Influence of pyridine-based ligands on photostability of MAPbI₃ thin films

Mayuribala Mangrulkar, Sergey Yu. Luchkin, Aleksandra G. Boldyreva, Pavel A. Troshin and Keith J. Stevenson

Experimental Setup

Materials:

N, N dimethylformamide (DMF, anhydrous, 99.99%), Aqueous Tin oxide (15% concentration), Toluene and Ethyl acetate were purchased from Sigma-Aldrich and used as received. PCBA, PTA, MAI, PbI_2 and bathophenanthroline (**1**), 4,4'-bipyridine (**2**), 4-hydroxy-1,10-phenanthroline (**3**), bathocuproine (**4**), 8-hydroxyquinoline (**5**) and 1,10-phenanthroline (**6**) powders were used.

Preparation of Precursor Solutions:

To prepare thin films, 0.3M solution of MAPbI₃ combined with additives **1–6** was used. Here additives were added by 5%, percentage by weight. Further, 1.4M solution of MAPbI₃ was used to prepare devices. Later, additive **2** was added into the precursor solution and filtered with 0.45um PTFE filters. Filtered solutions were used for film and device fabrication and characterisation.

Film and Device Preparation:

Film Preparation:

Glass substrates were cut into 25 mm* 25 mm size and cleaned. Deionised water, acetone and isopropanol were used to give an ultra-sonication bath for 15 minutes in this particular sequence for cleaning substrates. Upon cleaning, substrates were plasma treated for 5 minutes. Then, transferred into Argon filled glovebox. Perovskite film on glass substrate was spun at 3000 rpm and annealed at 100℃ for a minute. These perovskite films were further used to conduct thin-film photostability test.

Device preparation:

Glass substrates coated with Indium Tin Oxide(ITO) were cut into 25 mm* 25 mm size and cleaned. Deionised water, acetone and isopropanol were used to give an ultra-sonication bath for 15 minutes to clean the ITO substrates in this particular sequence. Upon cleaning, substrates were plasma treated for 5 minutes. Then immediately spin-coated with SnO_2 at 4000 rpm. This SnO_2 solution was made by adding deionised water to dilute the concentration of tin oxide from 15 % to 10 %. Water was added in the ratio of 2:1. Further, this solution was ultra-sonicated for 5 minutes and filtered using a 0.45um PES filter. Filtered solution was used to spin coat on cleaned substrates. Upon spin coating samples were annealed at 170℃ for 15 minutes and transferred into the glovebox. In the glovebox, these substrates were heated at 150 ℃ for 10 minutes. All the subsequent layers after SnO_2 was spin-coated in Ar filled glovebox. Inside the glove box, first, PCBA (0.6 mg/ml in toluene) was spun at 3000 rpm and annealed for 5 minutes at 100℃. Further perovskite layers were spun at 4000 rpm. For the perovskite layer, the one-step spin coating was used, toluene was dropped after 20 seconds. These films were further annealed at 100 ℃ for 10 minutes. PTA (6 mg /ml in toluene) was spun on the perovskite layer at 3000 rpm. Then, polystyrene (PS) (0.4 mg/ml in ethyl acetate) was spun at 2000 rpm. Then, MoO_3 (10 nm) and Silver (100 nm) electrodes were thermally evaporated. These solar cells were used to examine device performance.

Thin Film Characterisation:

To explicitly understand the impact of the additives **1–6** in MAPbI₃ onto intrinsic photostability; the ageing of thin films was performed under the inert glovebox environment (H_2O <0.1ppm and O_2< 0.1 ppm). So that degradation due to moisture and air can be minimalised. For the ageing experiment, MAPbI₃ thin films with additives were

illuminated under the light intensity of 70-80 mW cm^{-2} around 50-60˚C up to 1400 h inside the glovebox. UV-Vis spectra were measured using AvaSpec-2048-2 UV–Vis fibre spectrometer integrated inside the glove box.

X-ray diffraction patterns were measured using a Bruker D8 Advance powder diffractometer (Cu-K$_\alpha$ radiation, 5-60° 2 theta range, 0.0219° increment step). Measurements were carried out in fixed illumination mode with no sample rotation. The time interval of 0.2 seconds, voltage 40kV, filament current 40 mA was used for all the measurements.

PL measurements were carried out using Automatic Research GmbH LBIC+PL+EL microscopy setup with Horiba spectrometer. All samples were measured with 532 nm laser wavelength at 0.05s integration time, 0.5 slit-width.

AFM topography images were obtained in a semicontact mode using Cypher ES atomic force microscope installed in an Ar-filled glovebox. We used single crystal diamond probes (HA_NC/FD) in order to reduce sticking of material from the photodegraded samples to the tip and hence avoid imaging artefacts

FTIR spectra were obtained using Bruker Alpha II with ATR module (diamond crystal).

Device Characterisation:

Current-Voltage measurements were performed under AM 1.5G (100 mW cm^{-2}) illumination solar simulator inside the glovebox. This instrument is provided by a Newport Verasol AAA class solar simulator. The intensity of the illumination was checked before each measurement using a calibrated silicon diode with known spectral responses. The *J-V* curves of all devices were measured while applying a metal mask with a 0.041 cm^2 window using the Advantest 6240A Source measurement units.
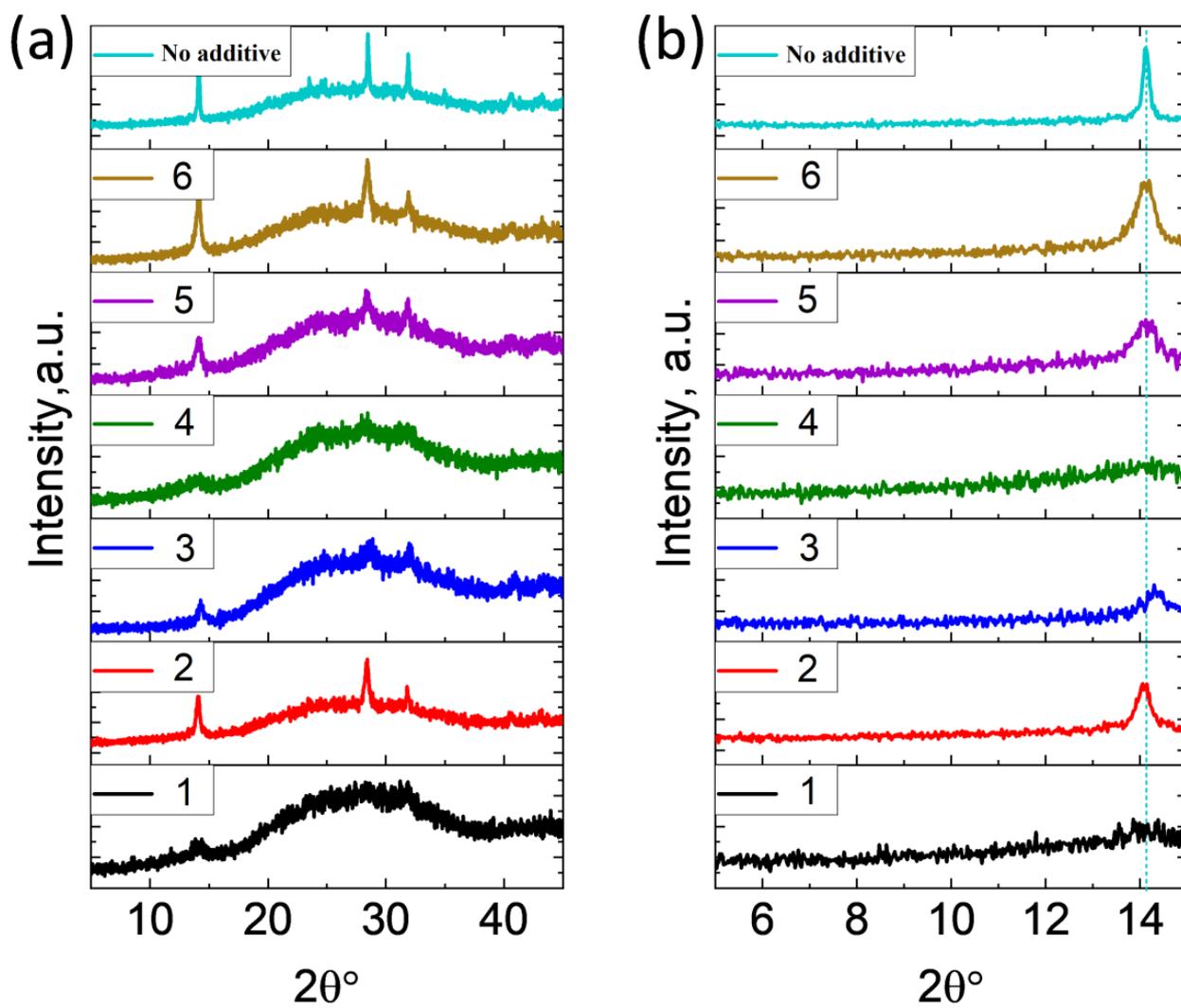
Figure S1 (*a*) XRD patterns of MAPbI$_3$ films with additives **1**–**6**. (*b*) Zoomed XRD patterns from 5˚ to 15˚
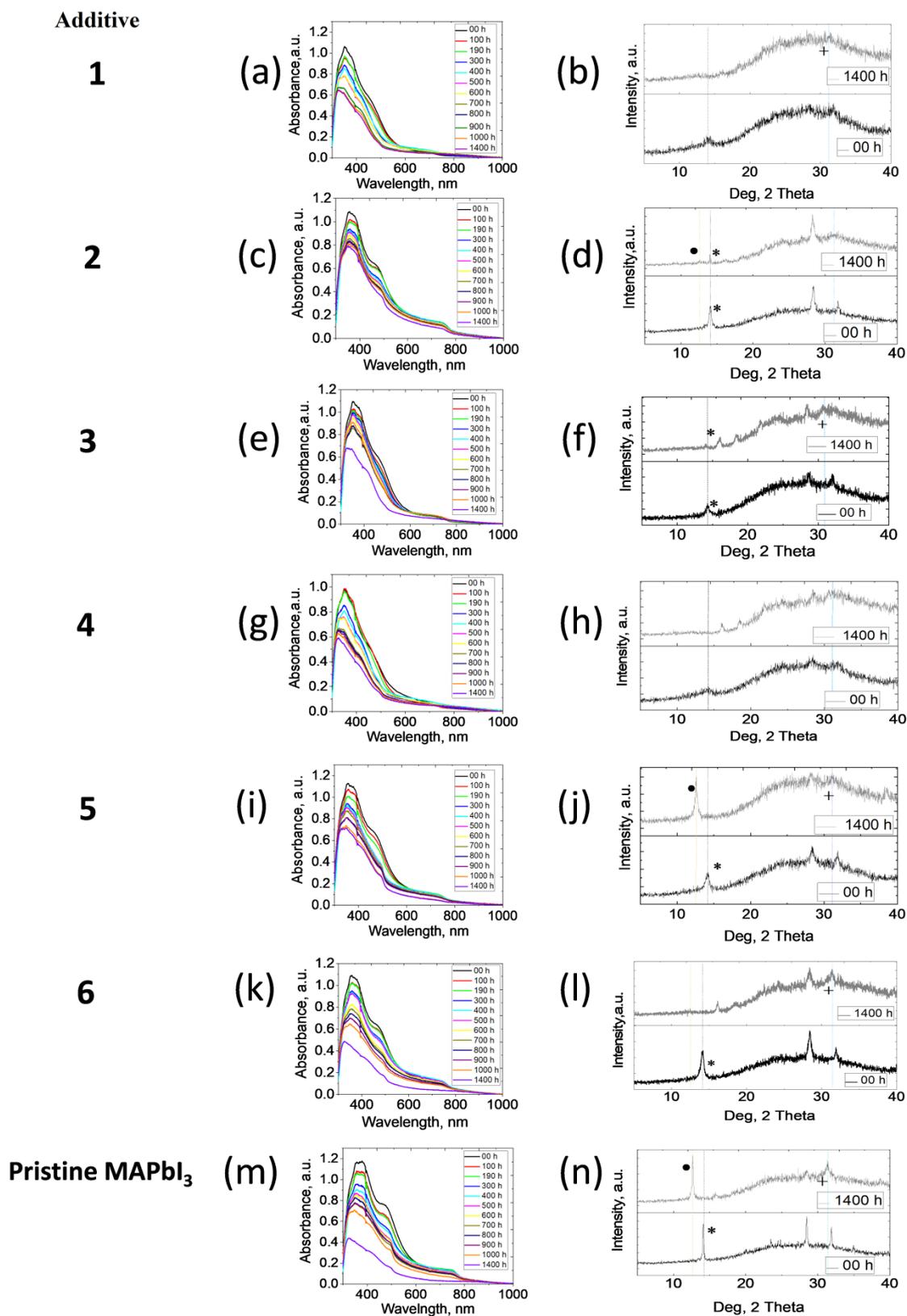
Figure S2 Evolution of UV-VIS spectra and XRD patterns of (*a*),(*b*) MAPbI$_3$+(**1**), (*c*),(*d*) MAPbI$_3$+(**2**), (*e*),(*f*) MAPbI$_3$+(**3**), (*g*),(*h*) MAPbI$_3$+(**4**), (*i*),(*j*) MAPbI$_3$+(**5**), (*k*),(*l*) MAPbI$_3$+(6) and (*m*),(*n*) pristine MAPbI$_3$, respectively. * presents perovskite, · presents PbI$_2$ and + presents Pb.
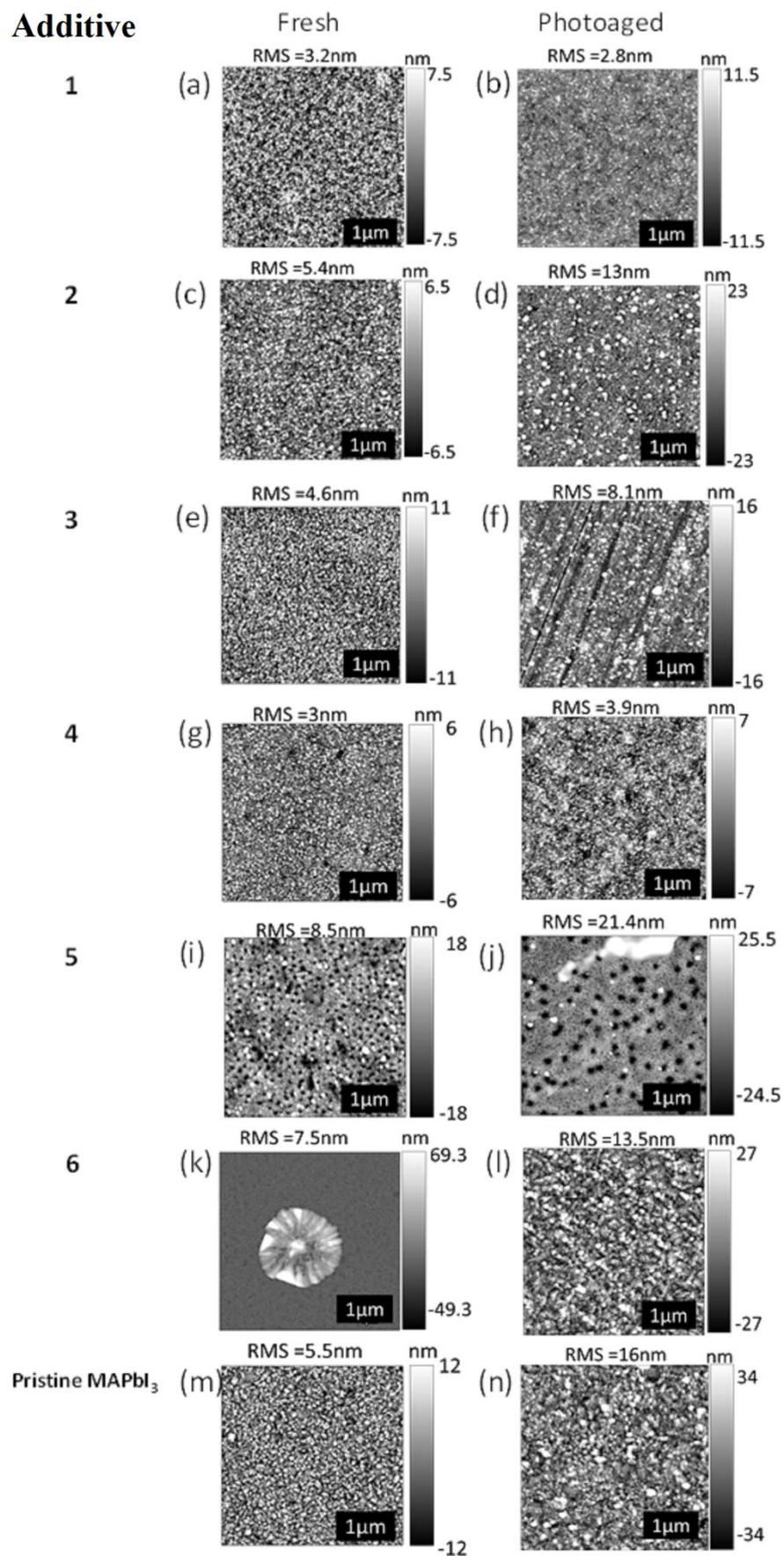
Figure S3 Comparison of morphology of MAPbI$_3$ films with additives **1–6**. AFM images of fresh and photoaged film with additives **1–6**.
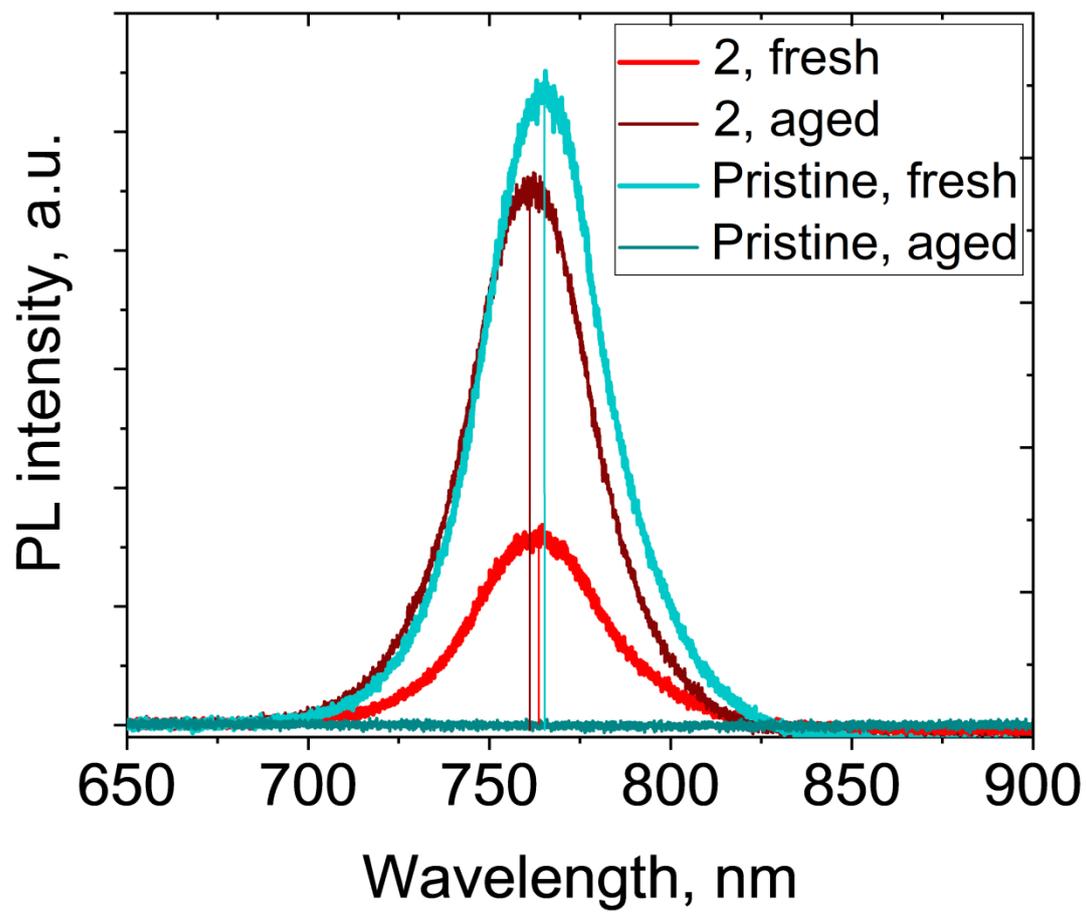
Figure S4 PL emission spectra of fresh and photoaged films with and without additive **2** in MAPbI$_3$.
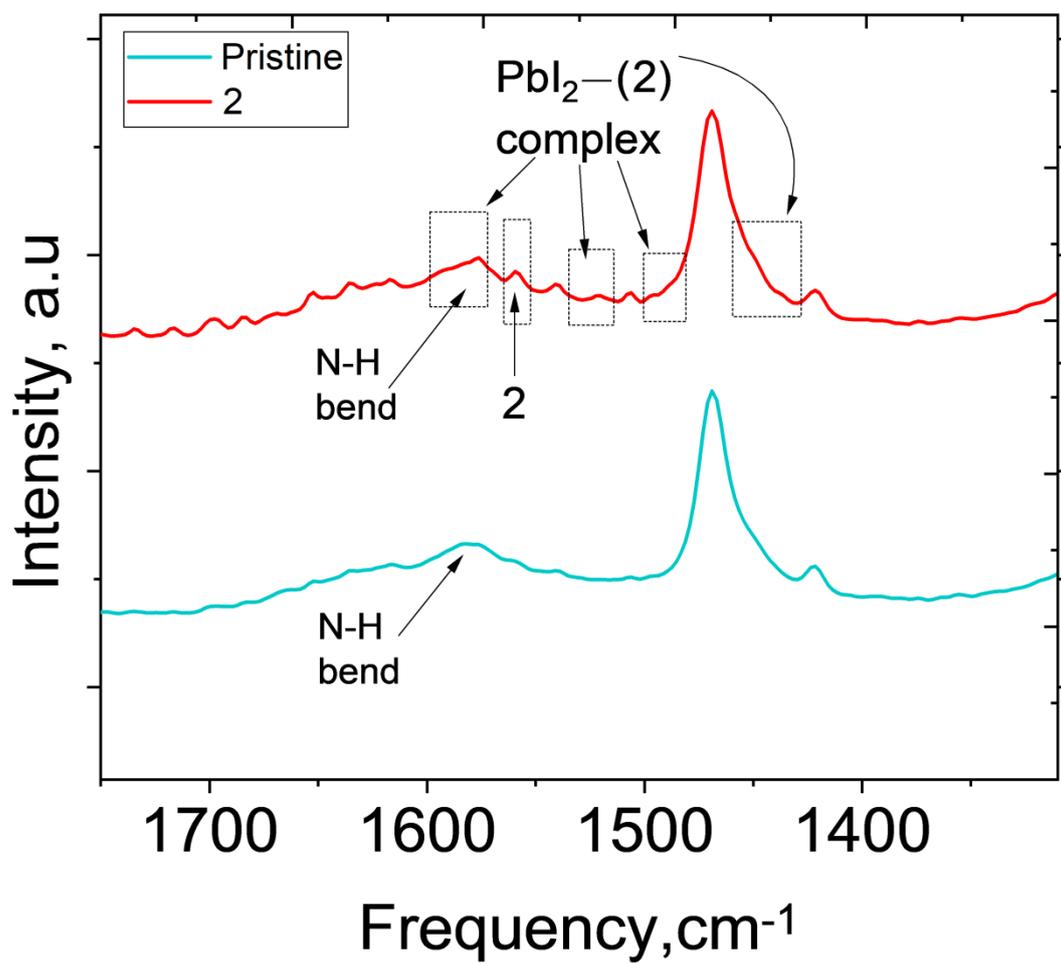
Figure S5 Zoomed FTIR spectra showing complex formation upon the addition of compound **2** in fresh film.
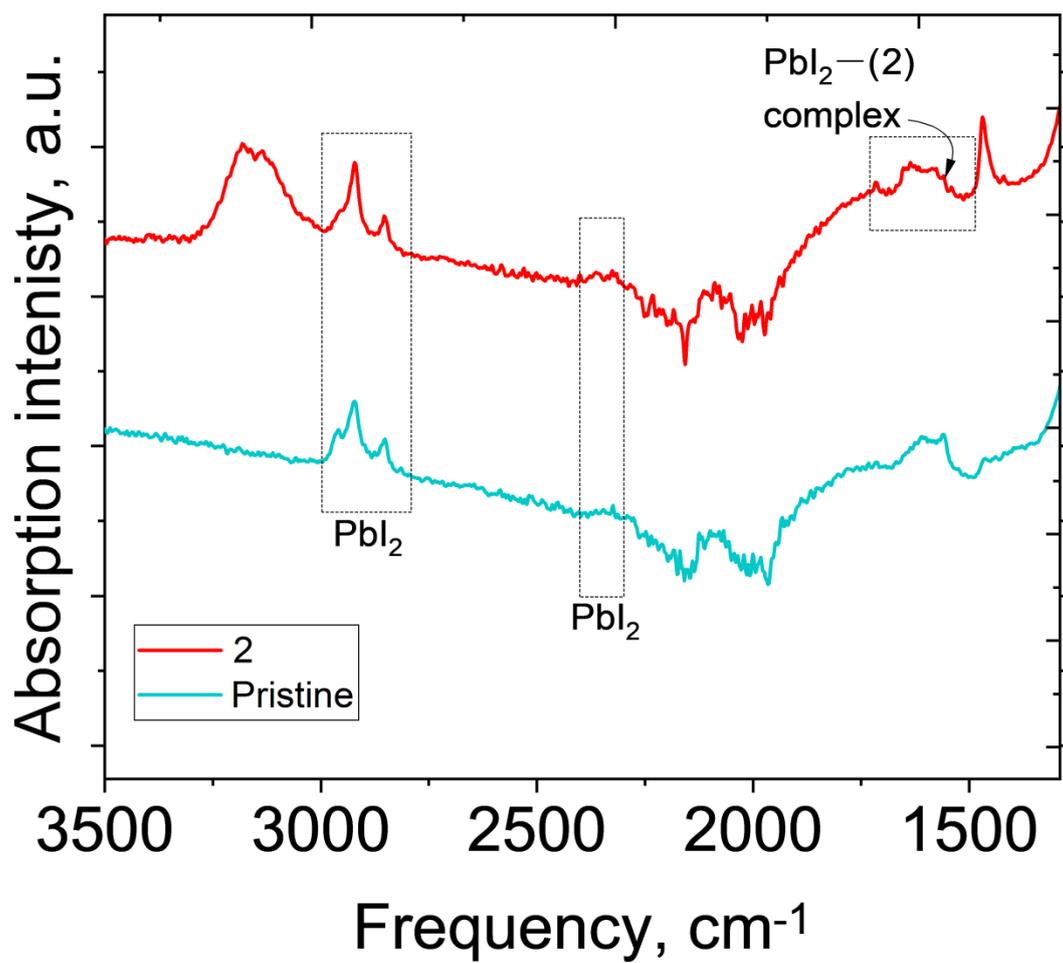
Figure S6 FTIR spectra of photoaged films of pristine $MAPbI_3$ and $MAPbI_3$+(**2**).
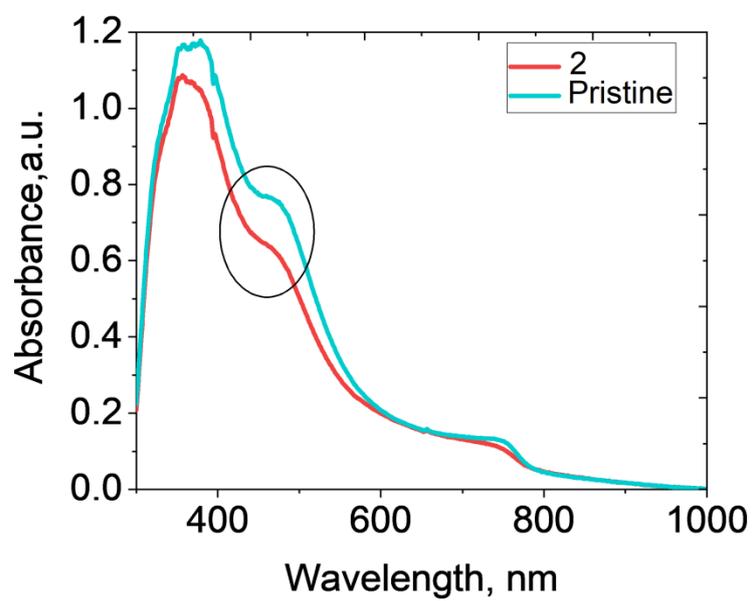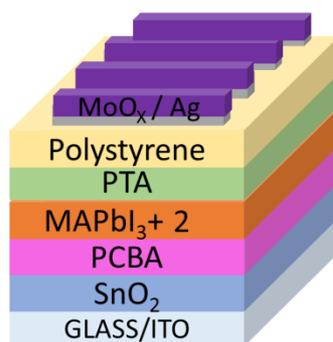
Figure S7 Absorbance reduction and wavelength shift of absorbance edge near 500 nm upon the addition of compound **2** to MAPbI$_3$.
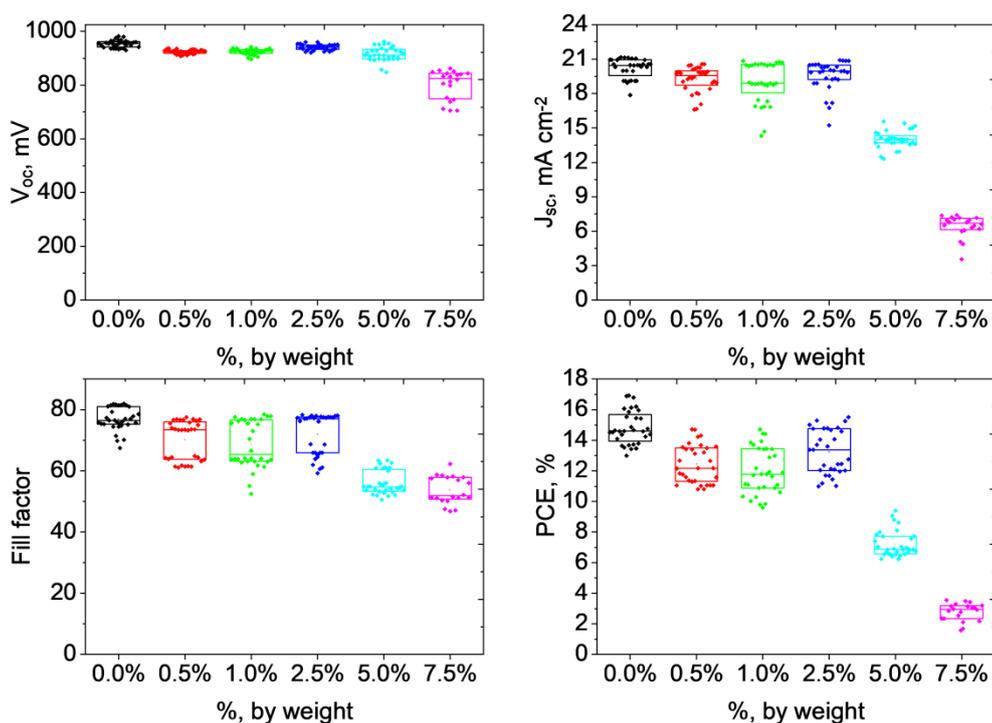
(a)

(b)

Figure S8 (*a*) Device architecture. (*b*) Impact of the addition of compound **2** on photovoltaic parameters.

Table S1 Dependence of best and average *J–V* parameters of the MAPbI$_3$+(**2**)-based solar cells on the concentration of additive **2**.

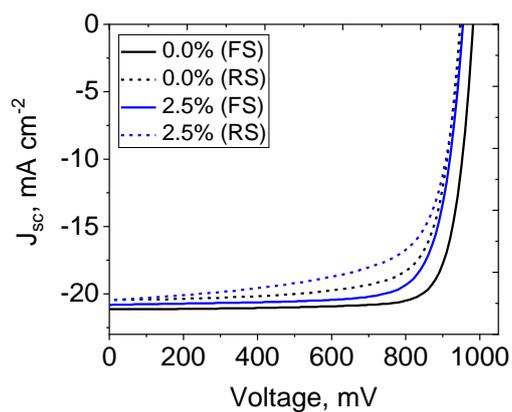| Concentration of 2		V$_{oc}$/mV	J$_{sc}$/mA cm^{-2}	Fill factor	PCE (%)
0%	**Best**	**981.84**	**21.13**	**81.52**	**16.91**
	Avg	953.40±13.73	20.20±0.84	76.87±3.78	14.8±1.09
0.5%	**Best**	934.08	20.56	76.62	14.72
	Avg	923.32±7.57	19.23±1.10	70.17±6.32	12.45±1.24
1%	**Best**	936.70	20.53	76.53	14.72
	Avg	923.89±10.71	18.98±1.79	68.64±7.70	12.00±1.53
2.5%	**Best**	**954.34**	**20.83**	**77.94**	**15.49**
	Avg	940.85±10.63	19.54±1.34	71.98±6.79	13.22±1.45
5%	**Best**	962.52	15.4	63.40	9.39
	Avg	916.04±26.49	14±0.75	56.02±3.85	7.20±0.85
7.5%	**Best**	862.17	7.16	57.52	3.55
	Avg	802.14±54.38	6.42±0.96	53.71±4.55	2.78±0.57

Figure S9 *J–V* curves of pristine MAPbI$_3$ and the best-PCE MAPbI$_3$ with 2.5% of additive **2**.

Table S2 *J–V* characteristics and hysteresis factor of the best solar cells made of pristine MAPbI$_3$ or 2.5% MAPbI$_3$+(**2**).

Concentration of 2	V$_{oc}$/mV	J$_{sc}$/mA cm^{-2}	Fill factor	PCE (%)	Hysteresis factor (HF)
0.0% (FS)	981.84	21.13	81.52	16.91	**0.1574**
0.0% (RS)	946.81	20.43	75.78	14.61	
2.5% (FS)	954.34	20.83	77.94	15.49	**0.1568**
2.5% (RS)	953.36	20.46	68.60	13.39	