

## A multifunctional ligand for defect passivation of perovskite film realizes air-stable perovskite solar cells with efficiencies exceeding 20%

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### Experimental

#### Characterization

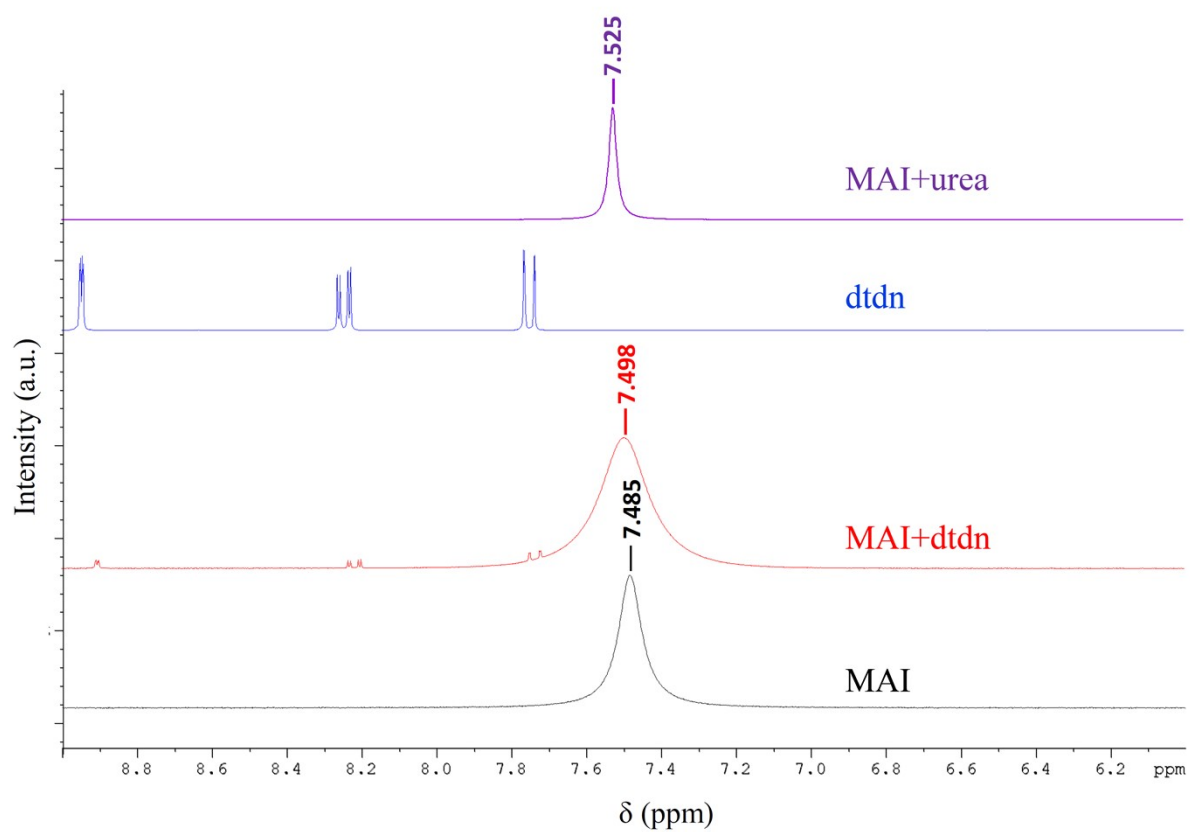
X-ray photoelectron spectroscopy (XPS) was performed using a ULVAC-PHI PHI 5000 Versaprobe II spectrometer and a monochromatic Al K $\alpha$  source. Scanning electron microscopy (SEM) images were recorded using a JSM-7000F microscope. Energy dispersive spectrometry (EDS) was used to determine the presence of elements. Crystallinity information was obtained using a Panalytical Empyrean X-ray diffractometer and CuK $\alpha$  radiation ( $\lambda = 0.1542$  nm). Absorption spectra were recorded using a JASCO V-650 spectrometer. TRPL spectra were recorded using a time-correlated single photon counting spectrometer (WELLS-001 FX, DongWoo Optron); the pulse laser had a wavelength of 440 nm and an average power of 1 mW; it was operated with a duration of excitation of 2  $\mu$ s. PL spectra were recorded using a FluroMax-4 HORIBA spectrometer with an excitation wavelength of 550 nm. Device performance data were measured inside a glove box. The current–voltage ( $I$ – $V$ ) properties of the devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) and a Dyesol simulator (AAA Class Solar Simulators) under AM 1.5 illumination (1000 W/m<sup>2</sup>); the illumination intensity was calibrated using a standard Si reference cell and a KG-5 filter. EQE spectra were recorded by using an Enlitech QE-R spectral response measurement system to calibrate the current densities of the devices. Electrochemical impedance spectroscopy (EIS) was performed using an electrochemical workstation (IM6, Zahner) over the frequency range from 1 MHz to 1 Hz, with an amplitude of 20 mV, under dark conditions; the EIS curves were fitted with Z-view software based on the electronic circuit model.

## Materials

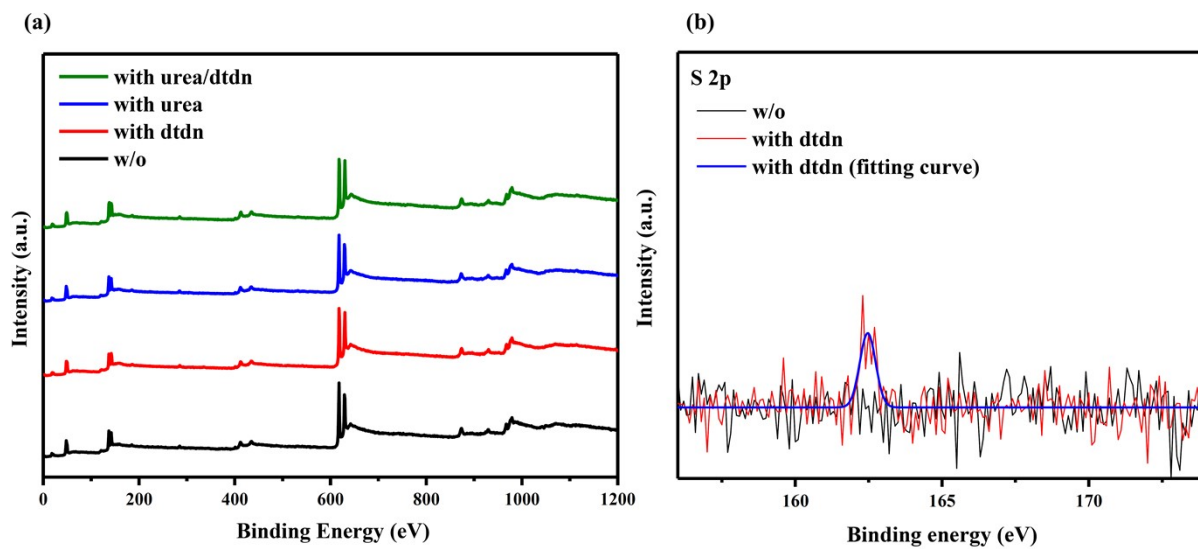
Dimethyl sulfoxide (DMSO, Sigma–Aldrich), N,N-dimethylformamide (DMF, Arcos Organics), lead iodide (Alfa Aesar), methylammonium iodide (Sigma–Aldrich), 6,6'-dithiodinicotinic acid (TCl), nickel(II) acetylacetonate, EtOH (ECHO), bathocuproine (BCP, Aldrich), PC<sub>61</sub>BM (Nano-C), and urea (J. T. Baker) were used as received

## Fabrication of PSCs

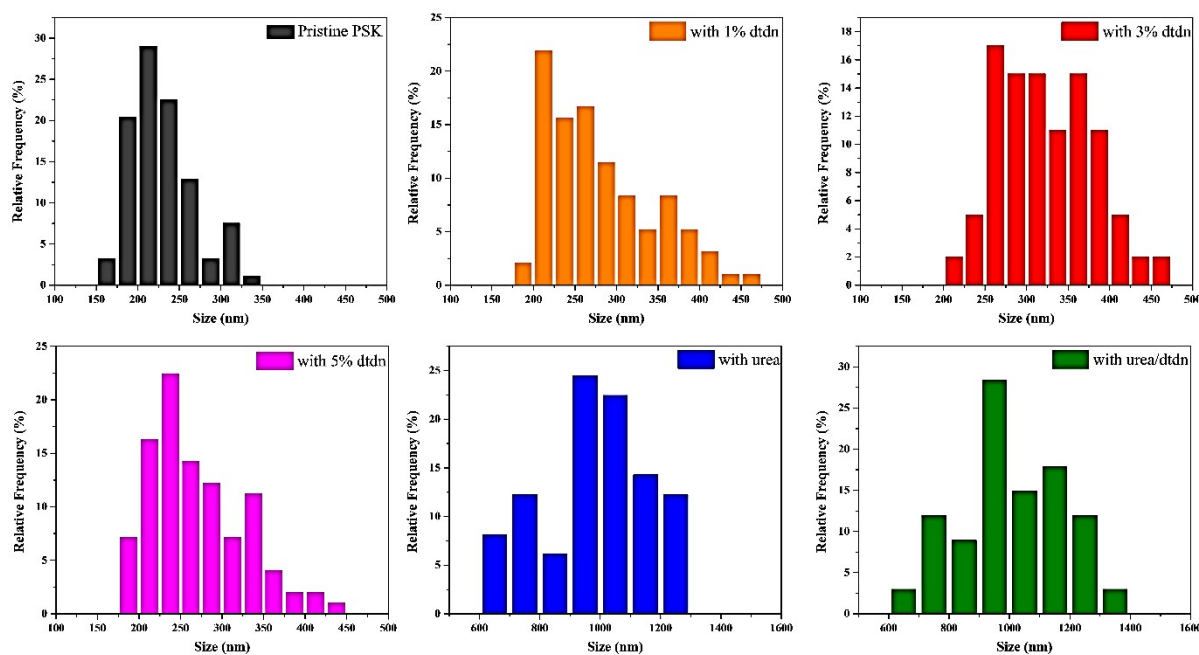
Indium tin oxide (ITO) substrates were pre-cleaned in an ultrasonic bath, sequentially with detergent aqueous solution, deionized water, acetone, and isopropyl alcohol, for 20 min each, then dried under a stream of N<sub>2</sub>. To manufacture inverted perovskite solar cells having the architecture ITO/NiO<sub>x</sub>/perovskite/PCBM/BCP/Ag, NiO<sub>x</sub> films were prepared by spin-coating (5000 rpm, 30 s) a solution containing the NiO<sub>x</sub> precursor onto plasma-treated ITO and then baking first at 250 °C for 30 min and then at 300 °C for 6 min. The NiO<sub>x</sub> precursor solution was prepared by dissolving nickel acetylacetonate (55 mg) in EtOH (2.5 mL) containing 1% HCl as a stabilizer. The ITO/NiO<sub>x</sub> substrates were transferred to an Ar-filled glove box for preparation of the perovskite films. A 1.4 M solution of the perovskite precursor was prepared by dissolving PbI<sub>2</sub> and MAI at a molar ratio of 1:1 in a mixture of DMF and DMSO (4:1, v/v). To obtain the additive-included perovskite films, an additive (urea and/or dtdn) was added to the perovskite precursor solution. The urea-incorporated perovskites were prepared by directly adding 1% urea solution into the perovskite precursor. To obtain the dtdn-incorporated perovskites, the perovskite precursor was first prepared (with or without urea) and then a 1, 3, or 5 vol % solution of dtdn (0.05 M in DMF) was added into the precursor solution. The normal perovskite precursor, the precursor with urea, or the precursor with dtdn was spin-coated onto the substrate in a two-step manner: first at 2000 rpm for 10 s and then at 4000 rpm for 22 s. During the second step, toluene (0.3 mL) was added dropwise onto the spinning substrate; the system was then annealed at 100 °C for 10 min. A solution of PC<sub>61</sub>BM in chlorobenzene (20 mg/mL) was spin-coated (2000 rpm, 30 s) onto the perovskite layer. A solution of BCP in isopropyl alcohol was spin-coated (6000 rpm, 10 s) onto the PC<sub>61</sub>BM layer. Finally, the devices were completed by evaporating Ag (100 nm) in a vacuum chamber; the active area of this electrode was fixed at 10 mm<sup>2</sup>.



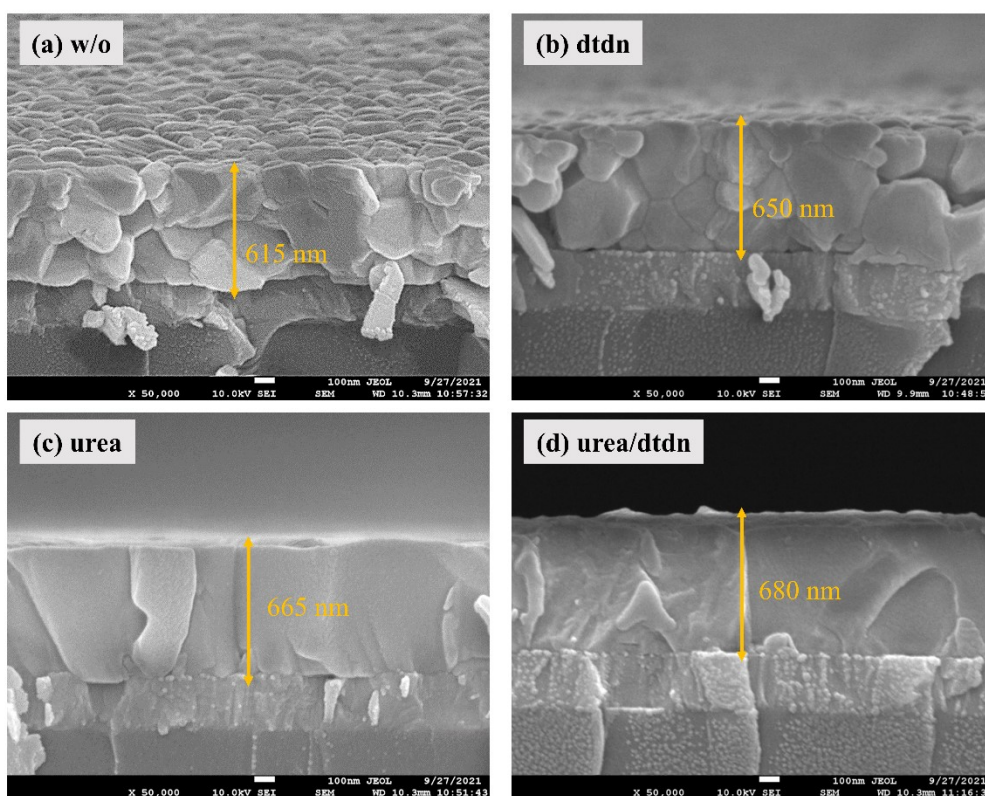
**Figure S1.** NMR spectra of MAI, MAI/dtdn, dtdn, and MAI/urea.



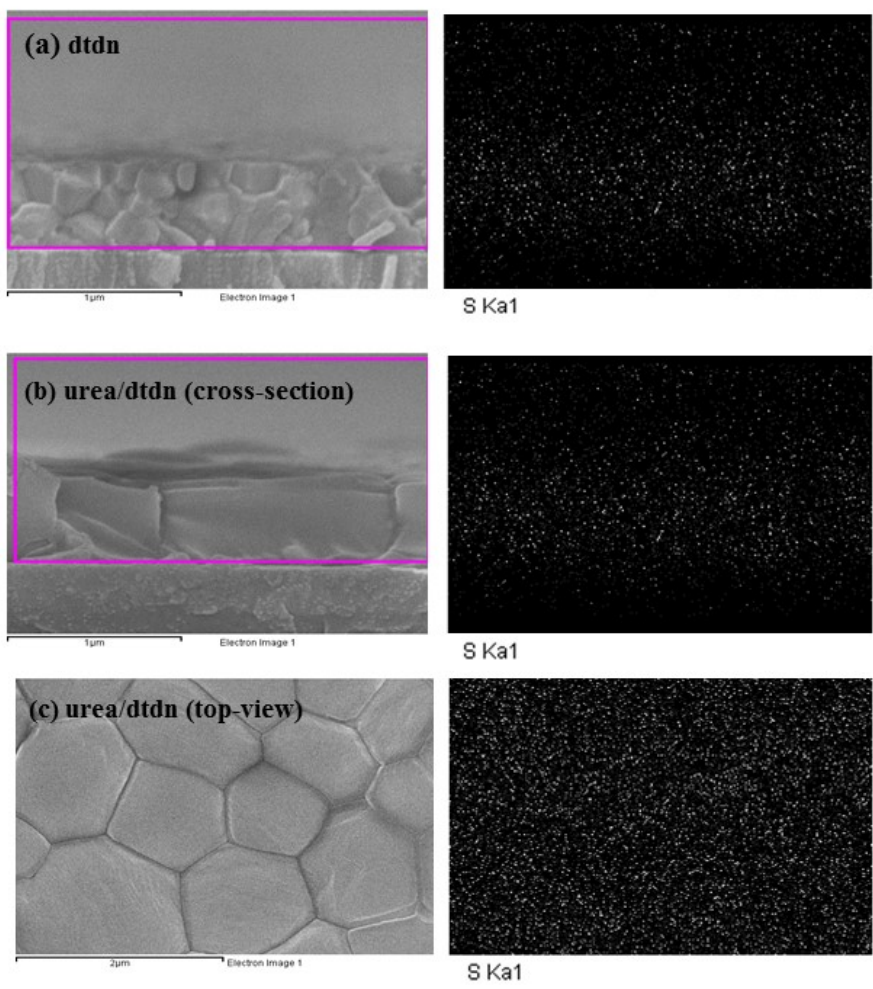
**Figure S2.** XPS spectra displaying the (a) Full-scale regions of perovskite films prepared with dtdn or urea and (b) S 2p regions of perovskite films prepared with dtdn.



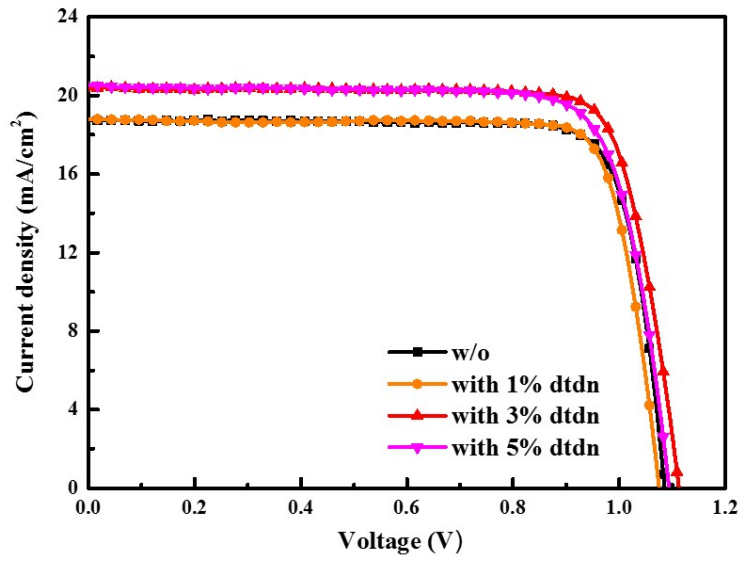
**Figure S3.** Statistical analysis in grain size of SEM images of perovskite with and w/o additives



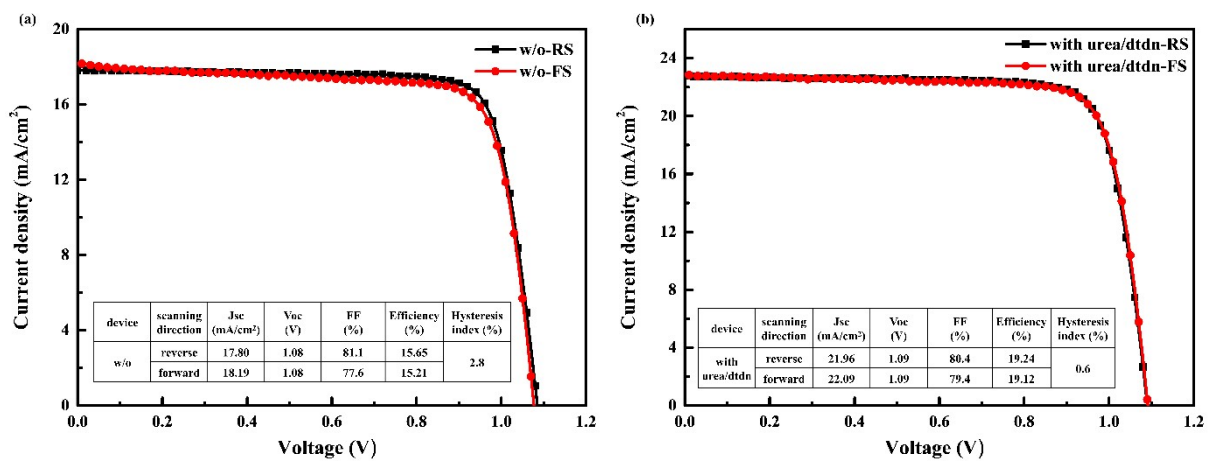
**Figure S4.** Cross-sectional SEM images of the (a) pristine perovskite film and (b–d) perovskite layers prepared with (b) 3% dtdn, (c) urea, and (d) urea/dtdn. (The scale bars are 100 nm).



**Figure S5.** (a, b) Cross-sectional SEM images and sulfur element mapping of perovskite films prepared with (a) dtdn and (b) urea/dtdn. (c) Top-view SEM images and sulfur element mapping of the perovskite film prepared with urea/dtdn.



**Figure S6.** *J*–*V* characteristic of PSCs incorporating perovskite films prepared with dtdn at various concentrations.



**Figure S7.** *J*–*V* curves and parameters obtained in forward and reverse scans of the pristine and optimal devices.

**Table S1.** Ambient stabilities of recently reported inverted PSCs.

Device configuration	Pristine PCE (%)	Modified PCE (%)	Ambient Stability	Ref.
ITO/NiOx/MAPbI <sub>3</sub> /PCBM/ BCP/Ag	16.76	20.64	94% stable after 720h (30 days) (40% RH)	This work
ITO/NiOx/Cs <sub>0.175</sub> FA <sub>0.750</sub> MA 0.075Pb(I <sub>0.880</sub> Br <sub>0.120</sub> ) <sub>3</sub> /PCBM/ZnO/Ag	17.37	19.01	72% stable after 60 days (in air,30%-40% RH) and 36% stable after 104 days (air, 50%-60% RH)	1
ITO/PTAA/FA <sub>0.8</sub> MA <sub>0.2</sub> Pb(I <sub>0.</sub> 8Br <sub>0.2</sub> ) <sub>3</sub> /PCBM/ZnO/Ag	18.3	21.5	82.8% stable after 1700 h (40% RH)	2
ITO/NiOx/Perovskite/ PCBM+C <sub>60</sub> /BCP/Cr/Au	18.62	22.1	93% stable after 6000 h (40% RH)	3
FTO/NiOx/MAPbI <sub>3</sub> /PCBM/ BCP/Ag	18.52	20.43	86% stable after 30 days (30% RH)	4
FTO/NiOx/Perovskite/ PCBM/Rhodamine101/Ag	13.6	19.06	80% stable after 1000 h (30%-40% RH)	5
ITO/NiOx/FA <sub>0.85</sub> MA <sub>0.15</sub> PbI <sub>2.</sub> 55Br <sub>0.45</sub> /Nb <sub>2</sub> O <sub>5</sub> /Ag	18.28	20.41	90% stable after 60 days (55±10% RH)	6
ITO/HTM/(exMMT/ MAPbI <sub>3</sub> )/PCBM/PEI/Ag	16.65	17.29	Almost zero loss after 4680 h (ambient)	7
ITO/PTAA/BDAl/Perovskit e/PCBM/BCP/Ag	20.09	22.31	87% stable after 850 h (20% RH)	8

**Table S2.** FWHMs and intensities of the XRD spectral signals at a value of  $2\theta$  of  $14^\circ$  corresponding to the (110) plane.

sample	FWHM (degree)	Intensity (a.u.)
w/o	0.493	3028
1% dtdn	0.476	4319
3% dtdn	0.473	4681
5% dtdn	0.489	3531
with urea	0.463	7090
with urea/dtdn	0.446	7966

**Table S3.** Fitting parameters for the bi-exponential decay function of the TRPL spectral data of perovskite films prepared with various additives.

sample	$\tau_1$ ( $A_1$ )	$\tau_2$ ( $A_2$ )	$\tau_{\text{average}}$
w/o	5.18 ns (27.1%)	46.25 ns (72.9%)	35.138 ns
With dtdn	4.76 ns (26.4%)	47.10 ns (73.6%)	35.925 ns
With urea	14.31 ns (21.4%)	51.73 ns (78.6%)	43.733 ns
With urea/dtdn	20.23 ns (27.3%)	60.81 ns (72.7%)	49.741 ns

**Table S4.** Fitted EIS parameters of PSCs incorporating perovskite films prepared with various additives.

Device (additives)	$R_s$ ( $\Omega$ )	$R_{\text{rec}}$ ( $\Omega$ )	CPE(F)
w/o	17.15	2229	$1.131 \cdot 10^{-8}$
with dtdn	6.24	4448	$1.074 \cdot 10^{-8}$
with urea	8.44	4672	$1.026 \cdot 10^{-8}$
with urea/dtdn	6.97	5916	$7.832 \cdot 10^{-9}$

**Table S5.** Parameters of J–V performance of urea-derived PSCs incorporating perovskite films prepared with dtdn at various concentrations.

Sample (additives)	$J_{\text{SC}}$ (mA/cm <sup>2</sup> )	$V_{\text{OC}}$ (V)	FF (%)	Efficiency (%)
with urea/ 1% dtdn	21.11	1.08	80.7	18.37
with urea/ 5% dtdn	20.83	1.08	78.6	17.66
with urea/ 7% dtdn	20.22	1.06	77.4	16.56



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