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Supporting Information

Suppressing the defect through thiadiazole derivatives modulating $CH_3NH_3PbI_3$ crystal growth for highly stable perovskite solar cells under dark

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Materials: FTO glass (<15 Ω/square) achieved from Nippon Sheet Glass Corporation. 2,2,',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9-spirobifluorene (spiro-OMeTAD), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), 4-tert-butylpyridine (TBP) and PbI_2 were purchased from YouXuan Tech. TDZDT and TDZT were purchased from Heowns Biochemical Technology Co., Ltd. Titanium diisopropoxide bis(acetylacetonate) was purchased from Alfar Aesar. N-butanol, Acetonitrile, methylamine solution (40% in methanol) were purchase from Shanghai Aladdin Biochemical Technology Co., Ltd. Dimethyl Sulphoxide (DMSO) and N,N′ -dimethylformamide (DMF) were purchased from J&K chemical Corporation. CH_3NH_3I (MAI) was synthesized according to literatures. All the materials were used as received without any other purification unless other-wise specified.

Characterization. Fourier transfer infrared spectra (FTIR) was recorded on Thermo NICOLET380 spectrometer. Surface morphology of the TiO_2/perovskite/HTM/Au film and energy dispersive spectrometer were obtained by using a scanning electron microscope (SEM, SUPRA 55VP, ZEISS), Atomic force microscope photo measured by ttomic force microscope (AFM Dimension Edge LS18021). X-ray diffraction (XRD) data was recorded on the Mini Flex 600 in the range 2θ=5-60° using CuKa1 radiation. Timeresolved photoluminescence (TRPL) spectra and Steady state fluorescence was recorded on Edinburgh Instruments (FLS 980, UK) collected at 780 nm and excitation at 465 nm. The IPCE of the devices was measured by focusing light from a 300W Xenon lamp (ILC Technology, USA) through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK). The space charge limited current (SCLC) measurement through Keithley source table (Keithley 2400,USA).

The J-V characteristics of the devices were measured under 100mW/cm^2 conditions using a 450 W Xenon lamp (Oriel), as a light source, equipped with a Schott K113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectra to the AM1.5G standard in the region of 350-750 nm. The current–voltage characteristics of the devices were obtained by applying external potential bias to the cell while recording the generated photocurrent 3 using a Keithley (Model 2400) digital source meter. The J–V curves of all devices were measured by masking the active area with a metal mask of area 0.09 cm^2.

Solar cell fabrication. FTO-coated glass substrates were washed sequentially in detergent, toluene, deionized water and ethanol. Compact TiO_2 layer was fabricated on the cleaned FTO glass through spin-coating the titanium diisopropoxide bis(acetylacetonate) in n-butanol (v:v=1:16) at 2000 rpm for 30 s, then heating at 500 ℃for 30 min in air. After cooling to RT, on top of this layer, mesoporous TiO_2 was made by spin-coating 30 nm sized commercial TiO_2 paste (Dyesol 30NRD, Dyesol) diluted in ethanol (1:5.5 w/w) at 4500 rpm for 20 s, the substrate was sintering at 500 ℃ for 30 min in air. The $CH_3NH_3PbI_3$ layer was fabricated by one step fast crystallization method and the precursor solution was prepared from 1.35M $Pb^{2+}$with different concentration TDZDT and TDZT dissolved in DMF and DMSO, the volume ratio of DMF/DMSO is 4:1. The spin-coating procedure was performed at 6000 rpm for 30 s. Chlorobenzene (100 mL) was dropped in the spin-coating step 25 s before the end of the procedure in glovebox. The perovskite film was then heated at 100 ℃ for 60 min on a hotplate. Subsequently, the HTM was deposited on top of the perovskite by spin-coating at 4000 rpm for 15 s. The spiro-OMeTAD solutions were prepared by dissolving spiro-OMeTAD in chlorobenzene (1 mL) at a concentration of 72.3 mg/mL with the addition of an acetonitrile solution with 30 mL TBP and 18 mL of 520 mg/mL Li-TFSI in glovebox. and devices were finalized by the thermal evaporation of 80 nm gold.

Table S1 The stretch of N-H and C=S bond of thiadiazole derivative

	N-H	C=S
TDZT	3460	725
TDZT·PbI_2	3454	715
TDZT·PbI_2·CH_3NH_2I	3456	719
TDZDT	3470	746
TDZDT·PbI_2	3458	708
TDZT·PbI_2·CH_3NH_2I	3462	714

Table s2 The $MAPbI_3$ (110) diffraction peak intensity of different additive containing

TDZT-containing mg/mL	**0**	**0.3**	**0.6**	**0.9**	**1.2**	**1.5**	**3.0**
Peak intensity (2θ=14.2°)	414	452	680	623	550	519	429
TDZDT-containing mg/mL	0	0.3	0.6	0.9	1.2	1.5	3.0
Peak intensity (2θ=14.2°)	414	610	787	661	526	469	460

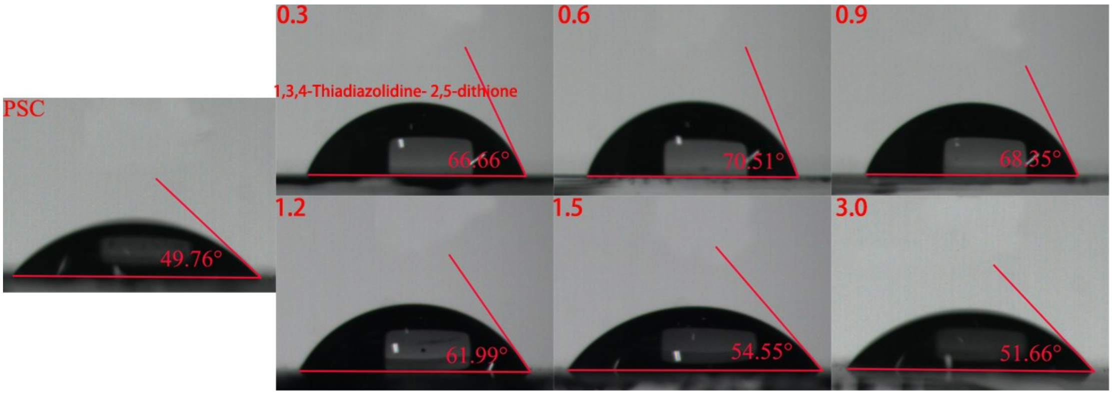


Figure S1. The contact angel between water and different concentration TDZDT containing perovskite films.

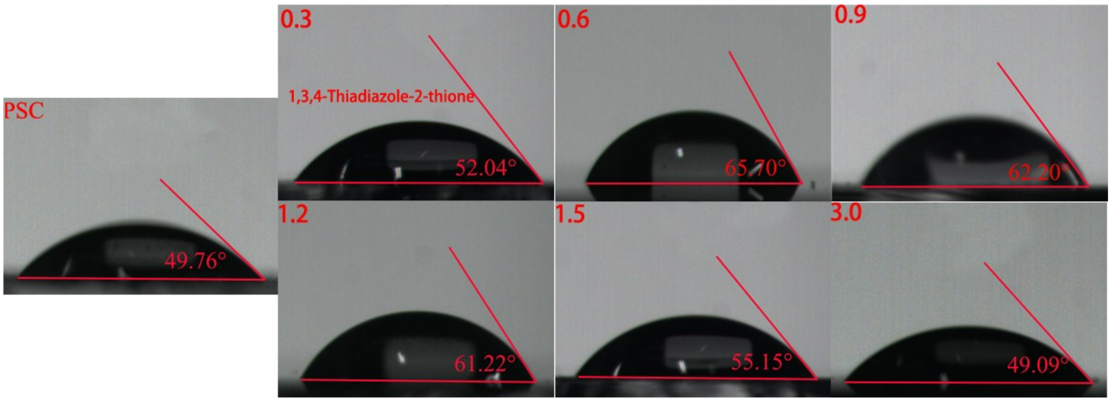


Figure S2 The contact angel between water and different concentration TDZT containing perovskite films

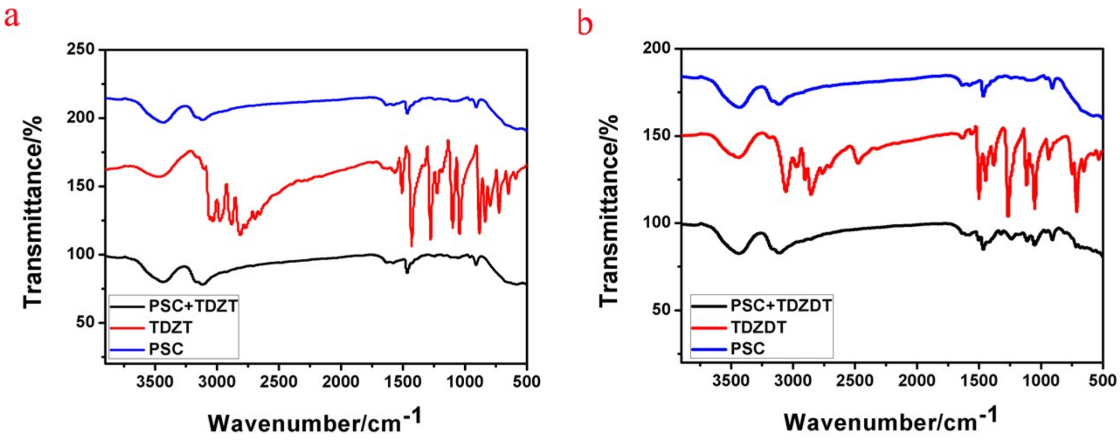
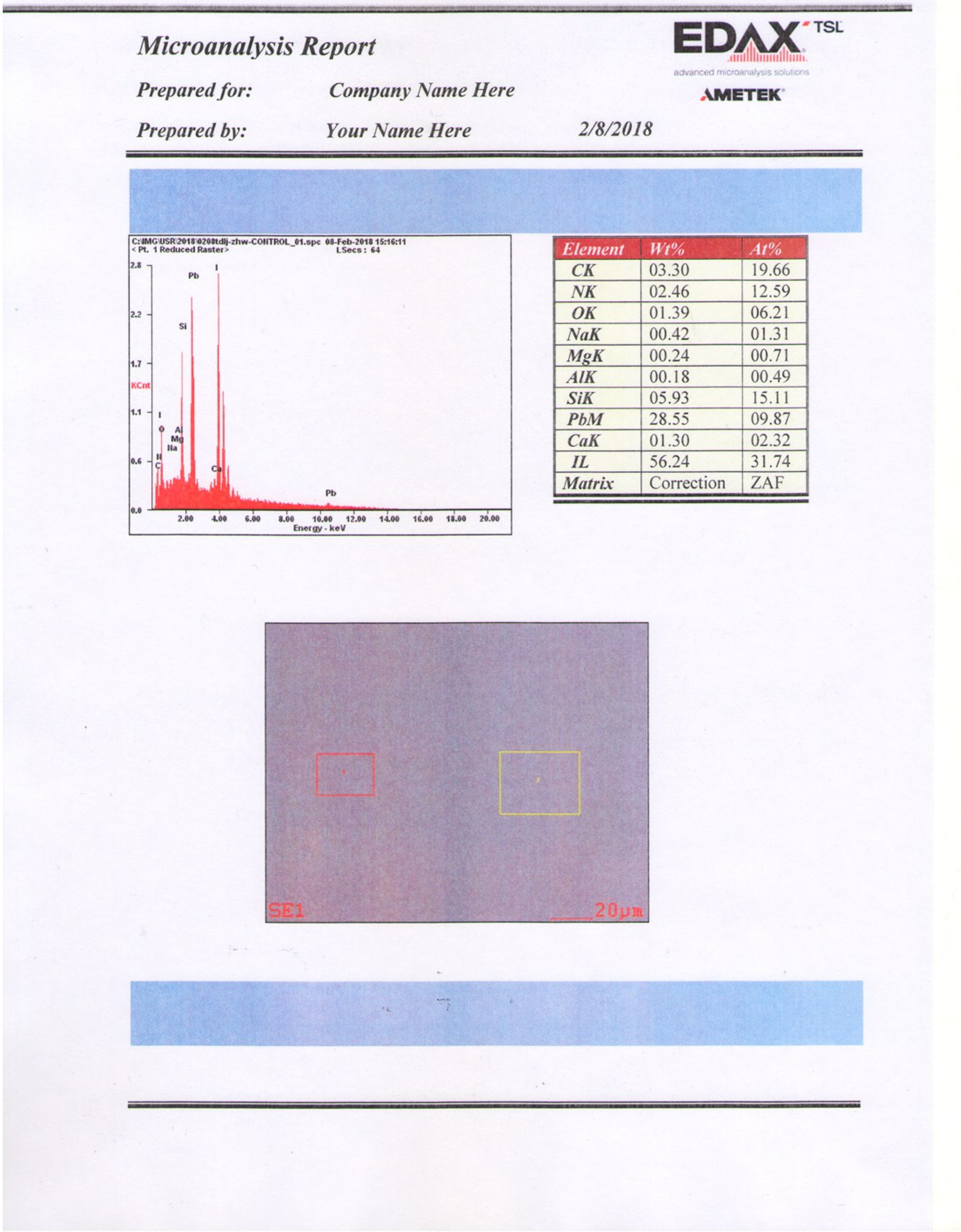


Figure S3 Fourier transform infrared spectroscopy (FTIR) for the perovskite film based on perovskite precursor with and without a) TDZT or b) TDZDT before annealing a



Microanalysis Report

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Prepared by: *Your Name Here* 2/8/2018

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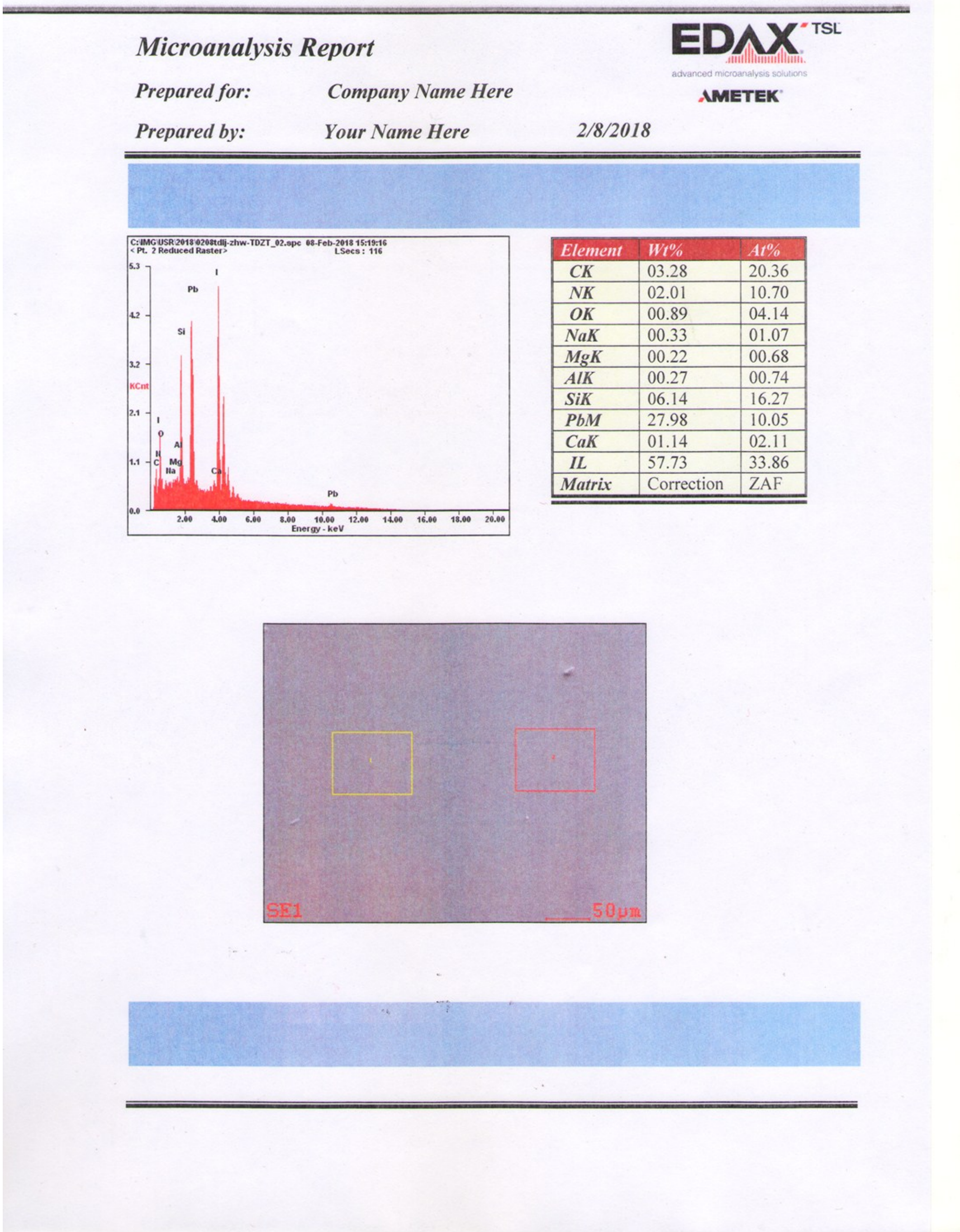
NK	02.46	12.59
OK	01.39	06.21
NaK	00.42	01.31
MgK	00.24	00.71
AlK	00.18	00.49
SiK	05.93	15.11
PbM	28.55	09.87
CaK	01.30	02.32
IL	56.24	31.74
Matrix	Correction	ZAF

b



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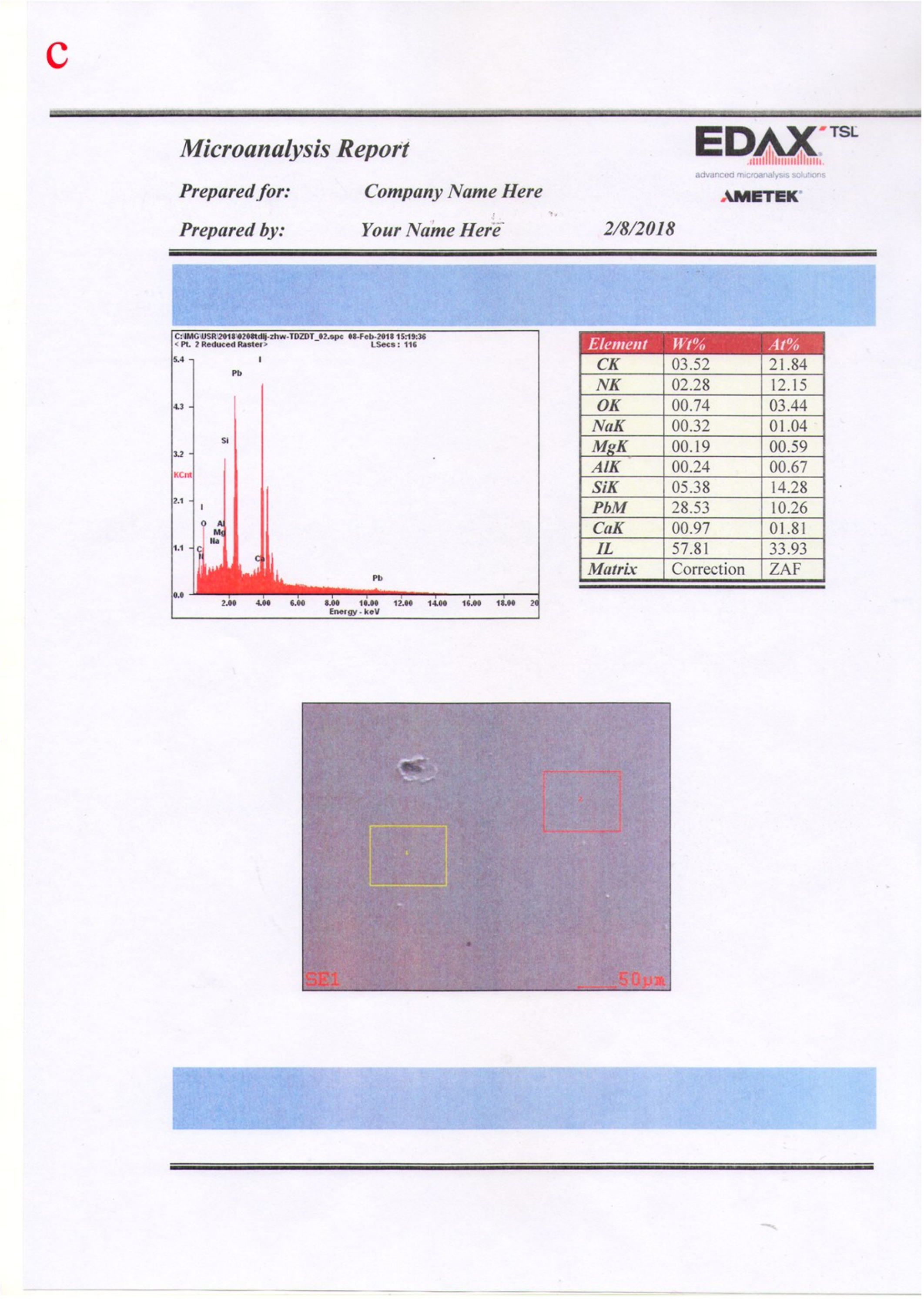
Element	*Wt%*	*At%*
CK	03.28	20.36
NK	02.01	10.70
OK	00.89	04.14
NaK	00.33	01.07
MgK	00.22	00.68
AlK	00.27	00.74
SiK	06.14	16.27
PbM	27.98	10.05
CaK	01.14	02.11
IL	57.73	33.86
Matrix	Correction	ZAF



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NK	02.28	12.15
OK	00.74	03.44
NaK	00.32	01.04
MgK	00.19	00.59
AlK	00.24	00.67
SiK	05.38	14.28
PbM	28.53	10.26
CaK	00.97	01.81
IL	57.81	33.93
Matrix	Correction	ZAF

Figure S4 Energy dispersive spectrometer analysis report of a) pristine , b) TDZT and c)TDZDT containing perovskite film.

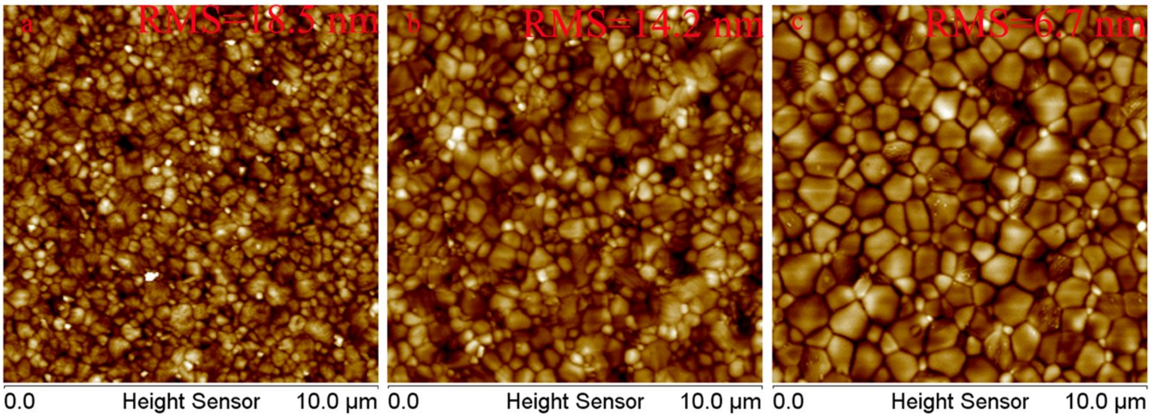

Figure S5 AFM images of a) pristine , b) TDZT and c)TDZDT containing perovskite film.

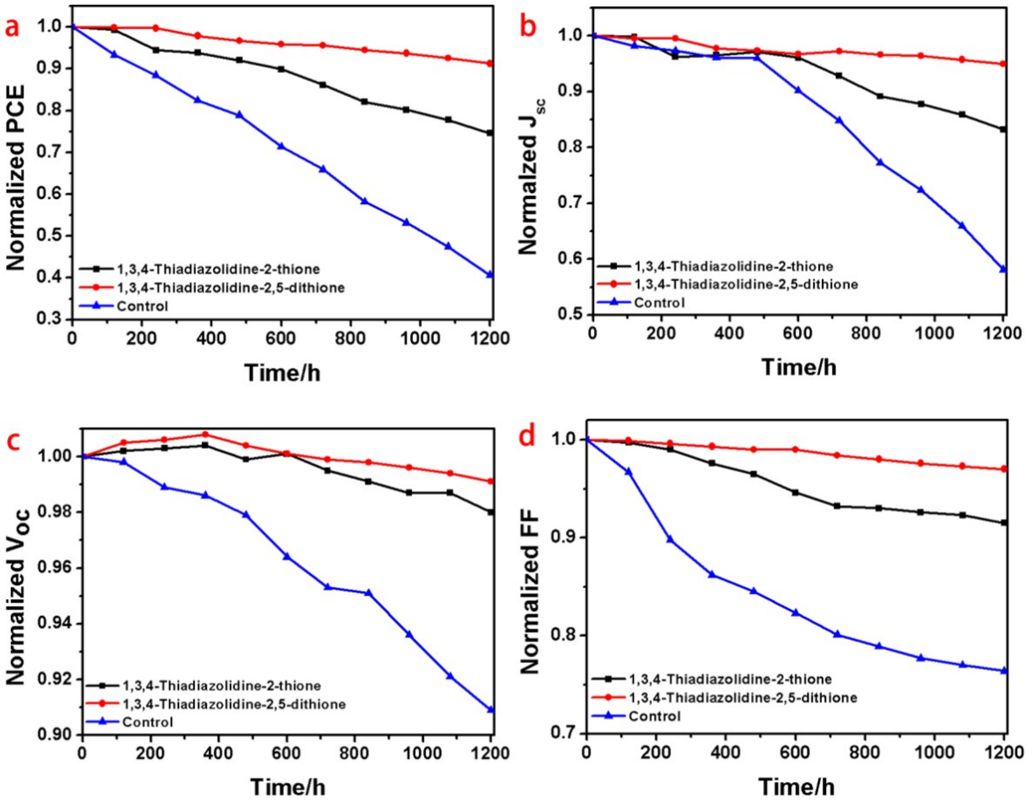

Figure S6 The a) PCE, b) *Jsc,* c) *Voc* and d) FF stability of corresponding perovskite solar cells in an ambient environment with 65±5% relative humidity under dark.

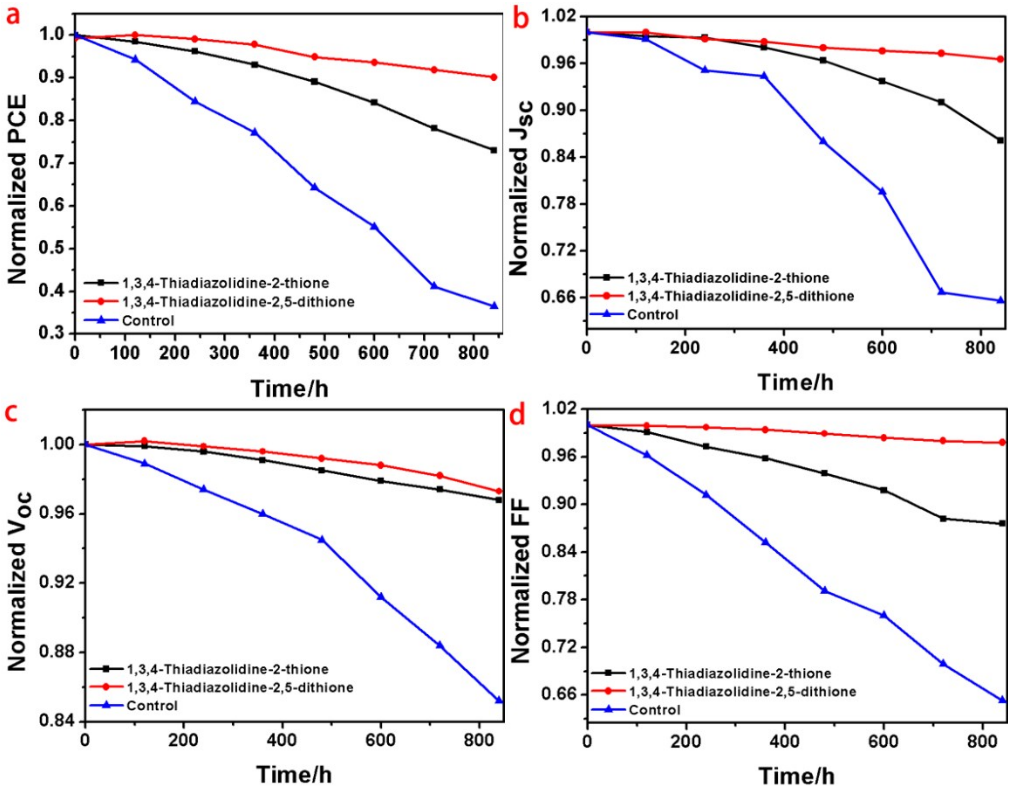

Figure S7 a) The PCE, b) *Jsc,* c) *Voc* and d) FF of corresponding perovskite solar cells in 30% relative humidity ambient air at 60-75℃ under dark.

Equation (a) y=2.54 + (23.77/(1.52×sqrt(π /2)))×exp(-2×((x-12.59)/1.52)^2)

Equation (b) y=2.76 + (27.88/(1.25×sqrt(π /2)))×exp(-2×((x-16.60)/1.25)^2)

Equation (c) y=-0.70 + (43.49/(1.14×sqrt(π /2)))×exp(-2×((x-18.36)/1.15)^2)

Equation S1 Histogram gaussian distribution of PCE 80 measurements for (a) pristine perovskite, (b) TDZT- and (c) TDZDT-containing perovskite based PSCs;