

## Dynamic Covalent Polymer Engineering for Stable And Self-Healing Perovskite Solar Cells

Peng Xu,<sup>ab #</sup> Jian Liu,<sup>a #</sup> Shuai Wang,<sup>b</sup> Jiujiang Chen,<sup>a</sup> Bin Han,<sup>a</sup> Yuanyuan Meng,<sup>a</sup>  
Shuncheng Yang,<sup>a</sup> Lisha Xie,<sup>ac</sup> Mengjin Yang<sup>\*ac</sup>, Runping Jia<sup>\*b</sup>, and Ziyi Ge<sup>\*ac</sup>

<sup>a</sup> Zhejiang Provincial Engineering Research Center of Energy Optoelectronic Materials and  
Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of  
Sciences, Ningbo 315201, P. R. China.

<sup>b</sup> School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai  
201418, P.R. China.

<sup>c</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy  
of Sciences, Beijing, 100049, P. R. China.

# equal contribution

E-mail: [yangmengjin@nimte.ac.cn](mailto:yangmengjin@nimte.ac.cn), [jiarp@sit.edu.cn](mailto:jiarp@sit.edu.cn) and [geziyi@nimte.ac.cn](mailto:geziyi@nimte.ac.cn)

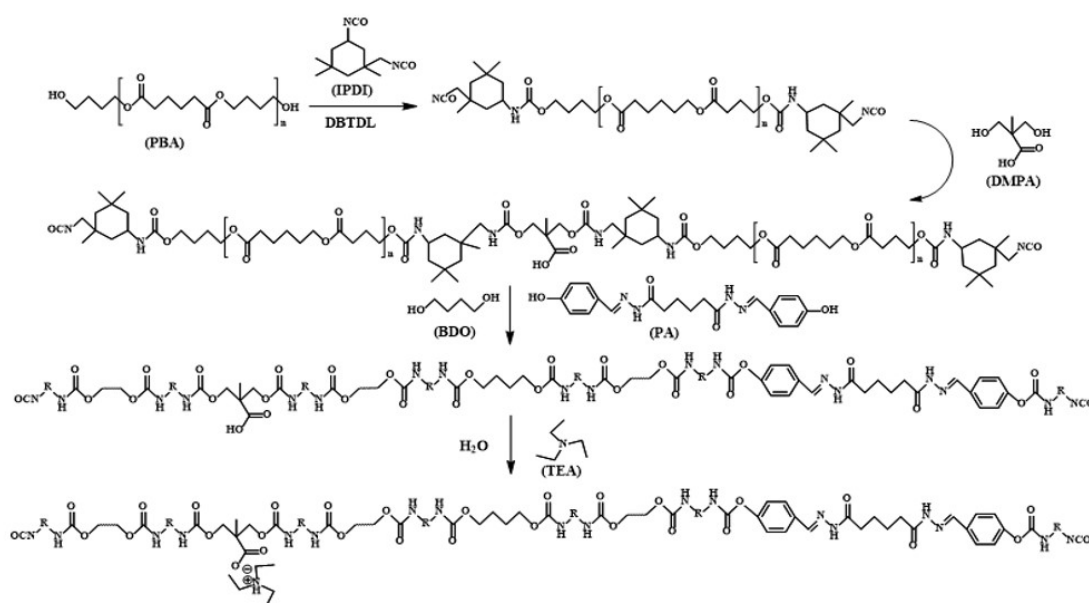


Figure S1 Synthesis steps of Ab-WPU

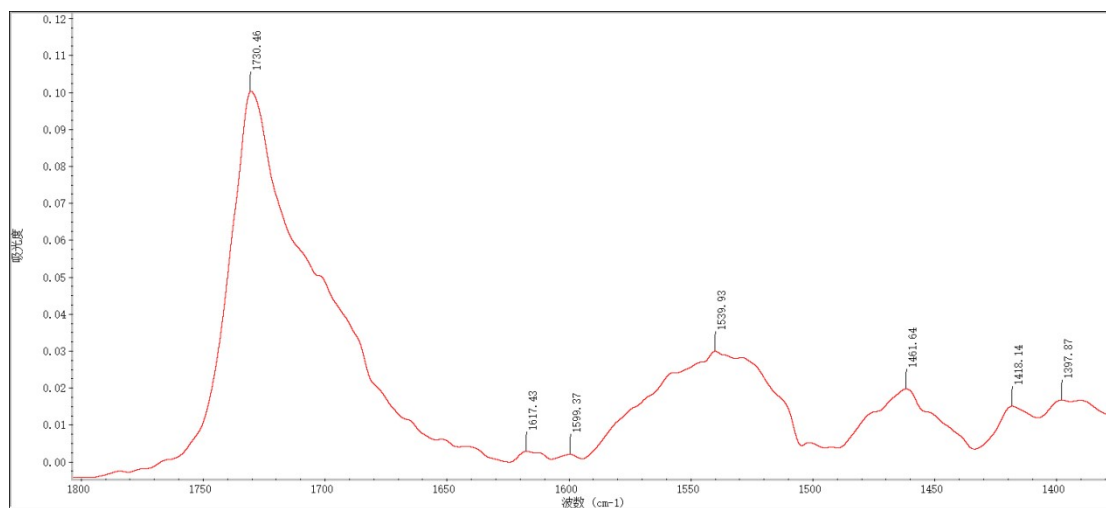


Figure S2 Ab-WPU infrared absorption (FTIR) spectroscopy

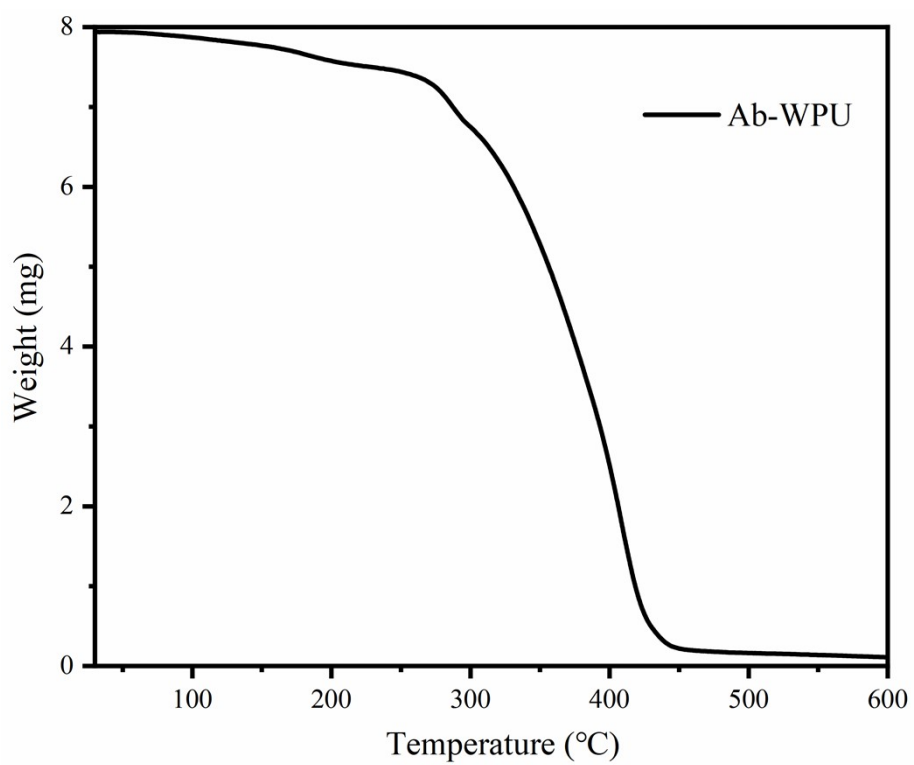


Figure S3 Thermogravimetric analysis (TGA) diagram of Ab-WPU

**60°C+PbI<sub>2</sub>@ ethanol solution**

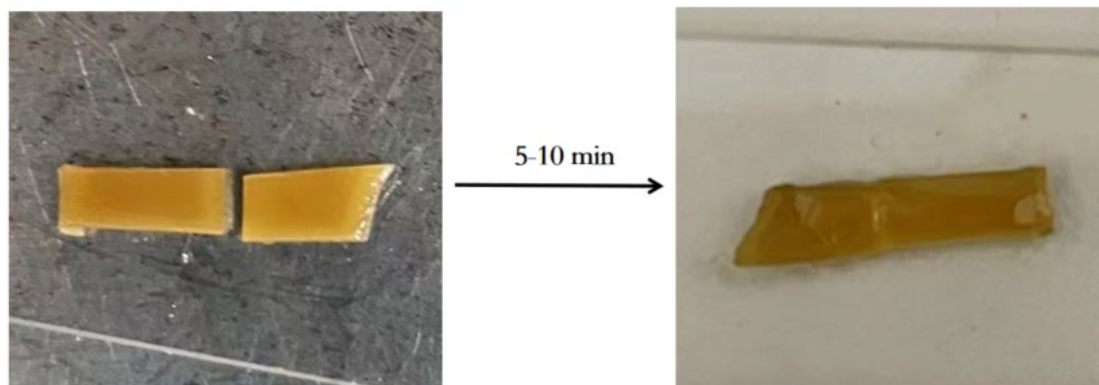


Figure S4 Ab-WPU self-healing diagram under heating and PbI<sub>2</sub> conditions

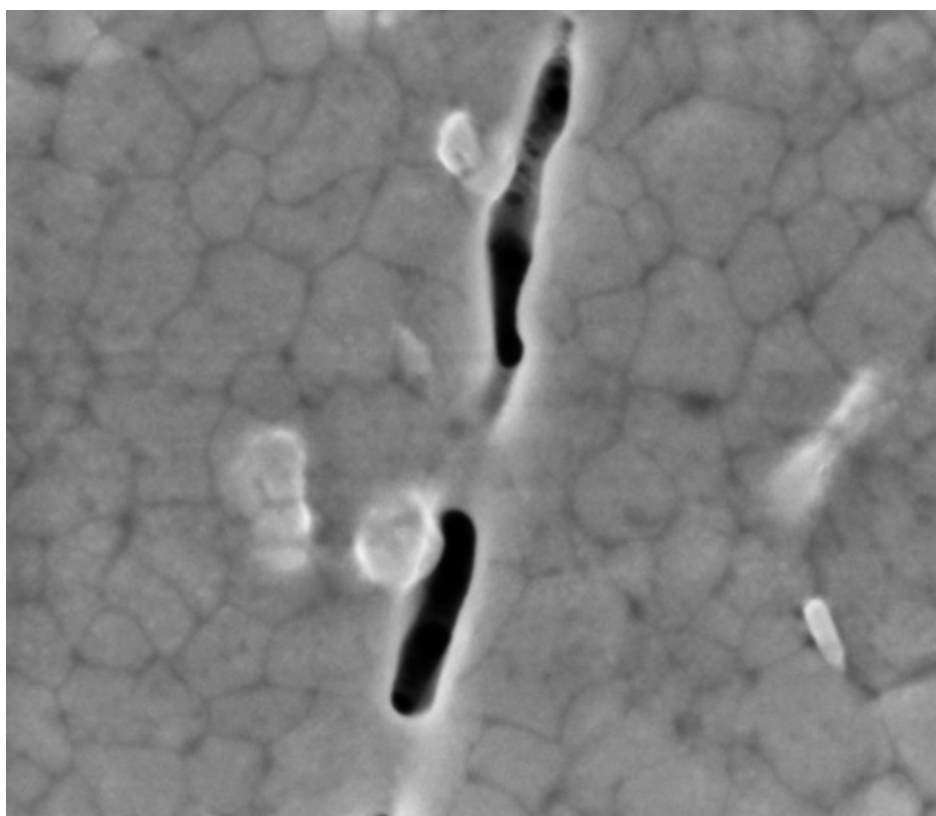


Figure S5 Crack morphology of perovskite film

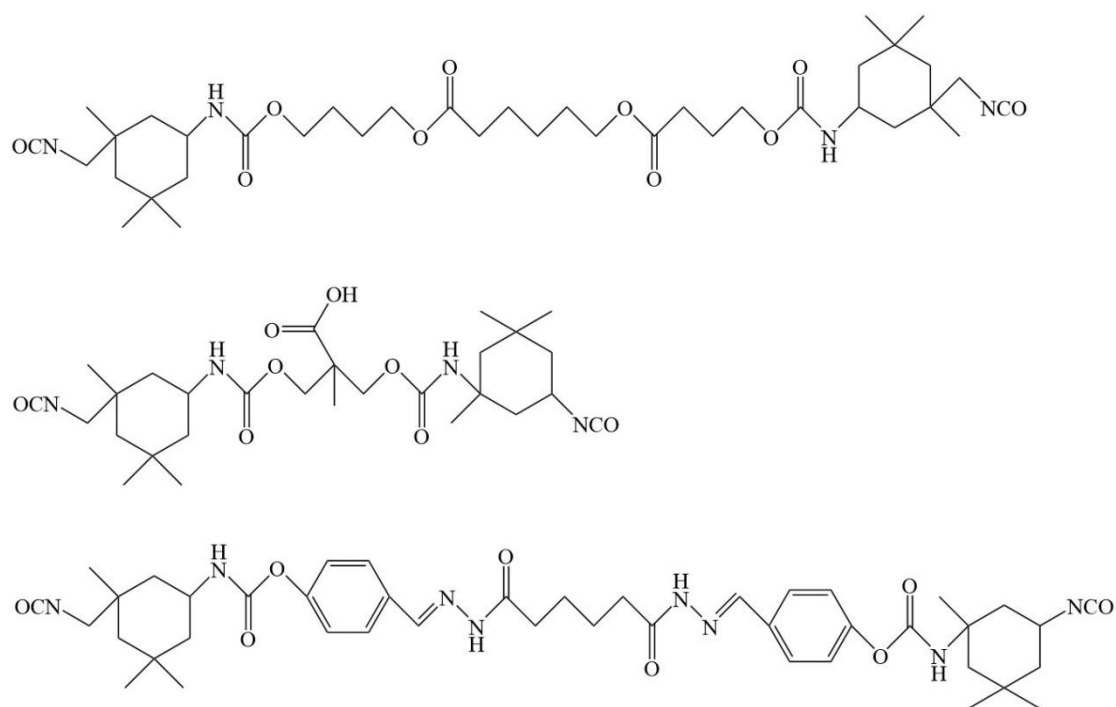


Figure S6 Three structural units split into Ab-WPU

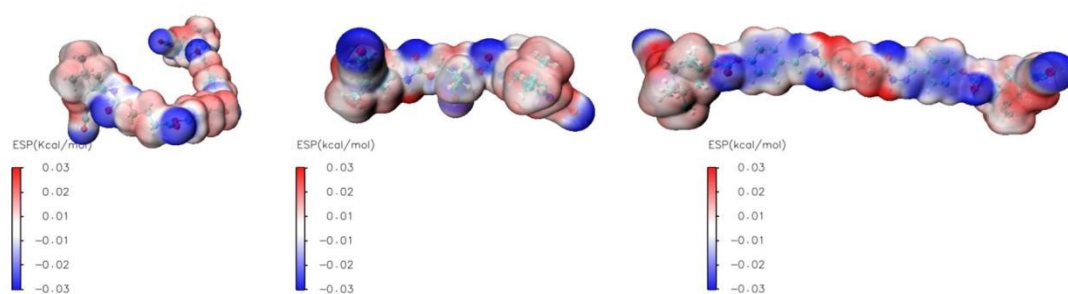


Figure S7 Charge distribution calculated by DFT for the three structural units split into Ab-WPU

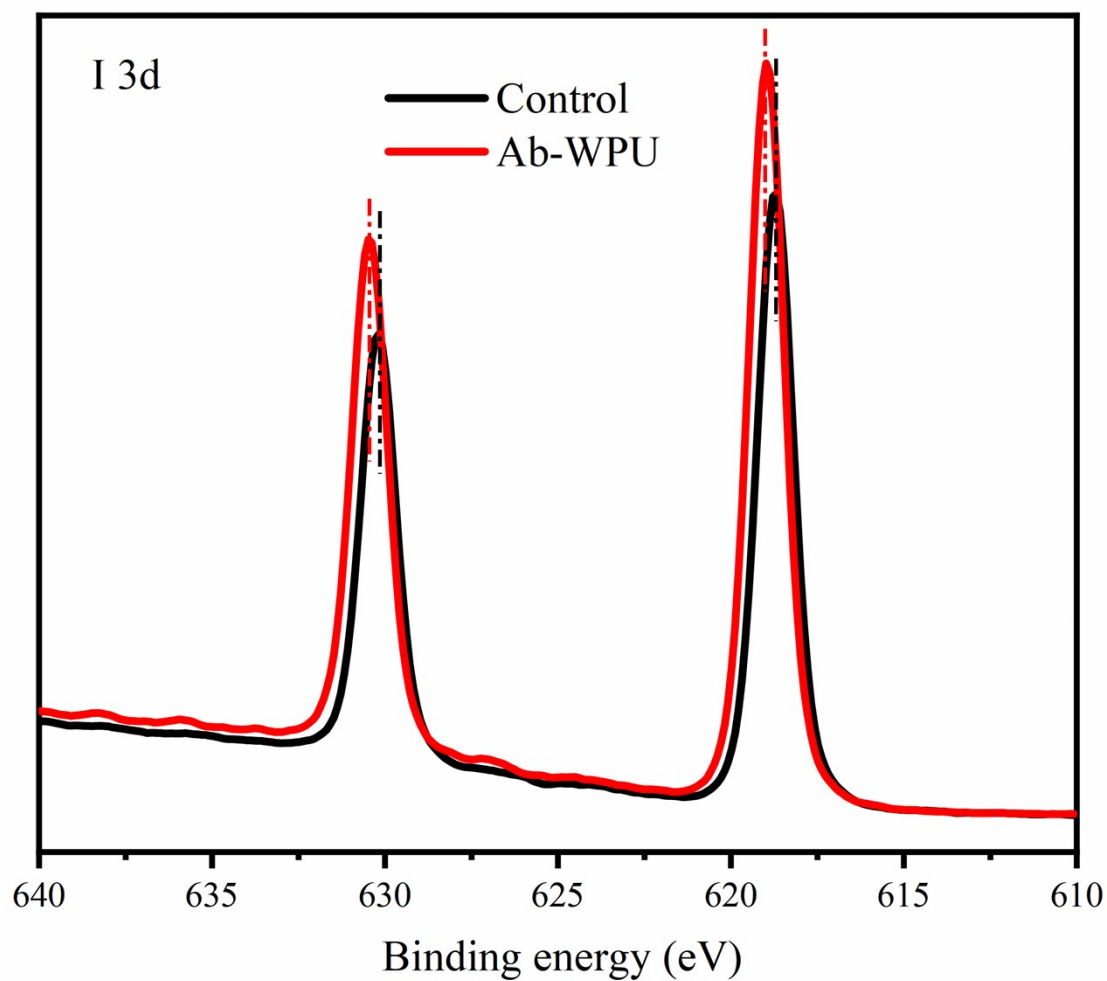


Figure S8 XPS comparison of perovskite layer without Ab-WPU modification and with Ab-WPU modification

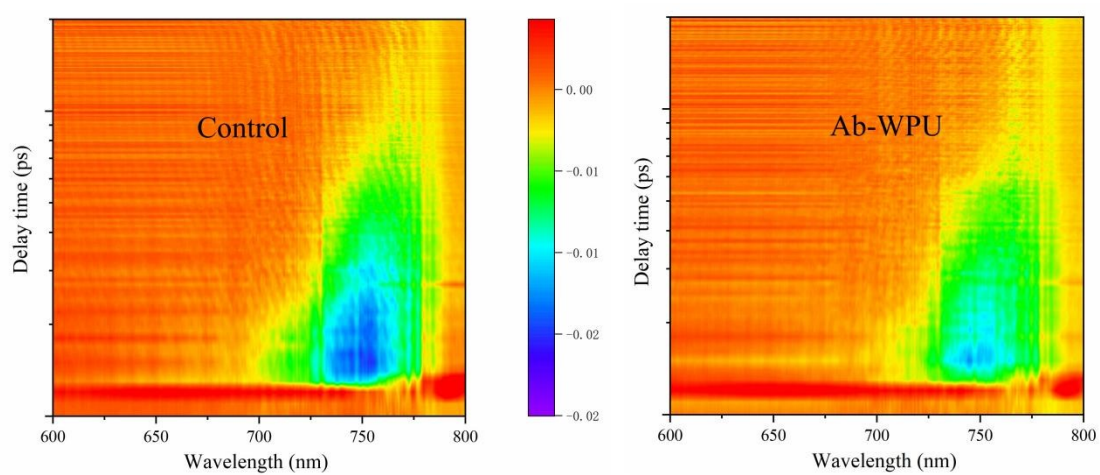


Figure S9 TA testing of perovskite films without and after Ab-WPU modification

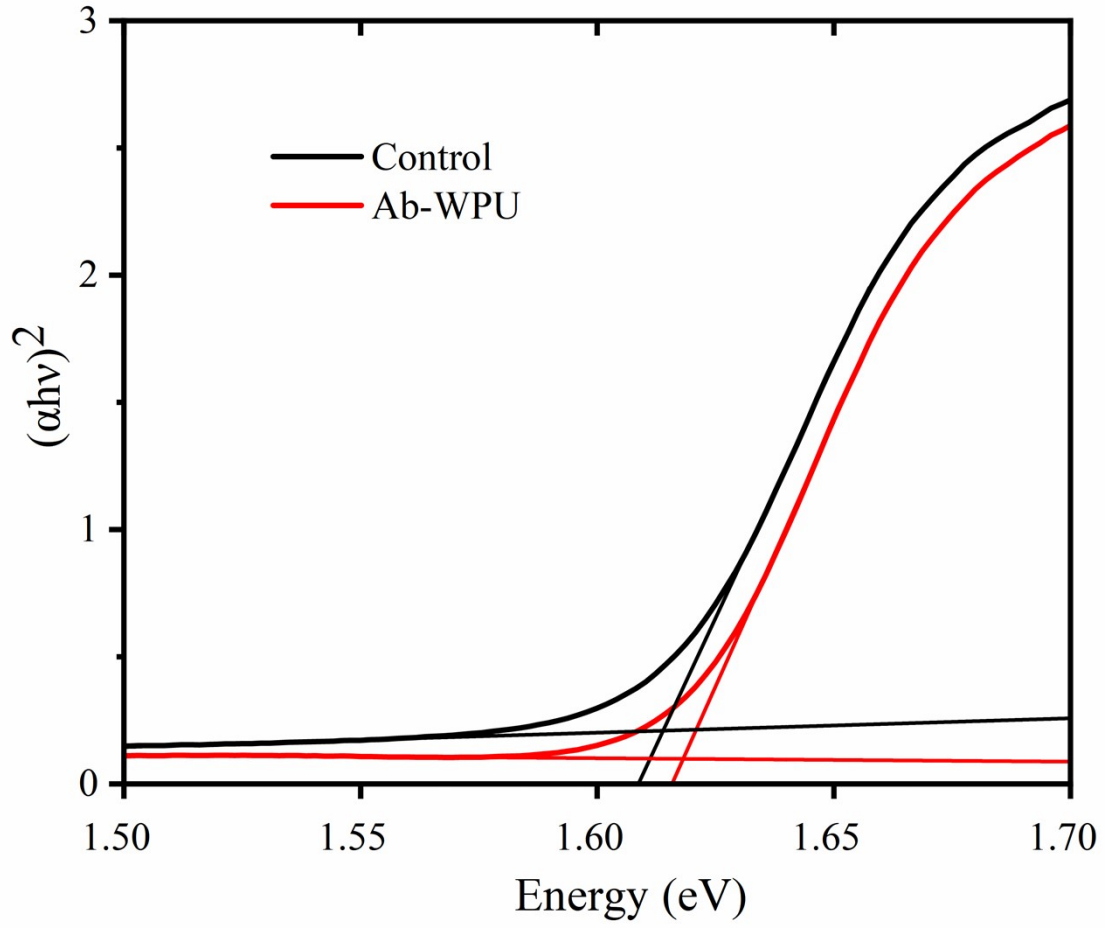


Figure S10 Tauc diagram of the perovskite film modified with Ab-WPU compared to the device

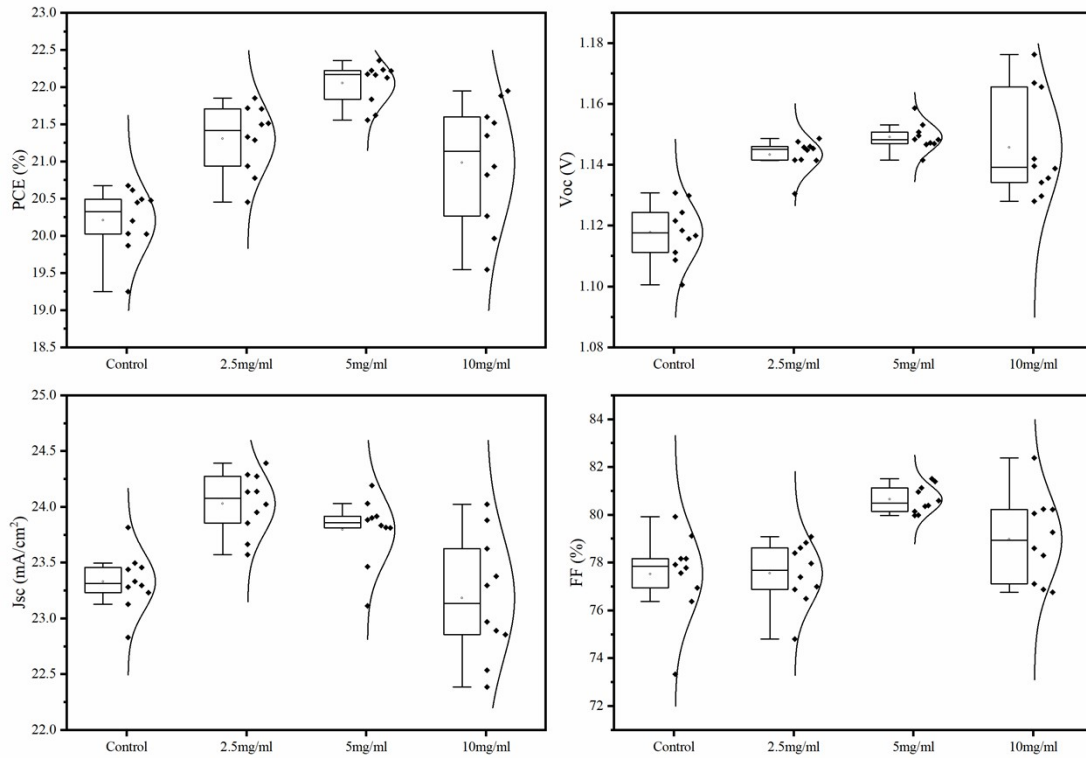


Figure S11 Performance statistics of 10 different batches of solar cells prepared before and after treating PSCs with different concentrations of Ab-WPU.

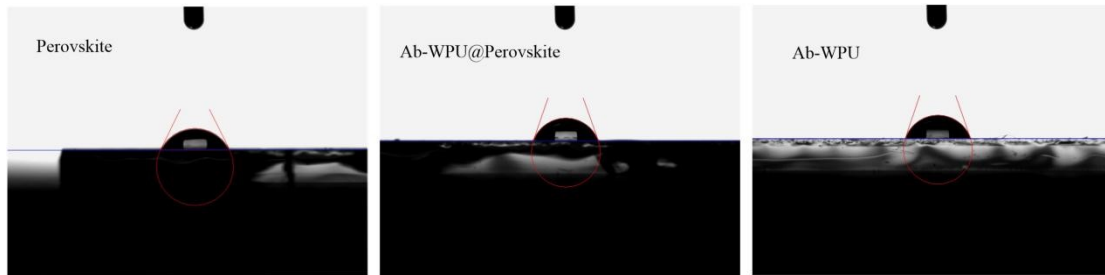


Figure S12 Comparison device, water contact angle of Ab WPU modified device and Ab-WPU

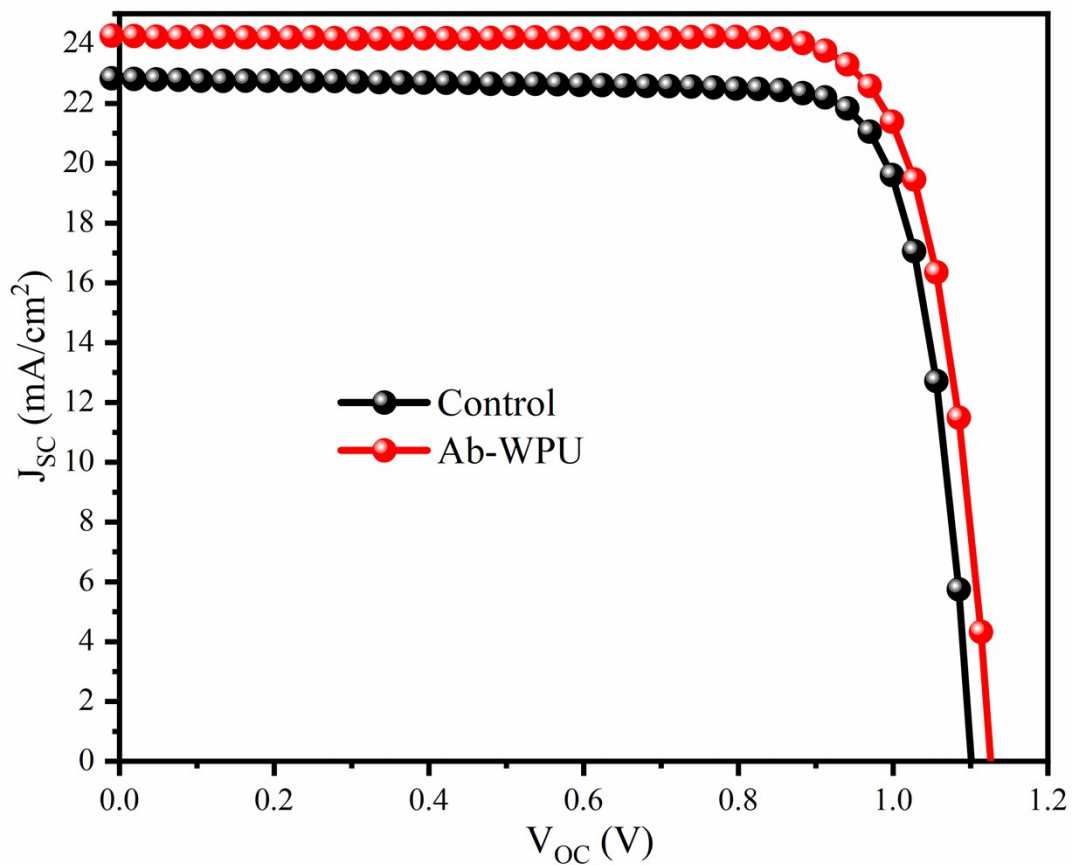


Figure S13 J-V curve of reference device and Ab-WPU modified device used for testing thermal stability

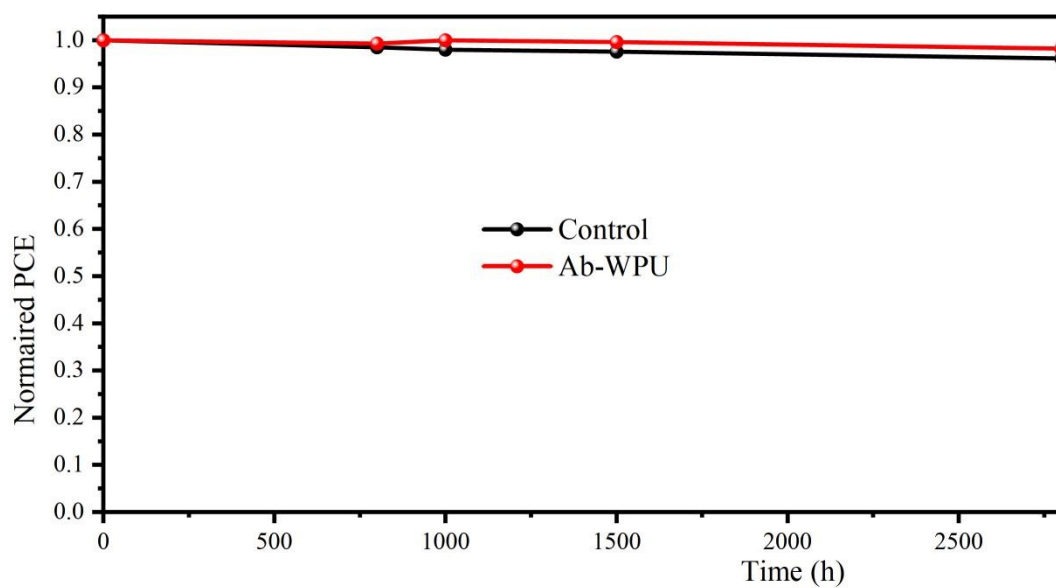


Figure S14 Normalized PCE plots of the stability of PSCs devices without additives and modified with Ab-WPU in an N<sub>2</sub> filled environment



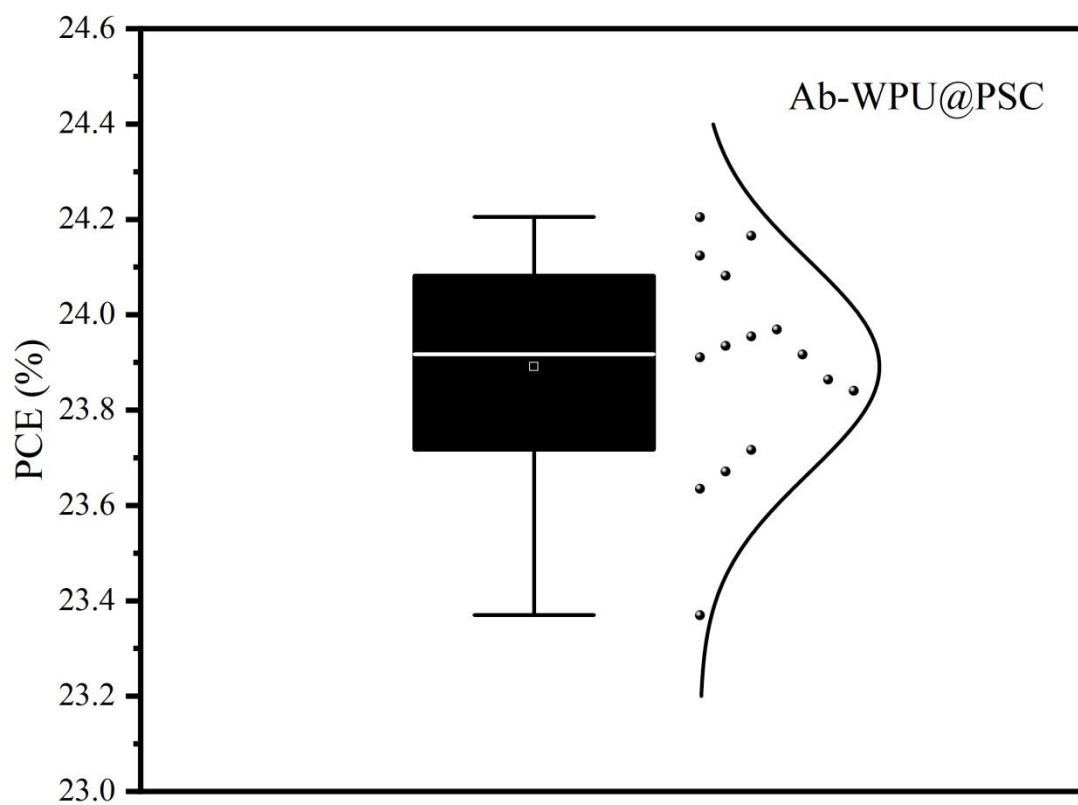


Figure S15 PCE statistics of 15 different devices of  $\text{FA}_{0.96}\text{Cs}_{0.04}\text{PbI}_{2.8}\text{Br}_{0.12}$  solar cells with Ab-WPU

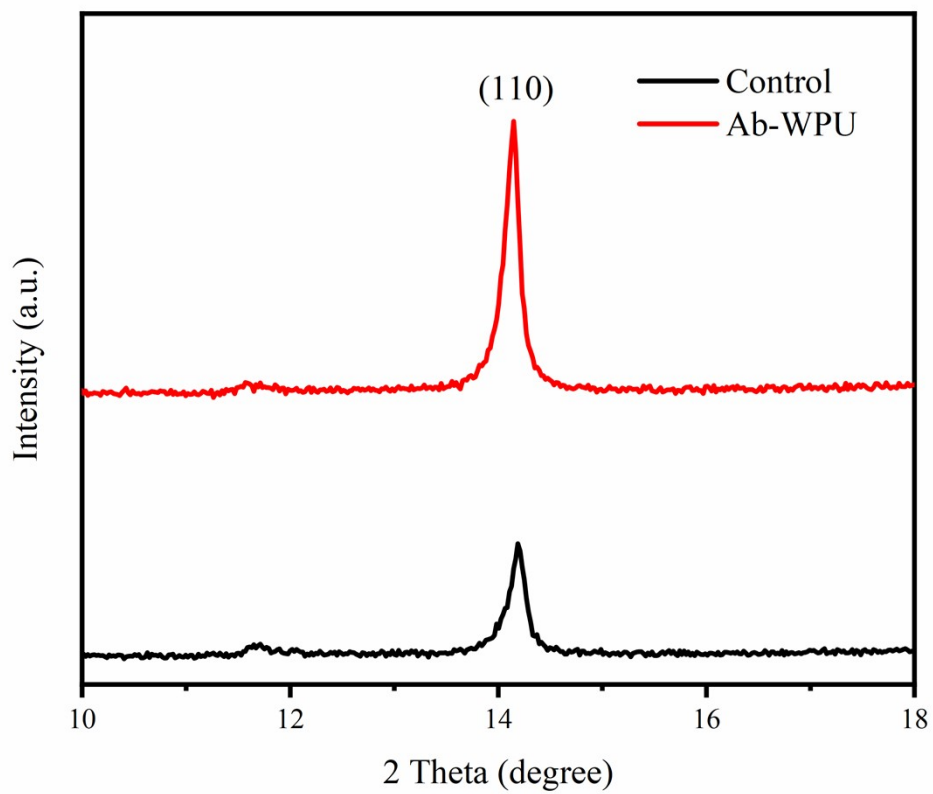


Figure S16 The XRD images of the perovskite layer without Ab-WPU modification and with Ab WPU modification

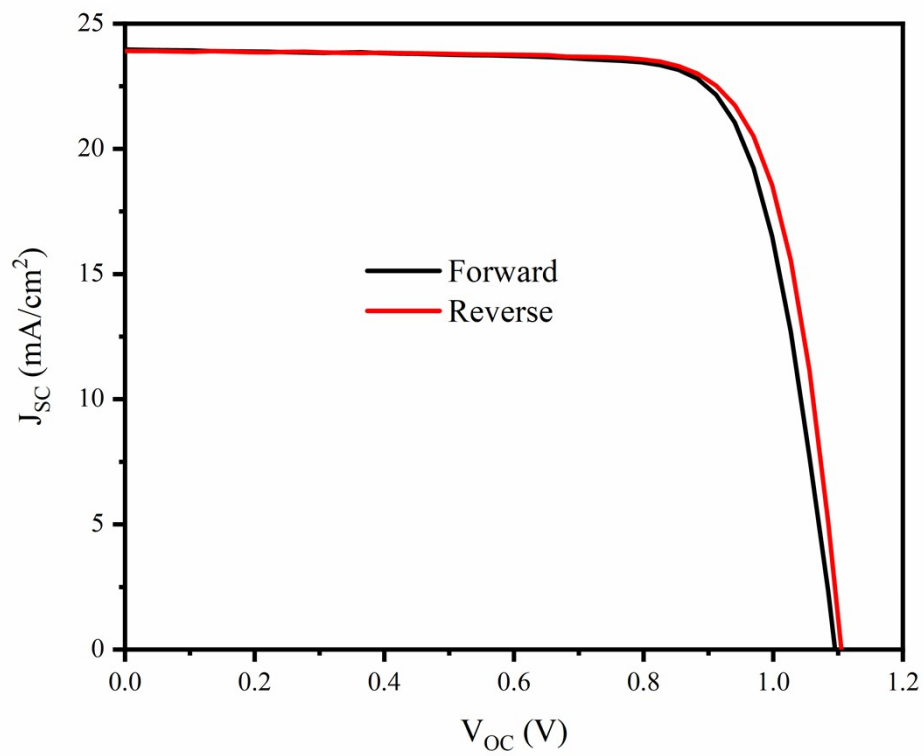


Figure S17 Forward and Reverse sweeps for Control devices

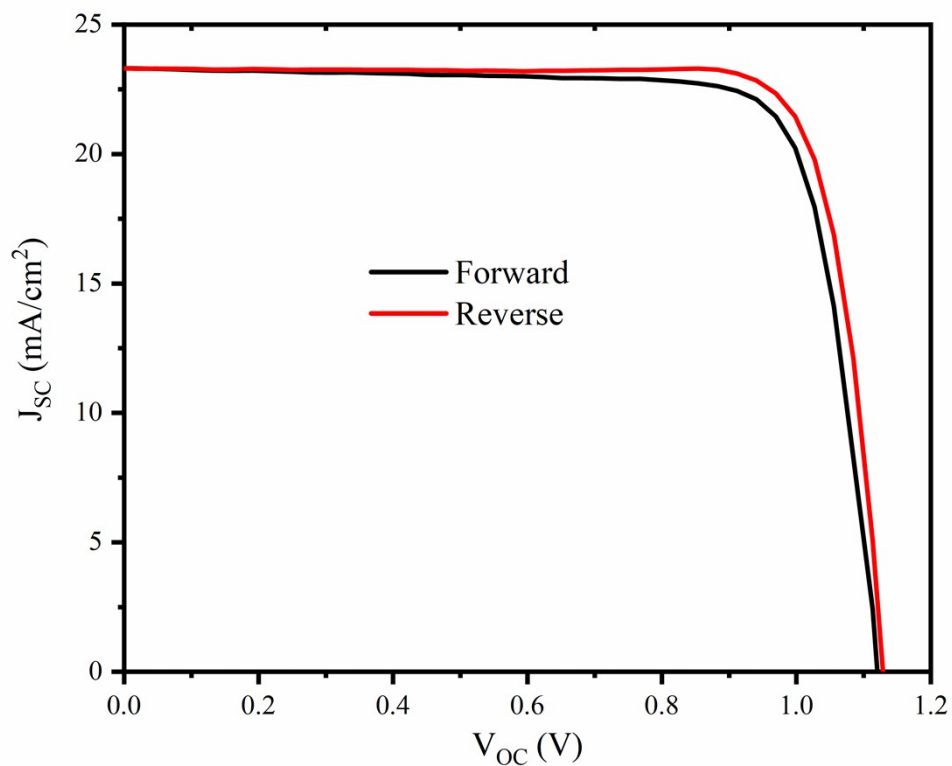


Figure S18 Forward and Reverse sweeps for Ab-WPU devices

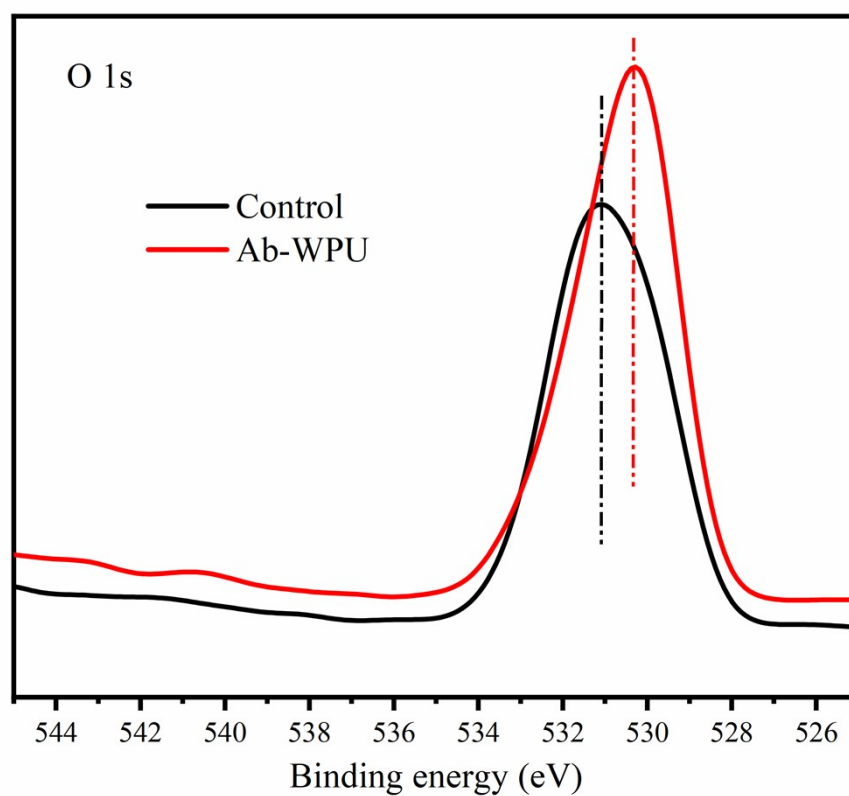


Figure S19 XPS comparison of perovskite layer without Ab-WPU modification and with Ab-WPU modification

Table S1 Photovoltaic performance parameters of the best devices of  $\text{FA}_{0.87}\text{Cs}_{0.13}\text{PbI}_{2.7}\text{Br}_{0.3}$  perovskite solar cells without additives and modified by Ab-WPU

Samples	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Control	1.13	23.22	78.06	20.49
5 mg/ml Ab-WPU	1.152	23.88	81.5	22.43

Table S2 Literature related to polyurethane modified perovskite layer

Structure	Journal	Date	PCE (%)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )
FTO/SnO <sub>2</sub> /PU-FAPbI <sub>3</sub> /Spiro-OMeTAD/Ag	Carbon	April 2022	21.36 <sup>1</sup>	1.15	22.44
FTO/c-TiO/PU-CsPbIBr <sub>2</sub> /Carbon	Angew. Chem. Int. Ed.	December 2021	10.61 <sup>2</sup>	1.293	11.58
ITO/NiO <sub>x</sub> /Perovskite/PC <sub>61</sub> BM/PEI/Ag	Nano Energy	June 2022	20.30 <sup>3</sup>	1.14	22.88
ITO/SnO <sub>2</sub> /SMPU-FAMAPbIBr <sub>3</sub> /Spiro-OMeTAD/Au	InfoMat	August 2022	21.33 <sup>4</sup>	1.18	24.21
(HPMC)/hc-PEDOT:PSS/SnO <sub>2</sub> /PU-perovskite/Spiro-OMeTAD/Ag	Advanced Functional Materials	March 2023	20.04 <sup>5</sup>	1.15	23.16

Table S3 Photovoltaic parameters of flexible comparison devices and Ab-WPU modified devices

Samples	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Control	1.13	23.22	78.06	20.49
5 mg/ml Ab-WPU	1.152	23.88	81.5	22.43

Table S4 Photovoltaic parameters of the reference device and Ab-WPU modified device used for testing thermal stability

Samples	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Control	1.099	22.80	81.61	20.45
5 mg/ml Ab-WPU	1.124	24.26	80.24	21.88

Table S5 Rigid and flexible device efficiency comparisons

Journal	Date	Rigid PCE (%)	Flexible PCE (%)
Advanced Functional Materials <sup>6</sup>	April 2022	24.40	22.04
Joule <sup>7</sup>	March 2023	24.9	22.3
Nano Energy <sup>3</sup>	June 2022	20.30	17.19
InfoMat <sup>4</sup>	August 2022		21.33
Advanced Functional Materials <sup>8</sup>	March 2023	22.43	19.03
Joule <sup>9</sup>	February 2023		23.4
Nano Energy <sup>10</sup>	February 2023	22.62	19.34
InfoMat <sup>11</sup>	August 2023	24.56	22.65
Nature Communications <sup>12</sup>	March 2023	23.26	22.10

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