Interface and Grain Boundary Passivation for Efficient and Stable Perovskite Solar Cells: The Effect of Terminal Groups in Hydrophobic Fused Benzothiadiazole-based Organic Semiconductor

Yanbo Gao[a1], Yanjie Wu[a1], Yue Liu[a], Min Lu[a], Lili Yang[b], Yinghui Wang[c], William W. Yu[a,d], Xue Bai*[a], Yu Zhang*[a] and Qilin Dai*[e]

[a] State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun, 130012, China.

E-mail: baix@jlu.edu.cn (X. Bai); yuzhang@jlu.edu.cn (Y. Zhang)

[b] Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Siping 136000, Jilin, China

[c] Femtosecond Laser Laboratory, State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, P. R. China

[d] Department of Chemistry and Physics, Louisiana State University, Shreveport, LA 71115, USA

[e] Department of Chemistry, Physics, and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, USA.

E-mail: qilin.dai@jsums.edu (Q. Dai)

Experimental section

FTO substrates were rinsed by deionized water, ethyl alcohol, acetone, and ethyl alcohol for 20 min and treated under UV-ozone for 15 min. Compact SnO_2 electron transporting layers (ETLs) were prepared by spin-coating aqueous solutions of SnO_2 onto the FTO substrates at 5,000 rpm for 30 s. The perovskite precursor solution was prepared by mixing FAI (172 mg), MABr (22.4 mg), PbBr2 (73.4 mg) and PbI2 (507.1 mg) in a mixed solvent of dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF). Then 40 μL CsI (1.5 mol/L-1 in DMSO) was put into the perovskite solution with ratio of 5:95 (v:v) to obtain the CsFAMA perovskite solution. The perovskite film was fabricated on the SnO2 layer by two spin-coating steps at 600 rpm for 6 s and 4000 rpm for 40 s, respectively. During the second step, 400 uL of chlorobenzene, or BTP-4X in CB at various concentrations was dropped on substrate at 20 s before the end of the spinning process. The concentrations of BTP-4X in chlorobenzene are 0, 1, 3, 5 and 7 mg/mL, respectively. The used BTP-4X organic semiconductors (purity：98%) were purchased from Solarmer Materials Inc and used as received. Then, perovskite film was annealed at 150 °C for 15 min. Spiro-OMeTAD solution was spin coated at 5000 rpm for 30 s onto perovskite layer. Spiro-OMeTAD solution was prepared by dissolving 72.3 mg Spiro-OMeTAD in 1 mL of chlorobenzene with 28.8 μL of 4- tert-butylpyridine and 17.5 μL Li-TFSI in acetonitrile (520 mg/mL). Finally, 100-nm thick Au was deposited on the top of Spiro-OMeTAD by thermal evaporation.

Characterization

Compositions and chemical states of elements of perovskite films were studied by X-ray photoelectron spectroscopy (XPS) (ESCALAB MARK II, VG Inc.) using an Al Kα as X-ray source, with a base pressure of 10^{-8} Pa in the analysis chamber. Crystal structure of samples were characterized by powder X-ray diffraction (Japan Rigaku D/max-ga X-ray diffractometer) using Cu Kα (λ=0.15406 nm). The scan step size was set to 0.02°, and the error is within ±0.0003 nm for lattice constant measurement. The power of XRD is 18 KW. The scanning electron microscope (SEM) and cross sections of the films were characterized by a SIRION field-emission scanning electron microscope. The EDS spectra were carried out by Nova_NanoSEM430. The J-V measurements of devices were taken using a Class A solar simulator (ABET Sun 2000) under a simulated AM1.5G spectrum and 100 mw/cm^2 illumination calibrated with a reference silicon cell (RERA Solutions RR-1002) using a Keithley 2400 as a source-meter. The electrical conductivity is performed by a Keithley 2400 as a source-meter in dark conditions, with current-voltage traces from +2.5 V to -2.5 V. The incident IPCE was performed by SolarCellScan100 (Zolix Instruments, Inc.). Electrochemical impedance spectroscopy (EIS) measurement was performed on a Princeton electrochemical workstation (Parstat Mc Princeton Instruments Co. Ltd., USA) in the frequency range of 0.1–100000 Hz, and the applied bias voltage was set as 0 V, respectively. The photoluminescence (PL) spectrum were performed by the Omni-λ300 Monochromator/Spectrometer of Zolix. The samples for the PL test were excited by a 500 nm laser. Cyclic voltammetry results were obtained with electrochemical workstation using polymer or non-fullerene acceptor films on platinum (1.0 cm^2) as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous argon-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile. Electrochemical onsets were determined at the position where the current started to rise from the baseline.

Table S1 Comparison of device performance parameters for the types and the concentration of small molecules

Devices BTP-4H	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0 mg/ml	23.39	1.116	73.74	19.25
1 mg/ml	23.25	1.125	74.10	19.38
3 mg/ml	23.16	1.136	74.60	19.62
5 mg/ml	23.02	1.148	75.26	19.88
7 mg/ml	22.96	1.110	73.51	18.73

Devices BTP-Cl	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0 mg/ml	23.39	1.116	73.74	19.25
1 mg/ml	23.46	1.142	74.56	19.97
3 mg/ml	23.62	1.153	75.78	20.63
5 mg/ml	23.79	1.160	76.06	20.99
7 mg/ml	23.70	1.120	74.05	19.65

Devices BTP-4F	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0 mg/ml	23.39	1.116	73.74	19.25
1 mg/ml	23.78	1.130	75.44	20.27
3 mg/ml	24.21	1.154	77.40	21.62
5 mg/ml	24.39	1.160	78.32	22.16
7 mg/ml	24.05	1.110	76.50	20.42

Table S2. Summary of application of organic materials in PSCs.

organic materials	PCE (%) (With organic material)	PCE (%) (Without organic material)	Ref.
4-aminobenzonitrile	21.02	20.22	47
2,5-di(thiophen-2-yl) terephthalic acid	21.45	19.1	48
OTG3	13.32	11.62	49
IT-4F	18.35	15.59	50
methimazole	20.10	17.62	4
phenothiazine,	15.50	14.38	51
BTP-4F	22.16	19.25	This work

Table S3 The hysteresis indexes for device modified with BTP-4X.

Devices	Forward	Reverse	Hysteresis index
Control	15.60	19.25	0.1896
BTP-4H	18.82	19.87	0.0528
BTP-4Cl	20.21	20.99	0.0371
BTP-4F	21.51	22.16	0.0293

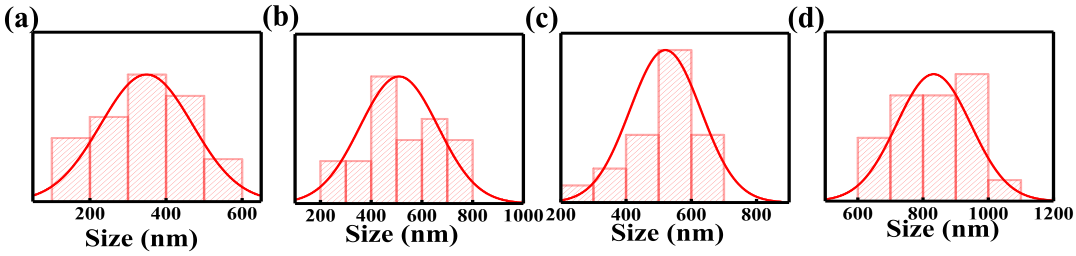

Figure S1 the grain size distribution of perovskite films without and with different small molecular additive. a) Control, b) BTP-4H, c) BTP-4Cl, d) BTP-4F.

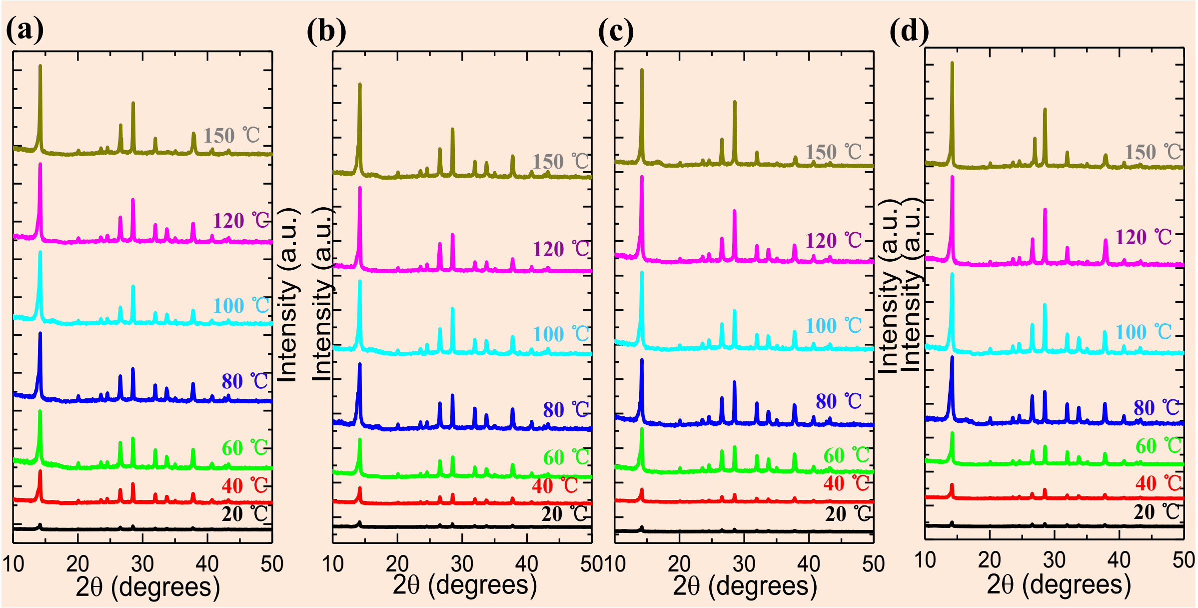

Figure S2 Temperature-dependent XRD data of the perovskite films modified with different organic molecules (e) Control perovskite film, (f) The perovskite films modified with BTP-4H, (g) The perovskite films modified with BTP-4Cl, (h) The perovskite films modified with BTP-4F.

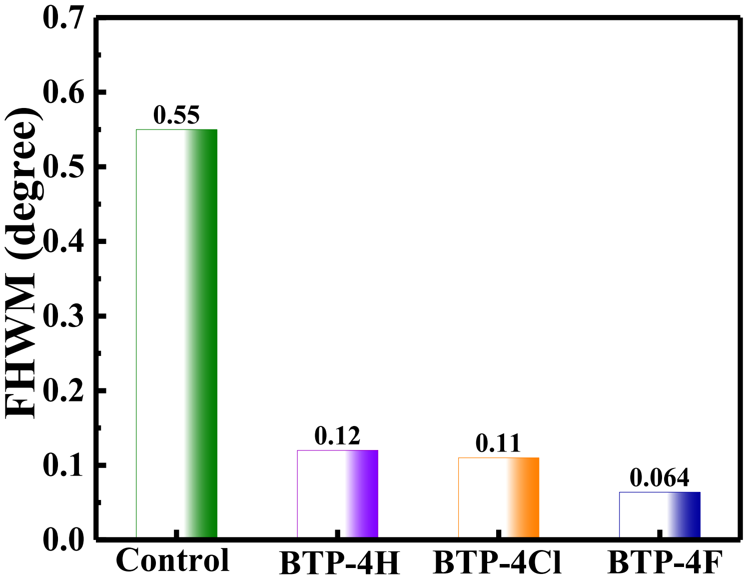

Figure S3 FWHM of the control CsFAMA film and the film with different small molecular additive.

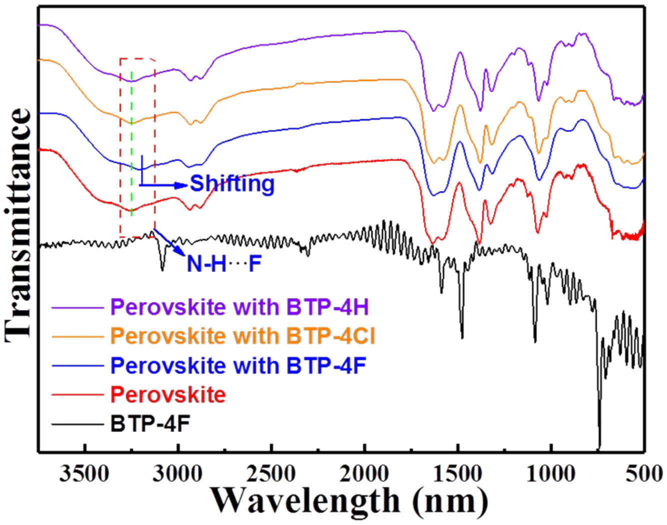

Figure S4 FTIR spectra of BTP-4F, perovskite film and perovskite films with BTP-4H, BTP-4F and BTP-4Cl.

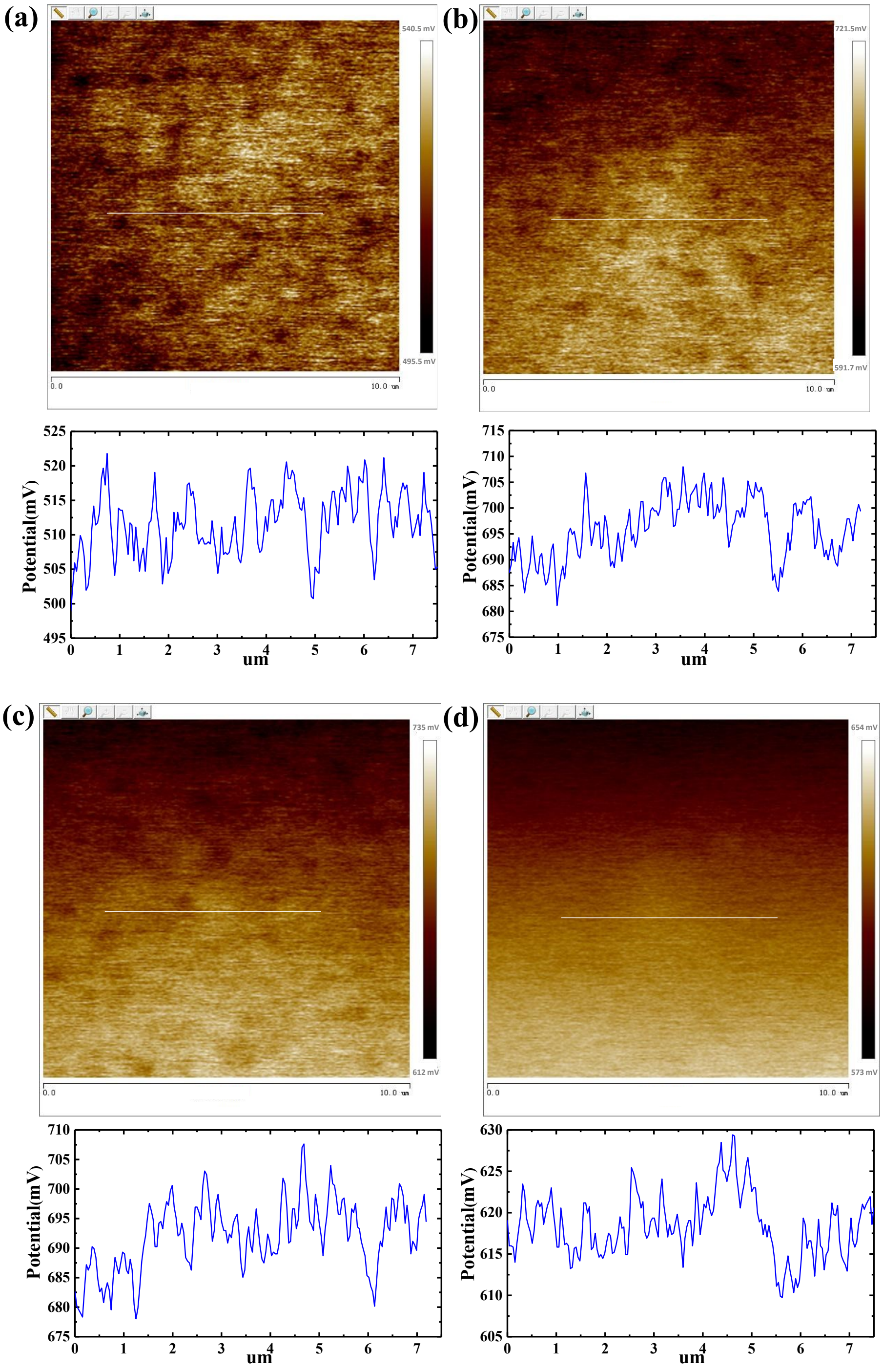

Figure S5 KPFM image of the control CsFAMA film and the film with different small molecular additive.a) Control, b) BTP-4H, c) BTP-4Cl, d) BTP-4F.

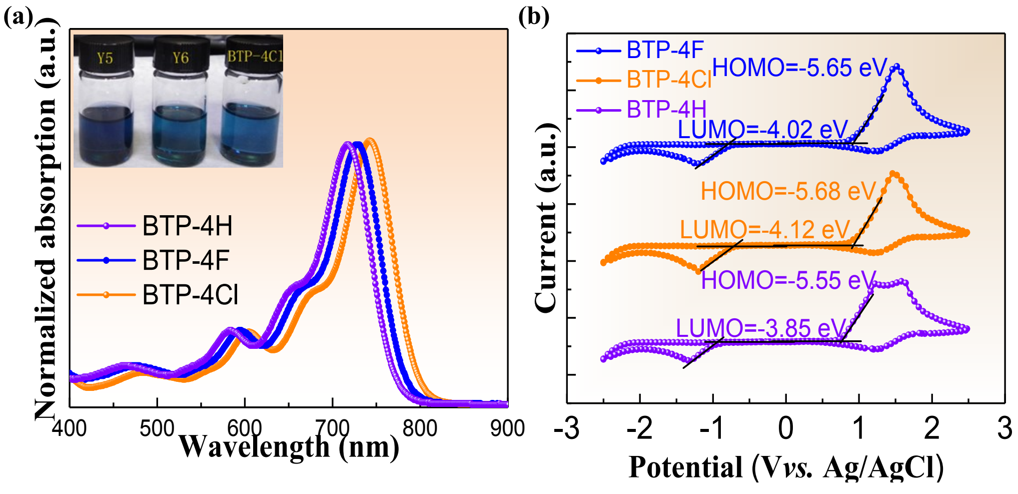

Figure S6 (a) Absorption spectra of BTP-4X in chloroform solution. (b) Cyclic voltammogram of BTP-4X in acetonitrile solution with 0.1 M Bu_4PF_6 as the supporting electrolyte.

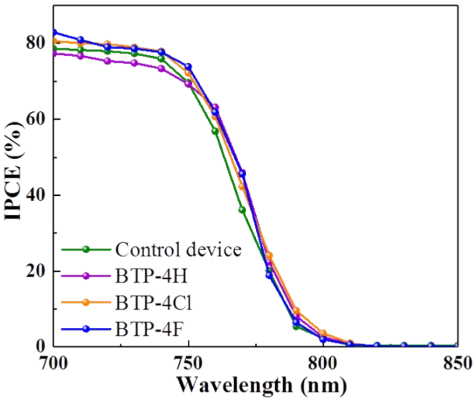

Figure S7 the IPCE spectra ranging of 700-850 nm of PSCs modified without and with BTP-4X ranging of 750-850 nm.

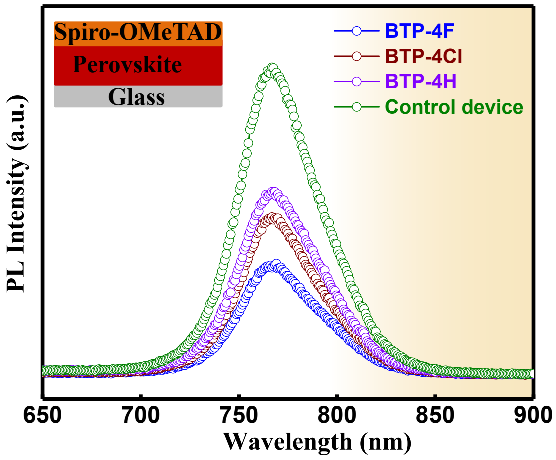

Figure S8 The PL of perovskite film with different additives.

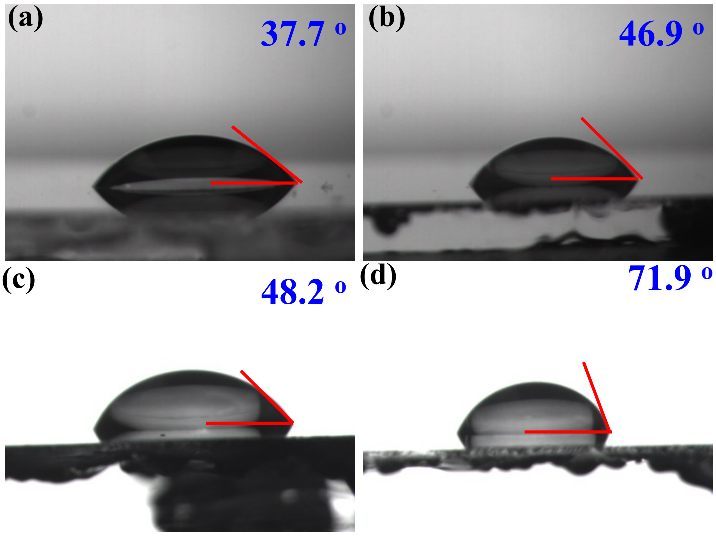

Figure S9 The images of water droplet contact angles on surfaces of pristine perovskite (a), perovskite films with BTP-4H additive (b), perovskite films with BTP-4Cl additive (c) and perovskite films with BTP-4F additive (d).

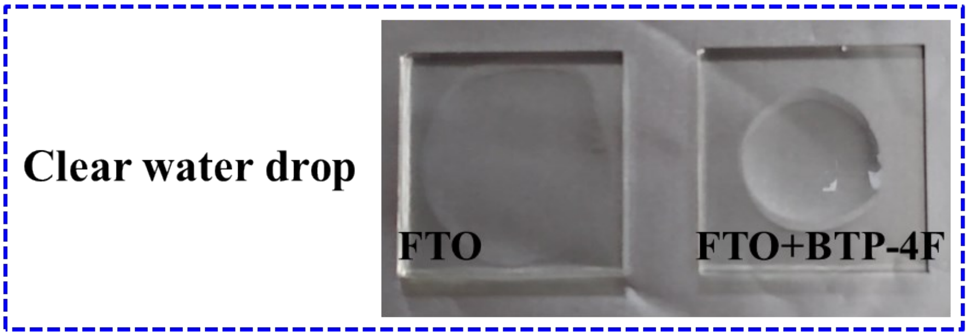

Figure S10 the photographs of FTO and FTO with BTP-4F.

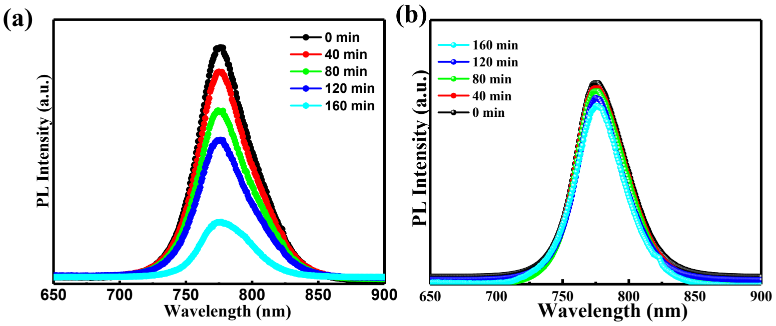

Figure S11 The PLof perovskite film without and with BTP-4F additives.

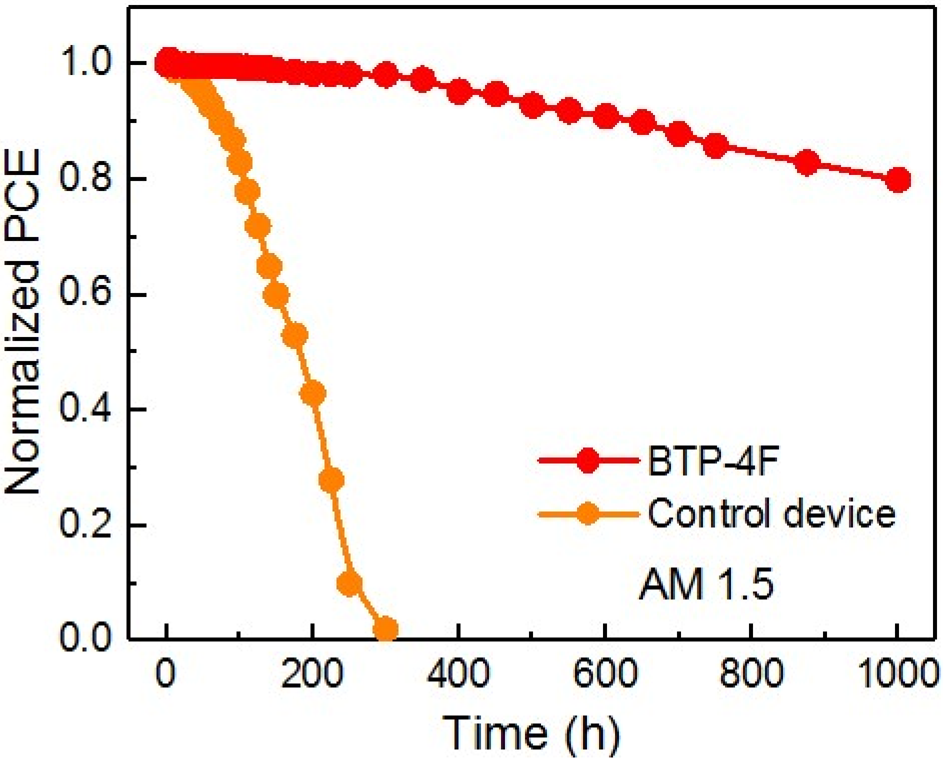

Figure S12 Light stability of devices aged under continuous AM 1.5 light soaking.