

**Defect passivation and humidity protection for perovskite solar cells enabled by
1-dodecanethiol**

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Experimental section

Materials:

Formamidine iodide (FAI) and methylammonium bromide (MABr) were obtained from Xi'an Polymer Light Technology Corp. Lead (II) iodide (PbI_2), Lead (II) bromide (PbBr_2), spiro-MeOTAD, lithium bis (trifluoromethylsulphonyl) imide (Li-TFSI), titanium isopropoxide (TTIP), bis(acetylacetonate) and 4-tert-butylpyridine (TBP) were purchased from Sigma-Aldrich. The isopropanol (IPA), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and chlorobenzene (CB) acquired from Sinopharm Chemical Reagent Co., Ltd. TiO_2 nanorod were acquired from DyeSol. All the materials and reagents above were used as received without further purification.

Device fabrication:

FTO glass ($15 \Omega \text{ cm}^{-1}$) was cleaned by sequentially ultrasonication in acetone, ethanol and deionized water for 20 min, respectively. Then, the cleaned substrates were dried by dry air flow and treated via UV for 10 min before spray pyrolysis of compact TiO_2 . The compact TiO_2 layer was deposited on FTO solution by spray pyrolysis at 450°C with a precursor which included 0.5 ml of TTIP and 5 mL of IPA. The thickness was estimated to be about 30 - 40 nm, in agreement with the literature, (G. Liu, H. Zheng, X. Xu, L. Zhu, X. Zhang and X. Pan, Chem. Mater. 2018, 30, 7691-7698,). A mesoporous TiO_2 layer was coated on the compact layer by spin-coated 30 nm TiO_2 paste (TiO_2 : ethanol = 1: 5.5 by weight) at a speed of 4000 rpm for 20 s. Then, mesoporous TiO_2 layer was gradually annealed from room temperature to 510°C for 3 h. The $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ precursor solution (1.4 M) was prepared by

dissolving FAI, MABr, PbI₂ and PbBr₂ in the mixed solvent of DMF and DMSO with a volume ratio of 4: 1. The perovskite film was deposited onto the mesoporous TiO₂ films by two-step spin-coating procedures which spun at 1000 rpm for 10 s and then 4000 rpm for 30 s. CB (80 μL) was dropped during the second spin-coating step as antisolvent. Next, the perovskite precursor film was thermal annealing at 105 °C for 30 mins. For ligand modification, 20 μL DDT are resolved in 1 mL IPA and spun on top of perovskite, followed by thermal annealing at 105 °C. The spiro-OMeTAD with the addition of Li-TFSI and 4-tBP in CB solvent act as hole transport layer was spun on top of the as-prepared perovskite film. Finally, 100 nm Au as a bottom electrode was by thermally evaporation.

Characterization:

XRD patterns of the perovskite films were recorded on a Rigaku Smartlab 9 kW diffractometer with Cu K α radiation. The data were collected in the 2 θ range from 5° to 60° at room temperature. The film morphology was investigated by using a high-resolution scanning electron microscope (SEM) with a Schottky Field Emission gun. Absorption spectra and reflectance spectra were recorded on an ultraviolet-vis (UV-vis) spectrophotometer (U-3900H, HITACHI, Japan). Steady-state PL spectra were measured using a spectrofluorometer (Photon Technology International) and analyzed with the software Fluorescence. The J–V curves were measured by using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) under 100 mW cm⁻² illumination (AM 1.5G). The absorbed effective area for each device was 0.09 cm² by masking a black mask. The incident photon to current efficiency (IPCE)

was collected as a function of wavelength from 300 to 900 nm (PV Measurements, Inc.), with a dual Xenon/ quartz halogen light source, measured in DC mode with no bias light used. Electrochemical impedance spectroscopy (EIS) was recorded at 0.8 V in the dark, in the frequency range of 1 Hz to 1 MHz by using an Autolab analyzer (Metrohm, PGSTAT 302N, Switzerland). The KPFM experiments were conducted on the FTO glass/perovskite film structure, using a KP RH040 (KP Technology Ltd.) system, where V_{CPD} was recorded for every millimeter of probe movement. The humidity aging tests were carried out in a sealed dark box. Inside the box we put the device ready for test and a water beaker, to increase the humidity. The relative humidity was found around 80%. The box was kept in the dark and the temperature was maintained at about 25 °C.

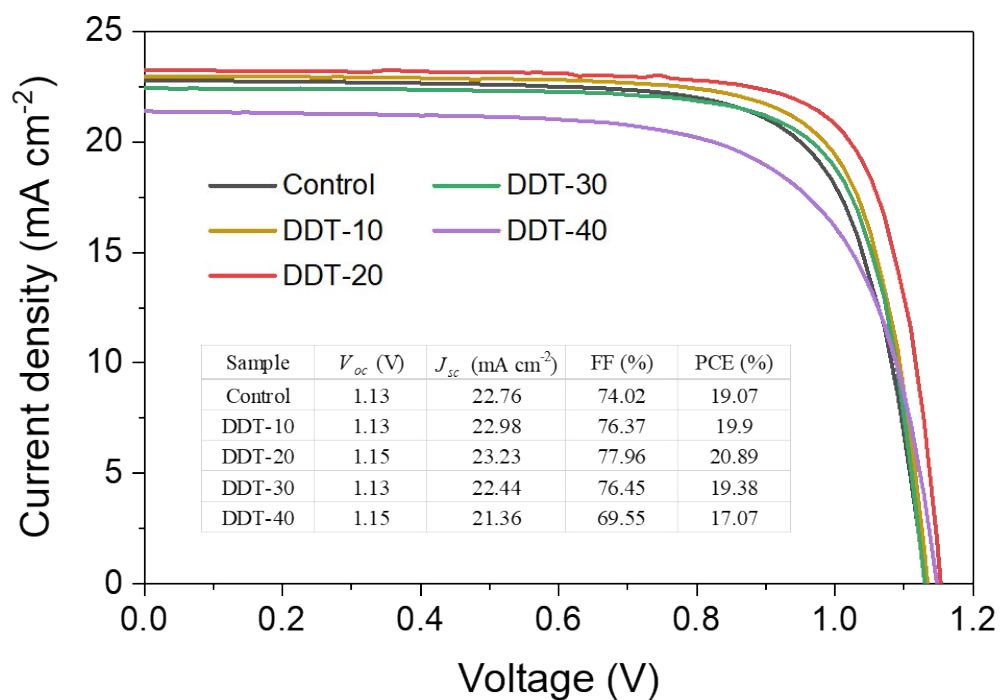


Figure S1. J–V curves of control and DDT-x PSCs. The notes, DDT-10, DDT-20, DDT-30, and DDT-40, represent 10, 20, 30, and 40 μ l DDT dissolved in 1 mL IPA solvent, respectively.

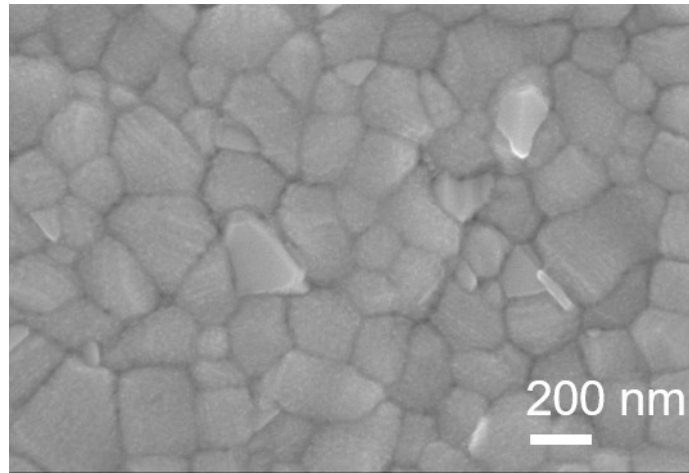


Figure S2. Top-view SEM images of control perovskite films.

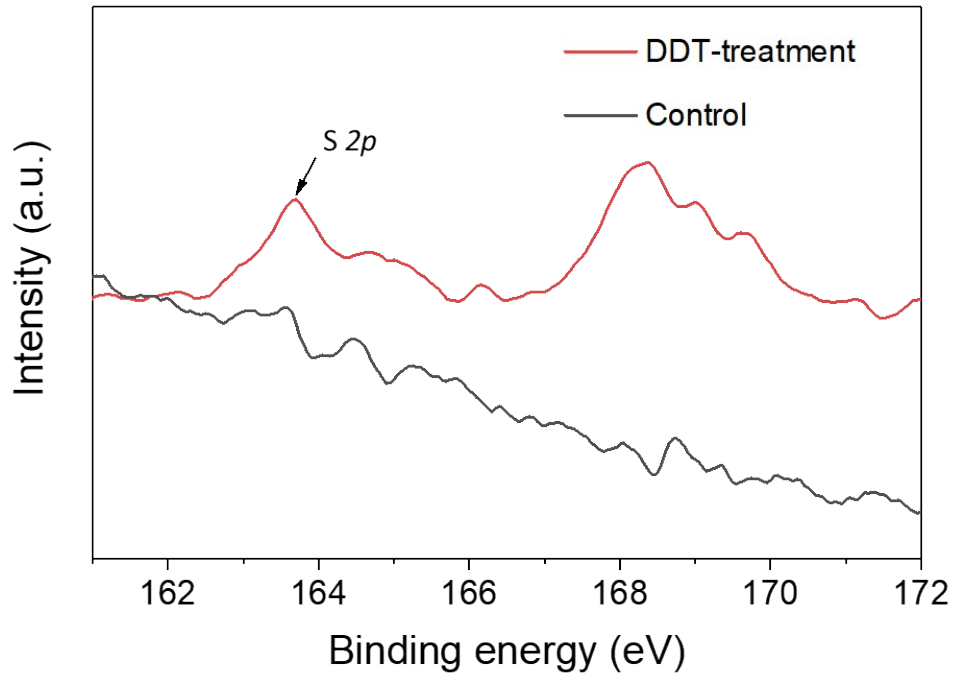


Figure S3. The XPS spectra for S 2p from the control and DDT-treatment perovskite films.

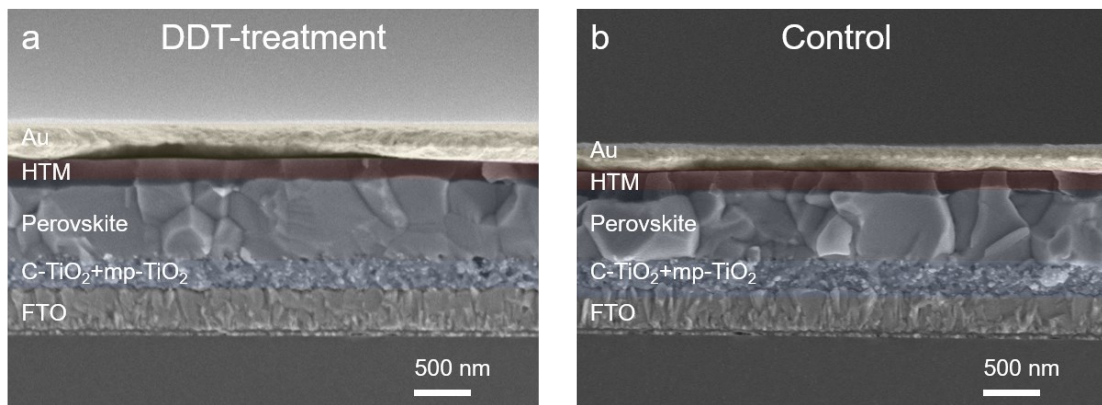


Figure S4. Cross-section SEM images of the DDT-treatment and control device.

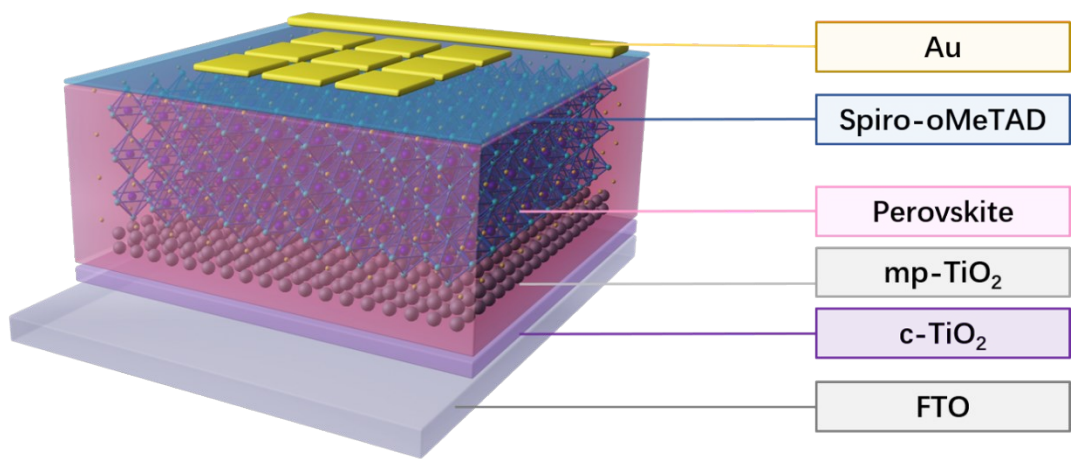


Figure S5. Schematic architecture of the PSC device.

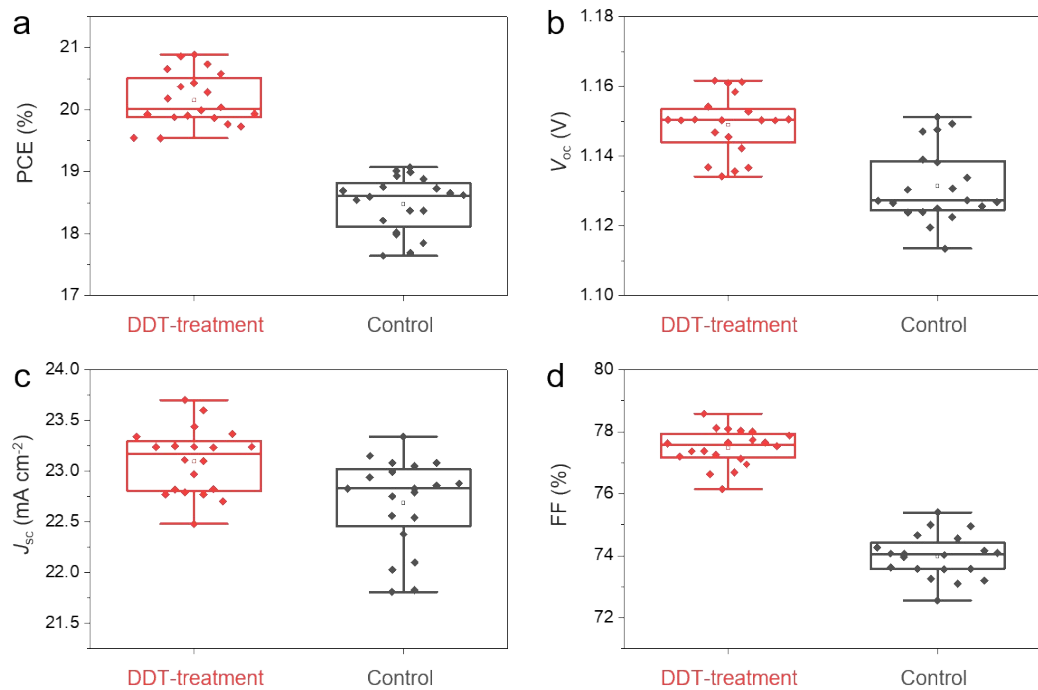


Figure S6. The statistical parameters of (a) PCE, (b) V_{oc} , (c) J_{sc} and (d) FF of DDT-treatment and control PSCs among 30 as-prepared devices.