Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information

Improving the Moisture Stability of Perovskite Solar Cells by Using PMMA/P3HT Based Hole-transport Layers

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Experimental section

Materials

ITO-coated glass (R_s = 20 $\Omega \cdot sq^{-1}$) substrates were purchased from Delta Technologies. Poly(3-hexylthiophene) (P3HT, electronic grade, M_w ~ 50 kDa) and zinc acetate dihydrate were purchased from Rieke Metals Inc., and Alfa Aesar, respectively. Ag (99.99%) and Au pellets (99.99%) were purchased from Kurt J. Lesker. PMMA (M_w ~ 350 kDa), lead(II) iodide (99%), methylamine (37% in absolute ethanol), hydriodic acid (57% in H_2O), 4-*tert*-butylpyridine (96%) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 99%) were purchased from Sigma-Aldrich. All solvents were purchased from Fisher Scientific. All chemicals were used without any further purification.

Characterization

A Cary 6000i spectrophotometer was used to record UV-vis spectra. Powder X-ray diffraction measurements were carried out on a PANalytical Empyrean diffractometer configured using a cobalt X-ray source (Co K_α, λ = 1.79 Å). The data were collected with a 0.0469° step size (2θ). Scanning electron microscopy was carried out on a Hitachi SU8010 microscope operating at a 1.0−5.0 kV landing voltage. AFM measurements were performed using a Dimensions Hybrid Nanoscope system (Veeco Metrology Group) under tapping mode in air.

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by previously reported procedures.[1, 2] Zinc acetate dihydrate (2.95 g, 13.4 mmol) was first dissolved in methanol (125 mL) at 70 °C followed by the addition of a solution of KOH (1.48 g, 23 mmol) in methanol (65 mL) over a period of 10-15 minutes. The reaction mixture was allowed to stir continuously at 65 °C for an additional 2.5 h. The reaction mixture was allowed to cool down to room temperature and the precipitate was washed twice with methanol (2 × 50 mL). Finally, chloroform (10 mL), n-butanol (50 ml) and methanol (5 ml) were added to prepare a translucent dispersion of ZnO nanoparticles (~ 6 mg/mL). The solution was filtered using a 0.45 μm PVDF syringe filter prior to use.

Synthesis of methylammonium iodide

Methylammonium iodide was synthesized according to literature procedures.[3, 4] First, a solution of methylamine (30 mL, 37% in EtOH) was added to 200 mL of ethanol and cooled to 0 °C, followed by the dropwise addition of hydriodic acid (30 mL). The reaction mixture was allowed to stir continually at 0 °C for 2 h. The product was recovered by removing the solvent on a rotary evaporator at 50 °C for 1 h. It was washed with diethyl ether (3 × 50 mL), dissolved in ethanol (50 mL), and reprecipitated in diethyl ether to obtain crystalline methylammonium iodide. The powder was dried under high vacuum for 1 day at 65 °C.

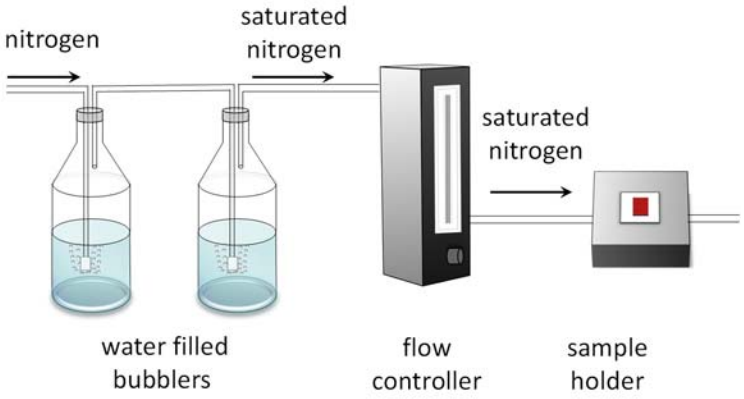

Fig. S1. Schematic illustration of the RH control setup for in situ UV/vis spectroscopy.

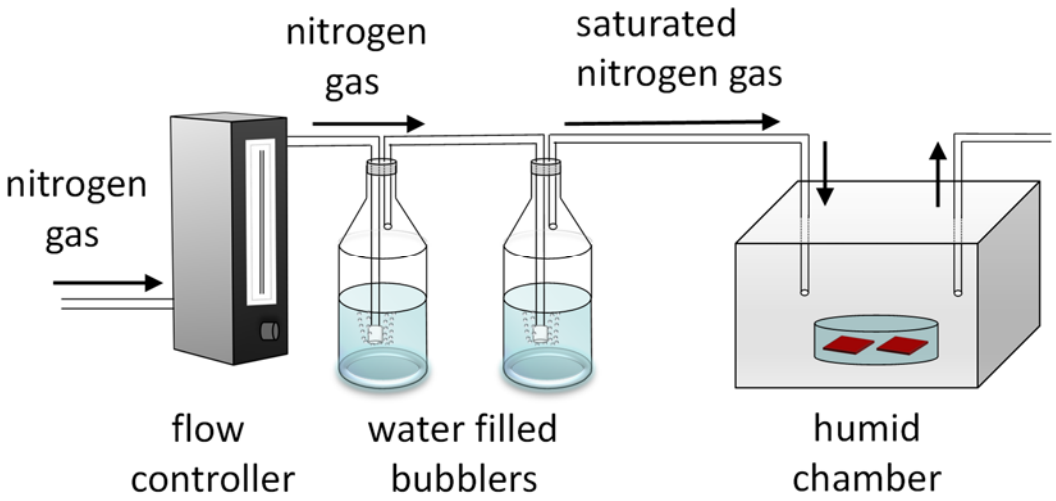

Fig. S2. Schematic illustration of the RH control setup for measuring device lifetime.

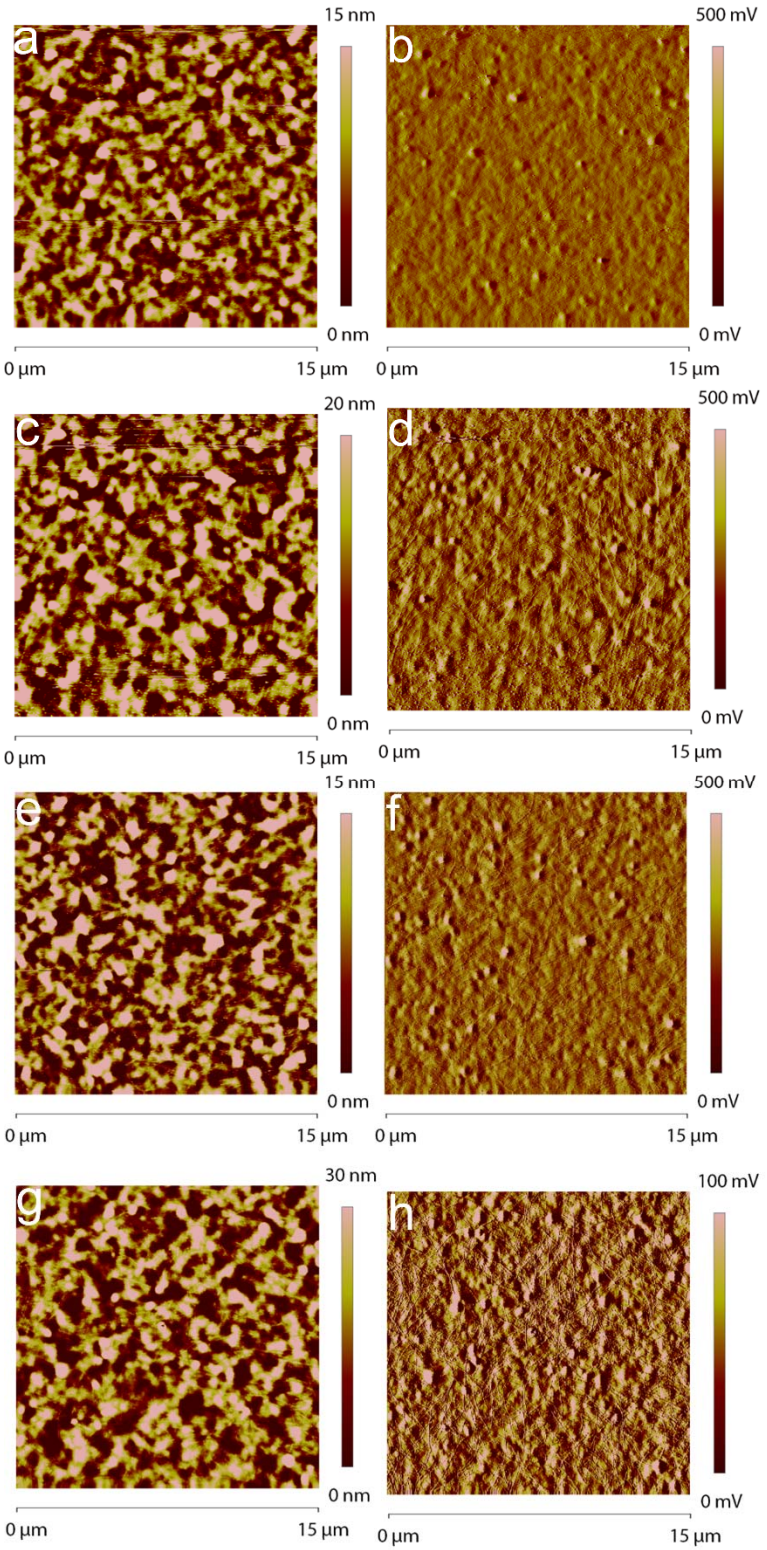

Fig. S3. AFM images of PMMA/P3HT thin films on SiO_2/ZnO/$CH_3NH_3PbI_3$/P3HT substrates with different PMMA/P3HT ratios: (a) 95:5, height image; (b) 95:5, phase image; (c) 90:10, height image; (d) 90:10, phase image; (e) 85:15, height image; (f) 85:15, phase image; (g) 80:20, height image; (h) 80:20, phase image.

Table S1. Average device performance parameters for ITO/ZnO/$CH_3NH_3PbI_3$/HTLs/Ag devices. The associated uncertainties represent plus-or-minus one standard deviation from the mean.

HTLs	**# of devices**	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	**Fill Factor (%)**	**PCE (%)**	**Best Efficiency (%)**
PMMA/P3HT 80:20	60	0.89 ± 0.06	16 ± 1	48 ± 5	6.8 ± 0.7	8.4
PMMA/P3HT 85:15	60	0.92 ± 0.04	16 ± 1	49 ± 5	7.5 ± 0.9	9.3
PMMA/P3HT 90:10	60	0.92 ± 0.06	16 ± 1	53 ± 6	8.1 ± 0.9	10.6
PMMA/P3HT 95:5	40	0.89 ± 0.04	11 ± 2	41 ± 5	4.2 ± 0.6	5.4
P3HT	30	0.97 ± 0.03	15.8 ± 0.8	62 ± 5	9.1 ± 0.9	11.0

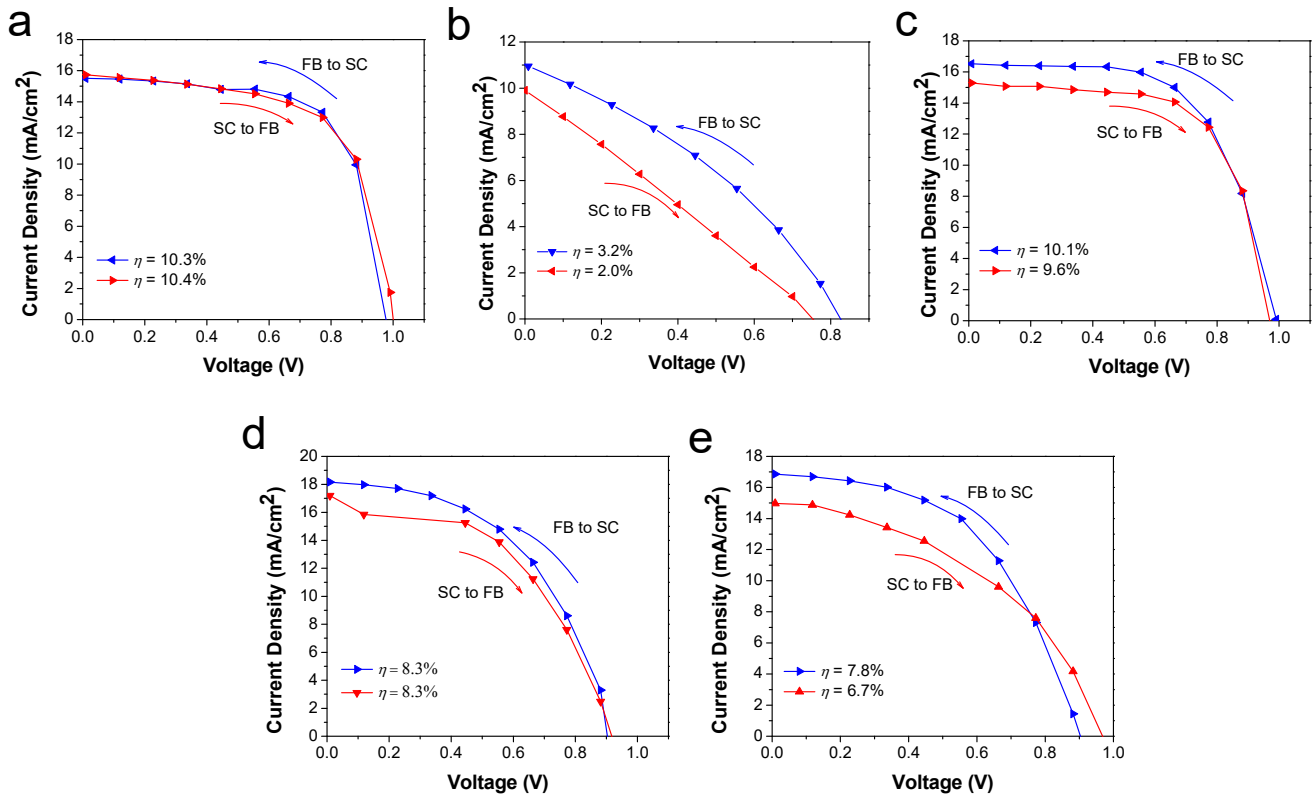

Fig. S4. *J-V* curves in both scan directions for devices with various HTLs: (a) P3HT; (b) 95:5 (c) 90:10, (d) 85:15, (e) 80:20 PMMA/P3HT. *J-V* curves were measured at a scan rate of 0.1 $V \cdot s^{-1}$.

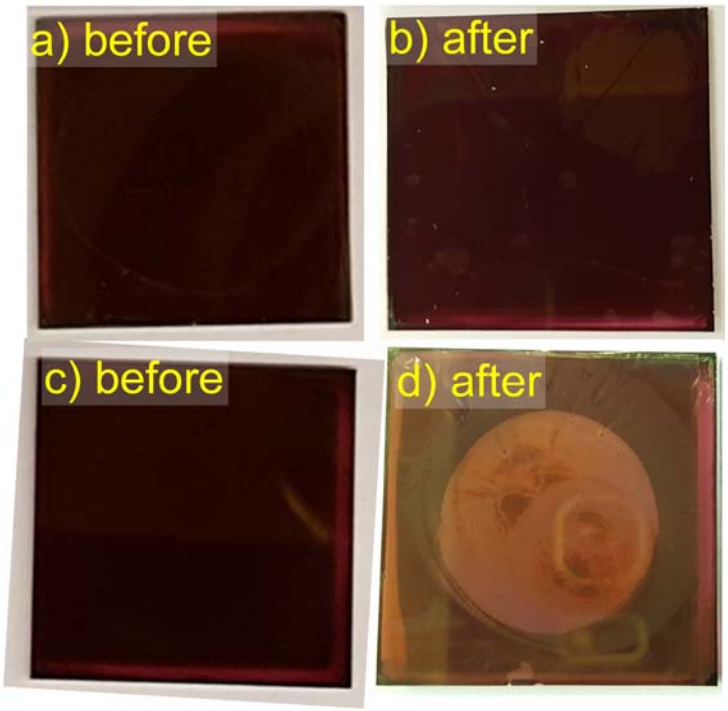

Fig. S5. Photographs of polymer-coated perovskite films exposed to liquid water for 1 minute: (a) 90:10 PMMA/P3HT-coated, before; (b) 90:10 PMMA/P3HT-coated, after; (c) P3HT-coated, before; (d) P3HT-coated, after.

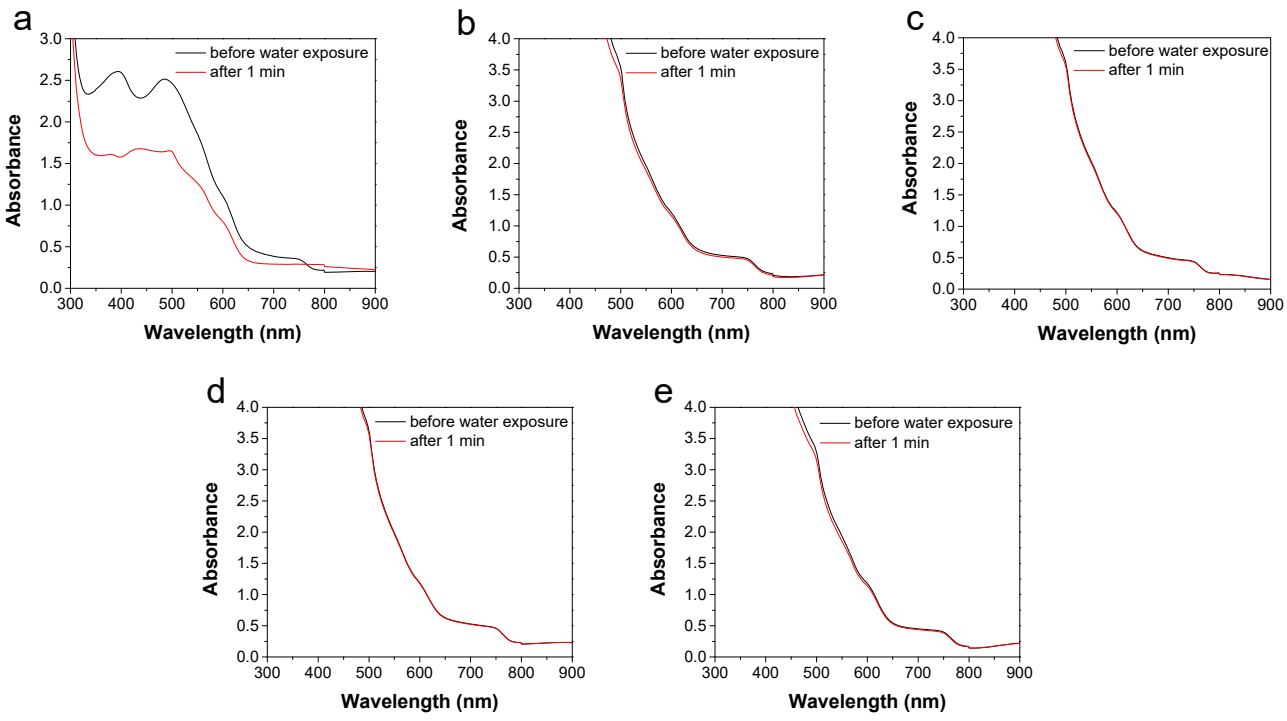

Fig. S6. Absorption spectra of polymer-coated perovskite films, before and after exposure to liquid water for 1 minute: (a) P3HT; (b) 95:5, (c) 90:10, (d) 85:15, and (e) 80:20 PMMA/P3HT.

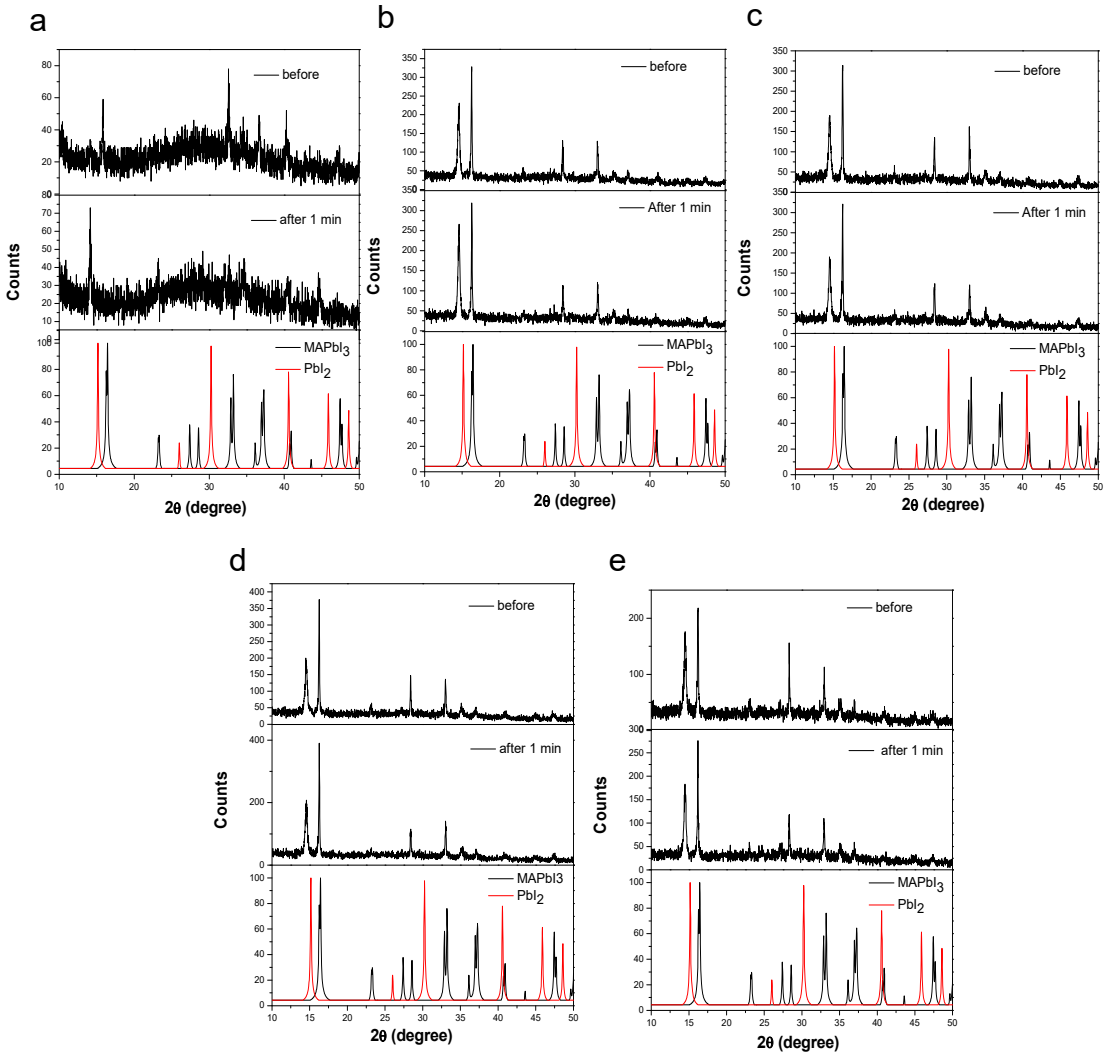

Fig. S7. pXRD patterns of polymer-coated perovskite films, before and after exposure to liquid water for 1 minute: (a) P3HT; (b) 95:5, (c) 90:10, (d) 85:15, and (e) 80:20 PMMA/P3HT.

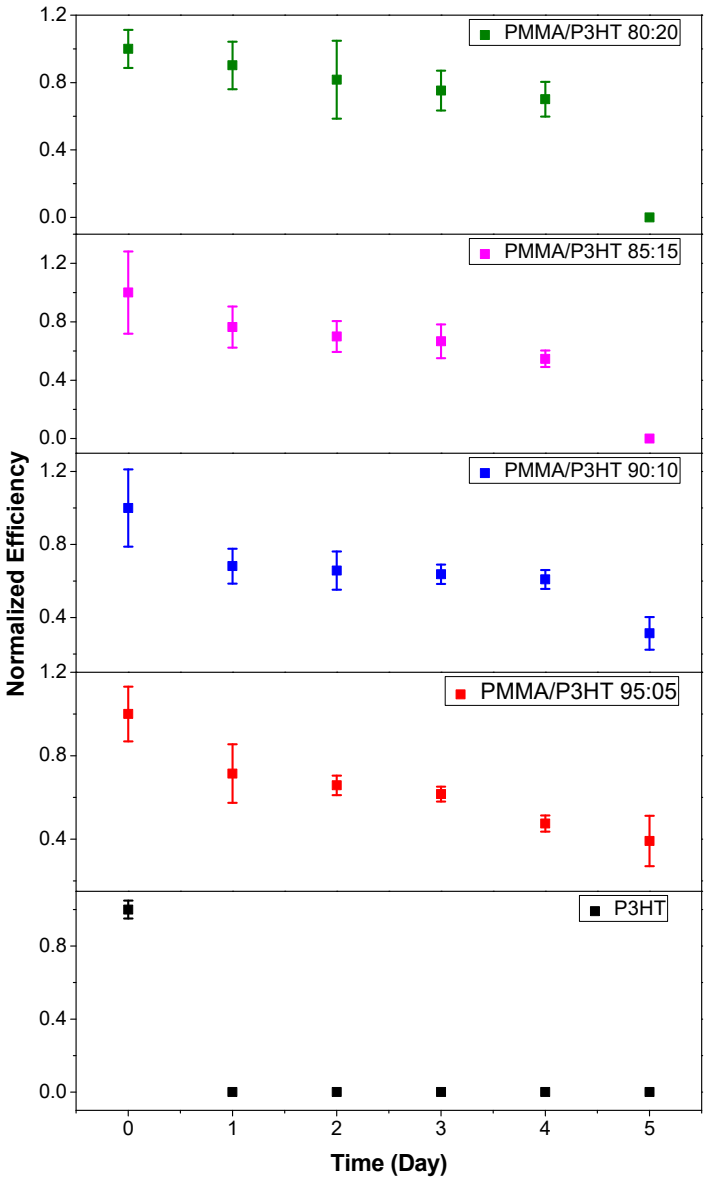

Fig. S8. Normalized power conversion efficiency as a function of time for perovskite solar cells with silver electrodes, stored in a 35-45% RH environment. Error bars denote plus-or-minus one standard deviation from the mean.

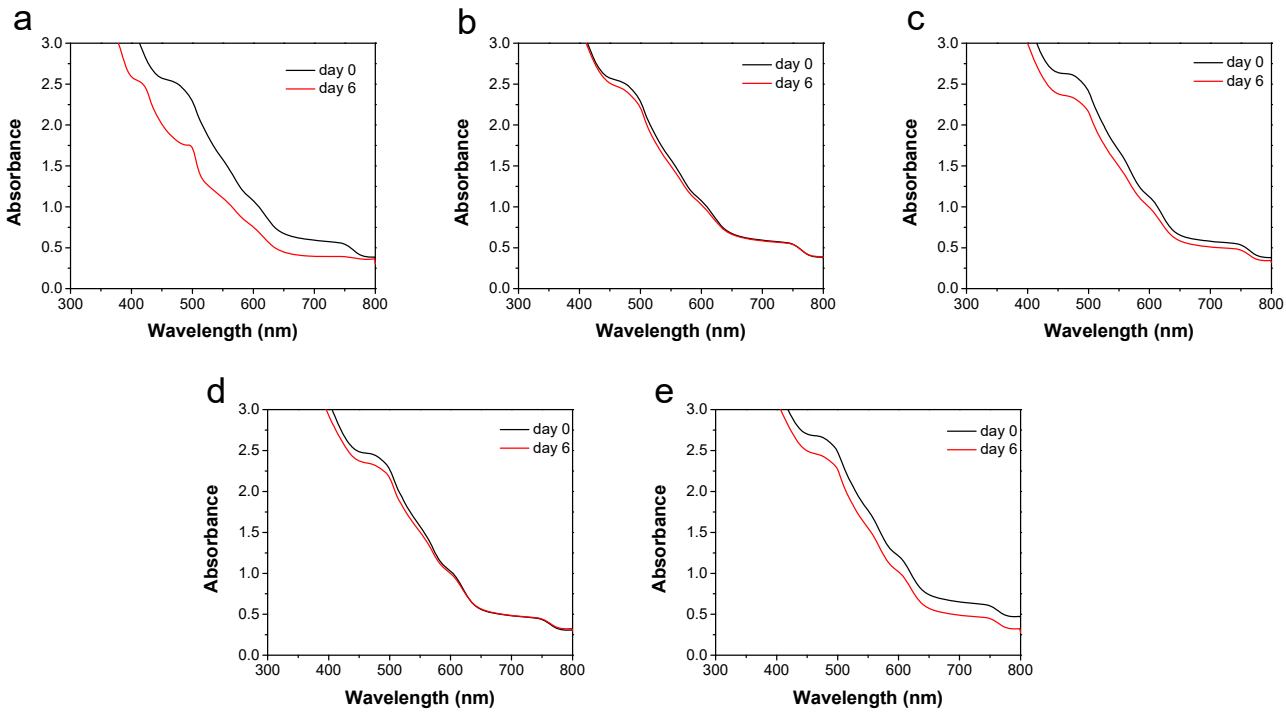

Fig. S9. Absorption spectra of perovskite solar cells with various HTLs before and after aging in air (RH = 35 – 45%): (a) P3HT; (b) 95:5, (c) 90:10, (d) 85:15, and (e) 80:20 PMMA/P3HT.

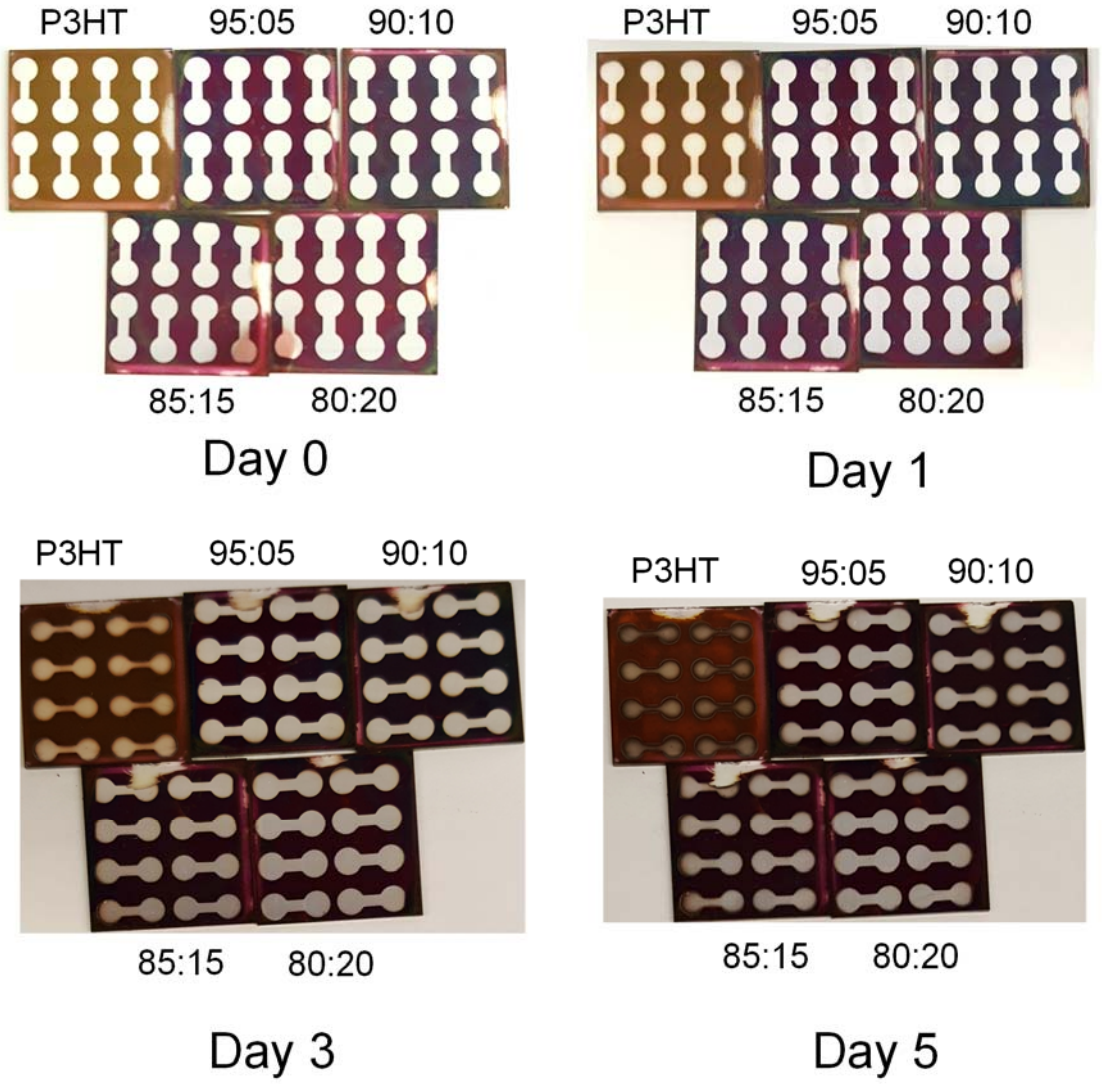

Fig. S10. Photographs of the ITO/ZnO/$CH_3NH_3PbI_3$/HTLs/Ag devices after aging in air; the corrosion of the silver electrode in the P3HT control samples is easily apparent.

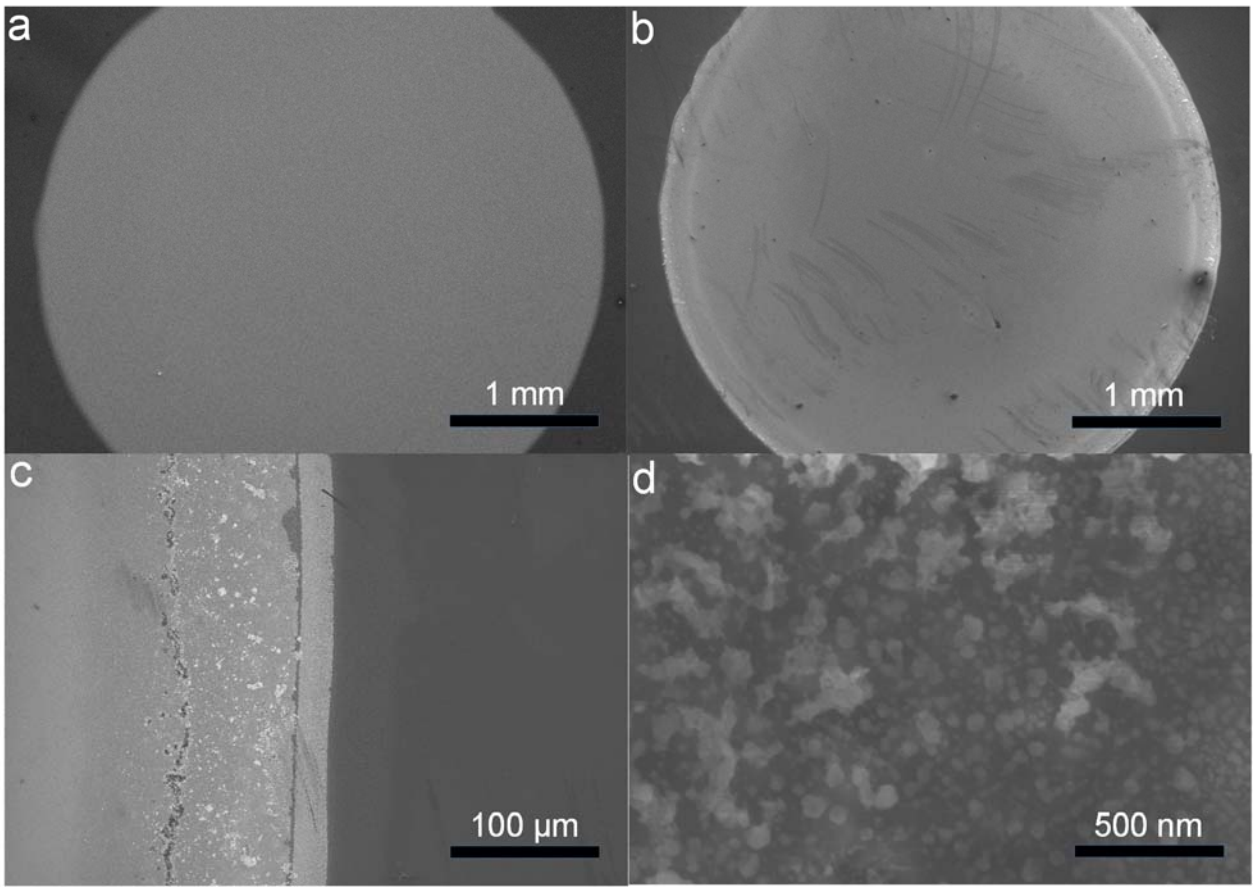

Fig. S11. SEM images of the silver electrode of a P3HT control device: (a) as prepared, and (b-d) after 6 days of aging in air; (c) and (d) are higher magnification images of the electrode edge.

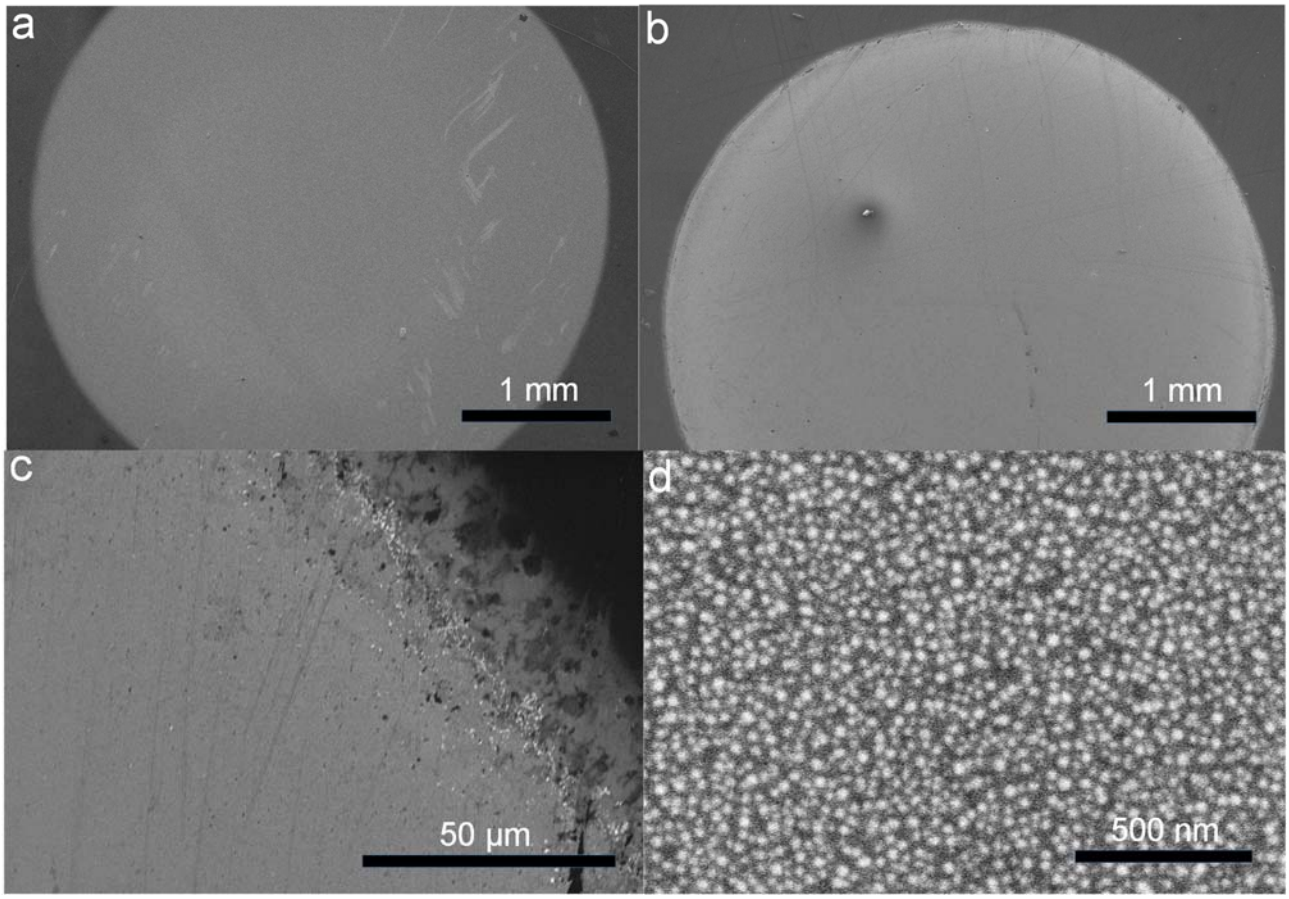

Fig. S12. SEM images of the silver electrode of a 95:5 PMMA/P3HT device: (a) as prepared, (b-d) after 6 days of aging in air; (c) and (d) are higher magnification images of the electrode edge.

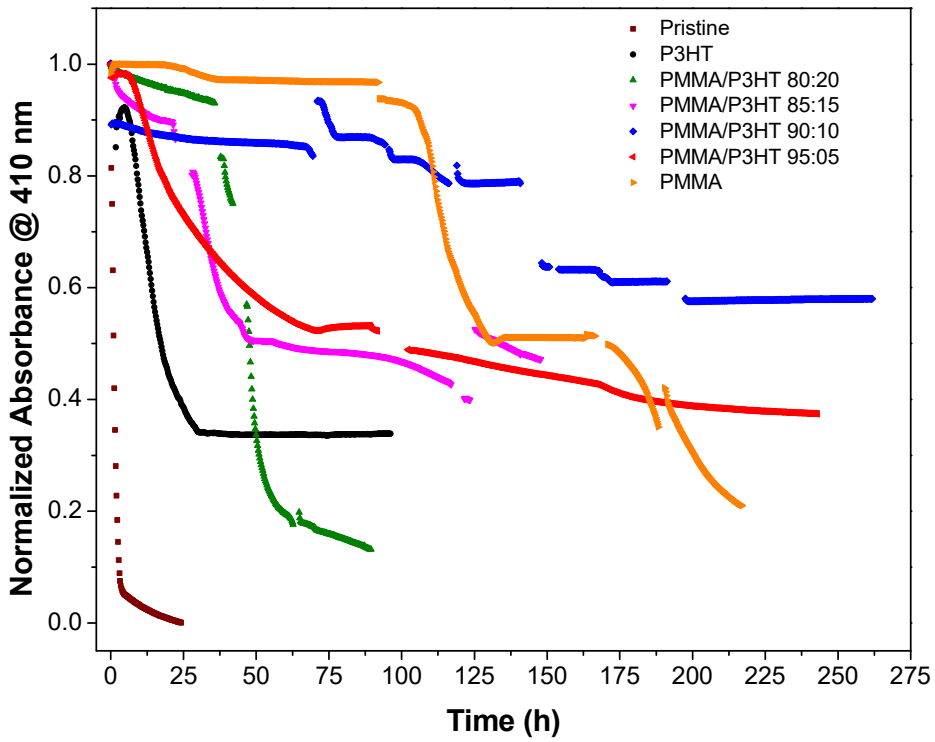

Fig. S13. Normalized absorbance at 410 nm as a function of time for polymer-coated perovskite films exposed to a 99 ± 1% RH environment.

References

1. W. J. E. Beek, M. M. Wienk, M. Kemerink, X. Yang and R. A. J. Janssen, *J. Phys. Chem. B*, 2005, **109**, 9505-9516.
2. D. Liu and T. L. Kelly, *Nat. Photonics*, 2014, **8**, 133-138.
3. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643-647.
4. H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel and N.-G. Park, *Sci. Rep.*, 2012, **2**, 591.