

## Supporting Information

# Functionalized polyamide acid additive for perovskite solar cells with high efficiency and stability

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## Experimental section

### 1. Materials

Lead (II) iodide (PbI<sub>2</sub>), [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and Poly [bis (4-phenyl) (2,4,6-trimethylphenyl)amine] (PTAA) were purchased from Xi'an p-OLED. The methylamine Hydroiodide (MAI) and Bathocuproine (BCP) were purchased from TCI. The N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB) were purchased from Sigma-aldrich. The isopropanol (IPA) were purchased from Macklin. Methylbenzene (TL) and acetone were acquired from Sinopharm. All purchased chemicals were used as received without further purification.

### 2. Fabrication of Perovskite solution

The MAPbI<sub>3</sub> precursor solutions were made by mixing PbI<sub>2</sub> and MAI in DMF and DMSO at a stoichiometric ratio of 1.05:1. Subsequently, In MAI:PbI<sub>2</sub> mixed solution, the concentration of PAA are 0.05, 0.1, 0.2 and 0.4 mg mL<sup>-1</sup>. The mixed solution was stirred the night at room temperature inside a nitrogen-filled glovebox with oxygen and moisture levels <0.1 ppm.

### 3. Device fabrication

ITO-coated glass (2 cm × 2 cm) was cleaned by sequential sonication in ultrapure water, acetone and isopropanol for 15 min each and dried in a warm table, and then treated in UV-O<sub>3</sub> atmosphere for 30 min. Put the substrates in a nitrogen-filled glovebox. The PTAA solution was spin-coated on substrate with 3000 r.p.m. for 30 s. The HTL films were then annealed at 110 °C for 10 min. Perovskite precursor solution with different PAA concentrations were spin-coated on the substrate with two processes of 1000 r.p.m. for 5 s and 5000 r.p.m. for 35 s. At 10 s before the end of the last spin-coating step, 150 μL of methylbenzene solvent was added dropwise onto the substrate. The substrates were then placed onto a hotplate at 100 °C for 30 min. The PCBM solution was spin-coated on top of the perovskite by spin coating at 3000 r.p.m. for 30 s. The ETM films were then annealed at 65 °C for 10 min and followed by thermal evaporating under vacuum of 80 nm Argentum electrode on the hole transport layer.

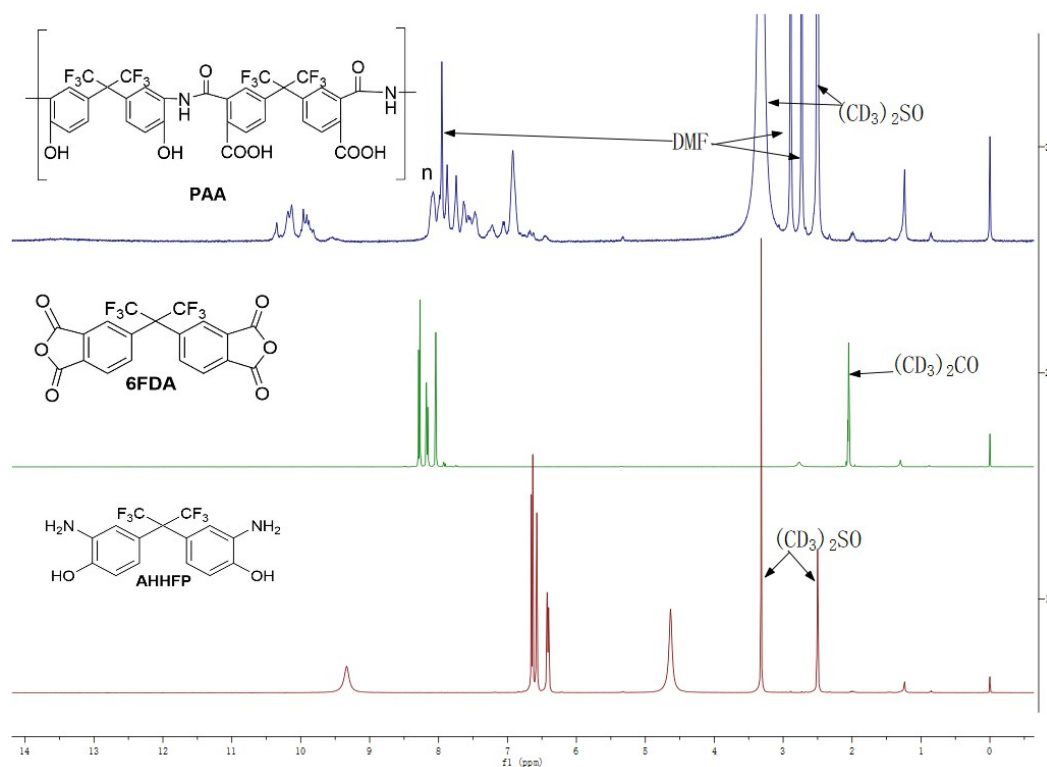
### 4. Device Characterization

*J-V* curves of the perovskite solar cells was measured by using the solar simulator (SS150-LPX150, Zolix) and a source meter (Keysight 2400C, Keysight). The solar simulator with 100 mW cm<sup>-2</sup> illumination AM 1.5G was calibrated by using NREL certified silicon reference cell (SRC-2020). The device area of 0.04 cm<sup>2</sup> was defined by masking a metal mask to avoid light scattering from the metal electrode onto the device during the measurement. External quantum efficiency (EQE) was obtained on a computer-controlled quantum efficiency instrument (QE-R, Enlitech).

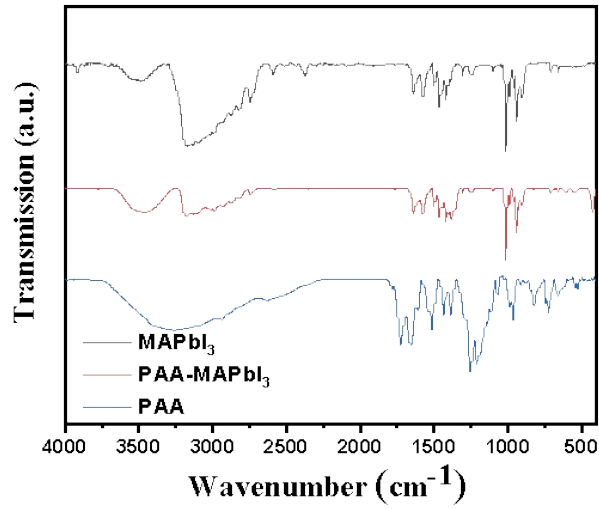
#### 4. Equipments

The UV-vis absorption spectra of deposited films were measured by a spectrophotometer (UV-2700, Japan), in MAI:PbI<sub>2</sub> mixed solution, the concentration of PAA are 0 and 0.2 mg mL<sup>-1</sup>. The XRD patterns of the films with 2θ range from 5° to 45° were obtained from an X-ray diffractometer (TD-3500, Tongda) with Cu Kα radiation. The Photoluminescence (PL) was measured at room temperature on a fluorescence spectrophotometer (FLS980, Edinburgh Instruments), and the steady-state emission was measured under a 785 nm light source excitation using a monochromatized Xe lamp. The time-resolved PL decays (TRPL) were monitored with a picosecond pulsed diode laser excitation source (frequency 1,000,000 Hz and a fluence of ~ 1 nJ cm<sup>-2</sup>) at a wavelength of 445 nm.

The top-view morphology of the perovskite films were observed using a field-emission scanning electron microscope (SEM, SU8220, Japan). Electrochemical impedance spectroscopy (EIS) were conducted by using an Autolab analyzer (Metrohm, PGSTAT 302N, Switzerland) at open-circuit voltage in the dark. Fourier transform infrared (FTIR) spectrum analysis was performed using an FTIR spectrometer (Nicolet 6700, Thermo-Fisher). The X-ray photoelectron spectrum (XPS) was performed using an X-ray photoelectron spectroscopy system (ESCALAB 250Xi, Thermo-Fisher) with Al Kα X-ray radiation (1486.6 eV) as the X-ray source. NMR spectra were recorded at ambient temperature using (Methyl sulfoxide)-d<sub>6</sub> as solvent, with proton, carbon, and fluorine resonances at 400, 100 and 375 MHz, respectively. All NMR data are reported in ppm relative to the solvent signal. The number average, weight average molecular weight range of PAA was observed using a Gel Permeation Chromatography (GPC) (Waters1515, Waters). The contact angle measuring of deposited films were measured by a contact angle measuring instrument. (OCA200, DPIC).



**Fig. S1.** <sup>1</sup>H NMR spectra of PAA, 6FDA and AHHFP. (The unsplit peaks of PAA in <sup>1</sup>H NMR spectrum is hardly to be assigned due to the polymerization. The absence of monomer peaks indicates this is a new product after a reaction between two monomers. On the other hand, a broad peak in the range of 12.5 to 14ppm indicates the possible presence of carboxylic acid group in PAA, suggesting a possible structure for PAA as shown in this figure.)

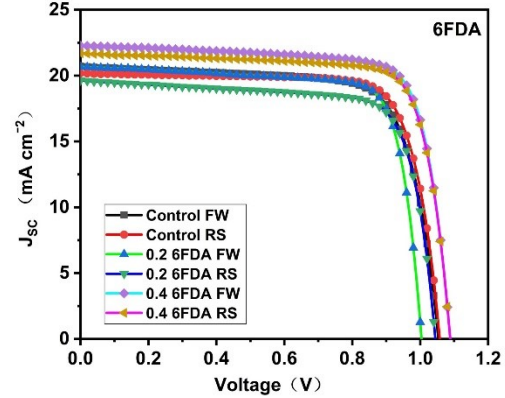


**Fig. S2.** FTIR spectra of MAPbI<sub>3</sub>, MAPbI<sub>3</sub>-PAA and PAA in a broad range.

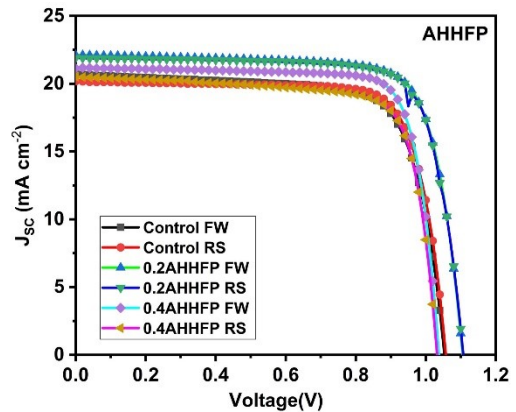
Peak	Mn (g/mol)	PD
PAA	20105	1.091

**Table.S1.** GPC of PAA.

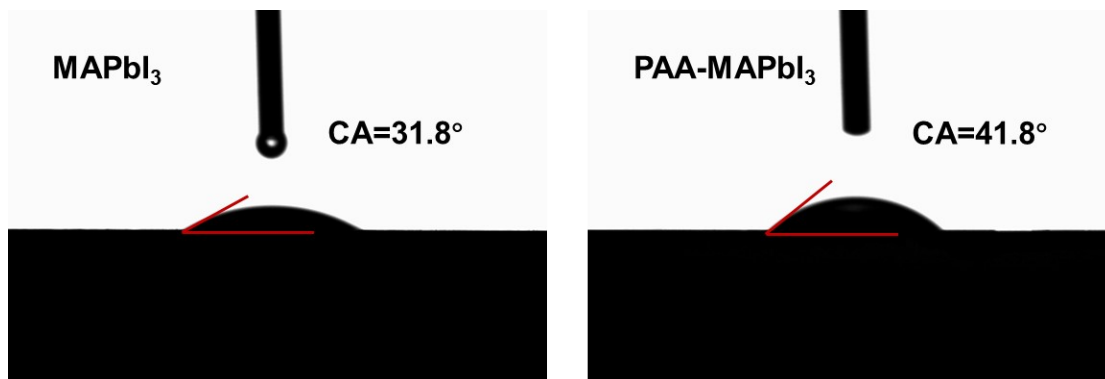
additive 6FDA		<i>V</i> <sub>oc</sub> (V)	<i>J</i> <sub>sc</sub> (mA/cm <sup>2</sup> )	PCE (%)	FF (%)
Control	FW	1.05	20.71	16.17	74.13
	RS	1.06	20.18	16.64	77.98
0.2mg/ml	FW	1.00	20.66	16.22	78.20
	RS	1.04	19.64	15.54	75.74
0.4mg/ml	FW	1.09	22.28	18.80	77.55
	RS	1.09	21.69	18.42	78.03



additive AHHFP		<i>V</i> <sub>oc</sub> (V)	<i>J</i> <sub>sc</sub> (mA/cm <sup>2</sup> )	PCE (%)	FF (%)
Control	FW	1.05	20.71	16.17	74.13
	RS	1.06	20.18	16.64	77.98
0.2mg/ml	FW	1.11	22.11	18.92	77.37
	RS	1.11	21.90	18.84	77.72
0.4mg/ml	FW	1.04	21.14	17.60	80.23
	RS	1.03	20.52	16.26	76.76



**Fig. S3.** Summary of the photovoltaic parameters for the PSCs without and with 6FDA and AHHFP, and the J-V curves for the devices with these additives at a variety of concentrations (0.2, 0.4mg mL<sup>-1</sup>)



**Fig. S4.** Contact angle of the perovskite films without and with PAA treatment.



**Fig. S5.** Photographs for solution of PAA, MAI and PAA mixed with MAI.