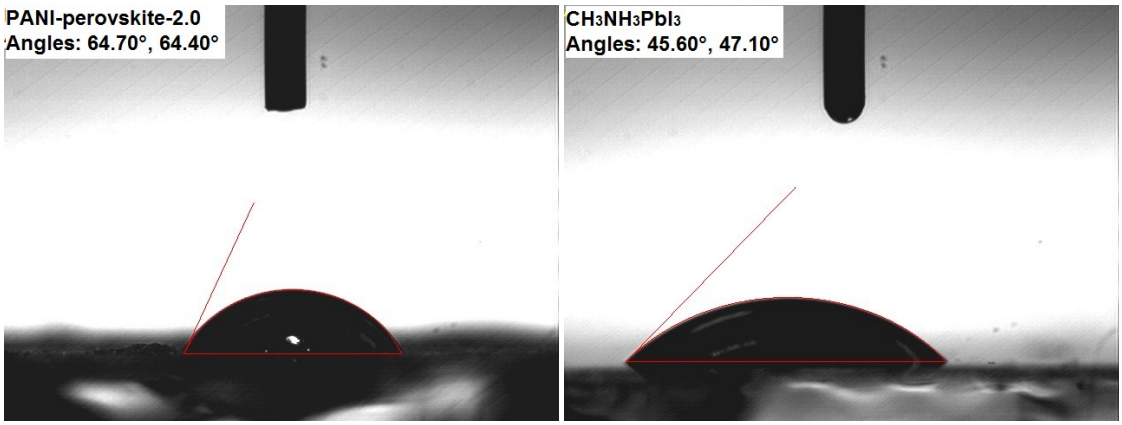

Figure S14. Contact angles of PANI-perovskite-2.0 (left) and $CH_3NH_3PbI_3$ (right) on a glass substrate.

Table S2. Electrical conductivities of the PANI, PANI-HI, PANI-PbI_2 and PANI-perovskite pellets.

Sample	Pellet Thickness (mm)	Conductivity (S/cm)
PANI	0.640	1.90×10^{-8}
PANI-HI	0.169	1.41×10^{-3}
PANI-PbI_2-1.0	0.270	2.23×10^{-6}
PANI-PbI_2-2.0	0.460	1.28×10^{-5}
PANI-perovskite-1.0	0.641	1.11×10^{-5}
PANI-perovskite-2.0	0.242	1.31×10^{-5}

References

1. C.M. Handley and C.L. Freeman, A new potential for methylammonium lead iodide, *Phys. Chem. Chem. Phys.,* **19**, 2313-2321 (2017).
2. D. W. Brenner *et al.*, A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons, *J. Phys. Condens. Matter,* **14**, 783 (2002).
3. S. J. Stuart *et al.*, A reactive potential for hydrocarbons with intermolecular interactions, *J. Chem. Phys,* **112**, 6472 (2000).
4. Singapore weather, http://www.weather.gov.sg/climate-climate-of-singapore/, (accessed 23 August, 2017).
5. J. Chang *et al.*, Enhancing the planar heterojunction perovskite solar cell performance through tuning the precursor ratio**,** *J. Mater. Chem. A* **4**, 7943-7949 (2016).