

**Supplementary Information**  
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**Synergistic Effect of Two Hydrochlorides Boosting 3D to  
Quasi-2D Tin-Based Perovskite Solar Cells with  
Significantly Enhanced Performance**

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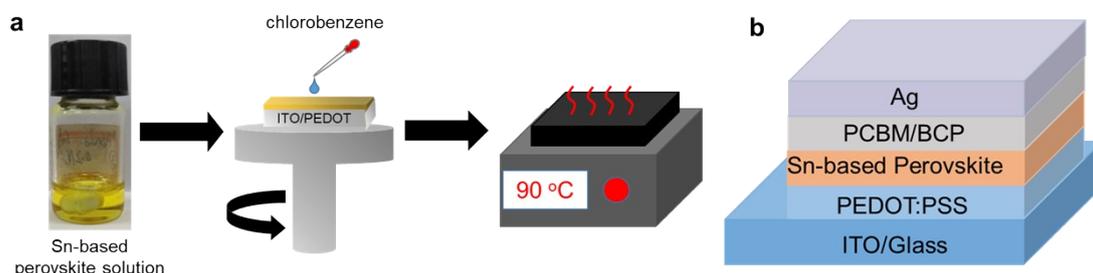
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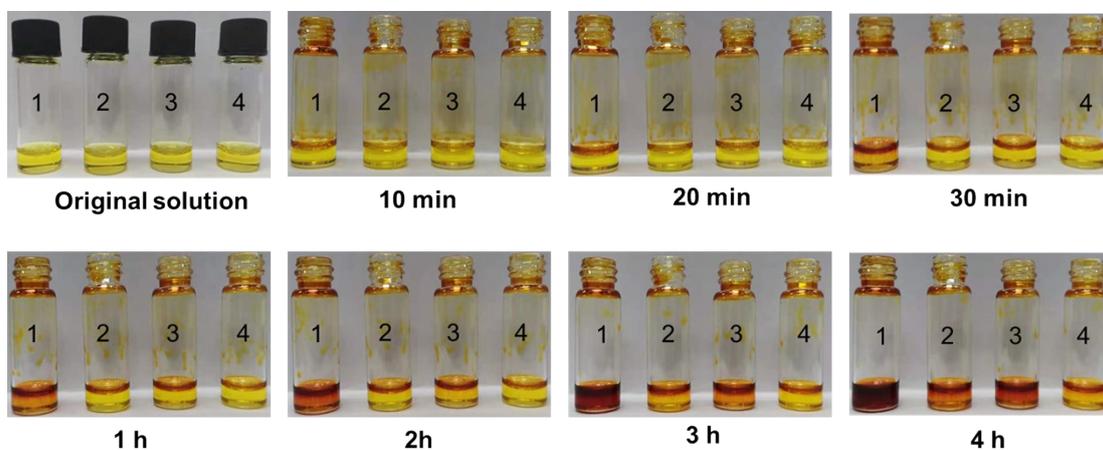
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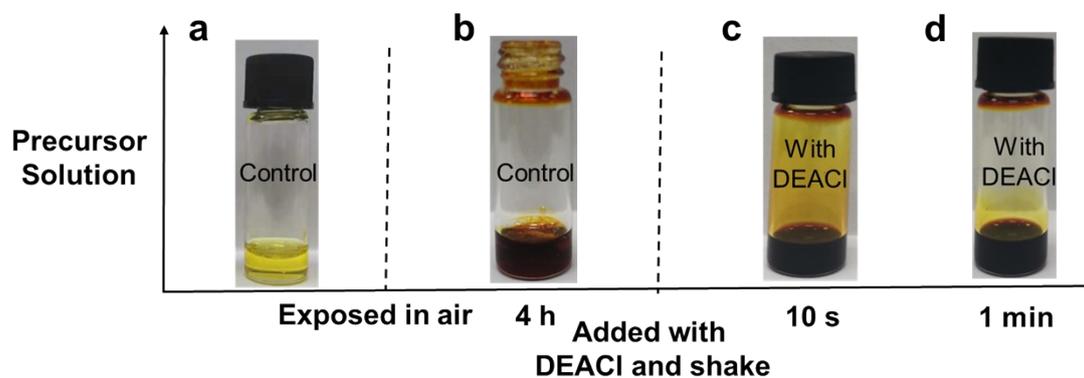
# T.L. and W. Y.Y. contributed equally to this work.



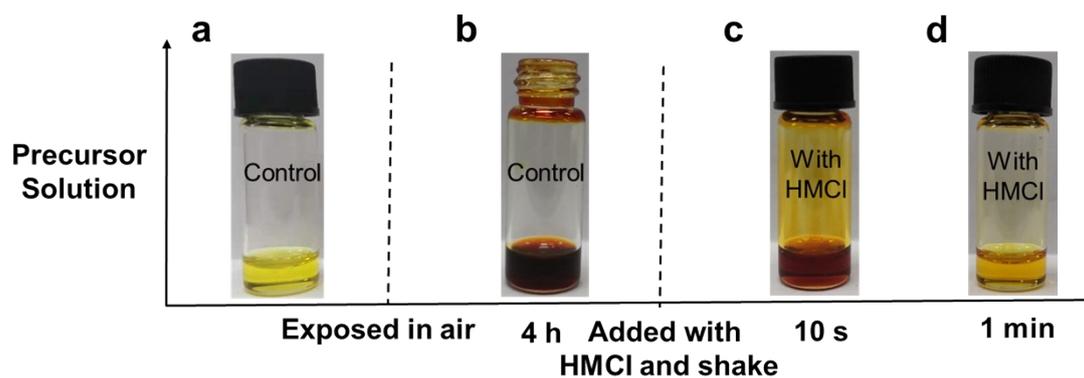
**Fig. S1.** (a) The progress of the Sn-based perovskite film via a one-step spin-coating method with antisolvent dripping. (b) Device structure of the 2D Sn-based PVSCs.



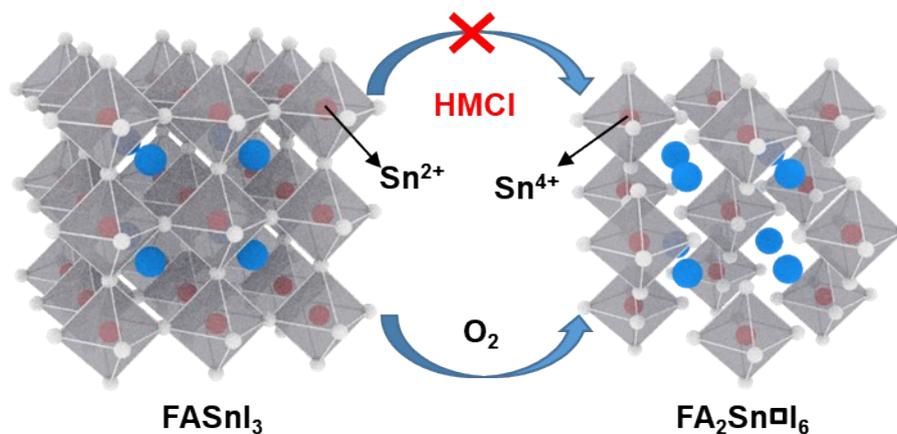
**Fig. S2.** Image of the precursor solution with different additives exposed in air for different time (the solution on the bottle wall can be considered as a mark to prove that the bottle has not moved during the shooting). The solution were marked as Sample 1: control solution; Sample 2: solution with DEACl; Sample 3: solution with HMC1; Sample 4: solution with HMC1 and DEACl.



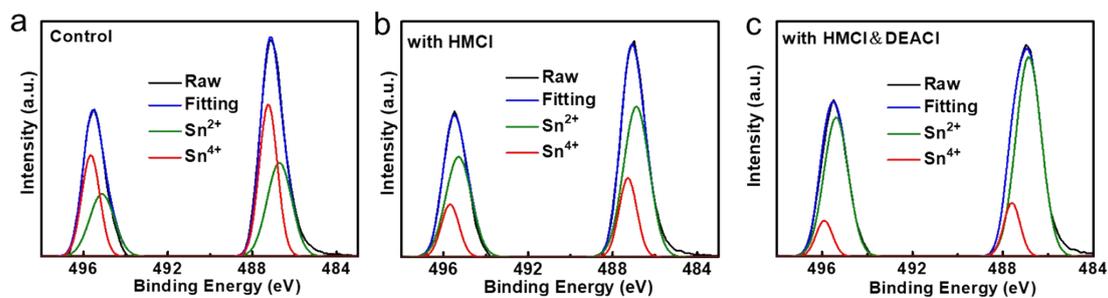
**Fig. S3.** Images of  $\text{FASnI}_3$  solution. (a)  $\text{FASnI}_3$  solution added with  $\text{SnF}_2$ . (b) solution exposed in air for 4 h. Add DEACl to the oxidized precursor solution and shake for (c) 10 s and (d) 1 min.



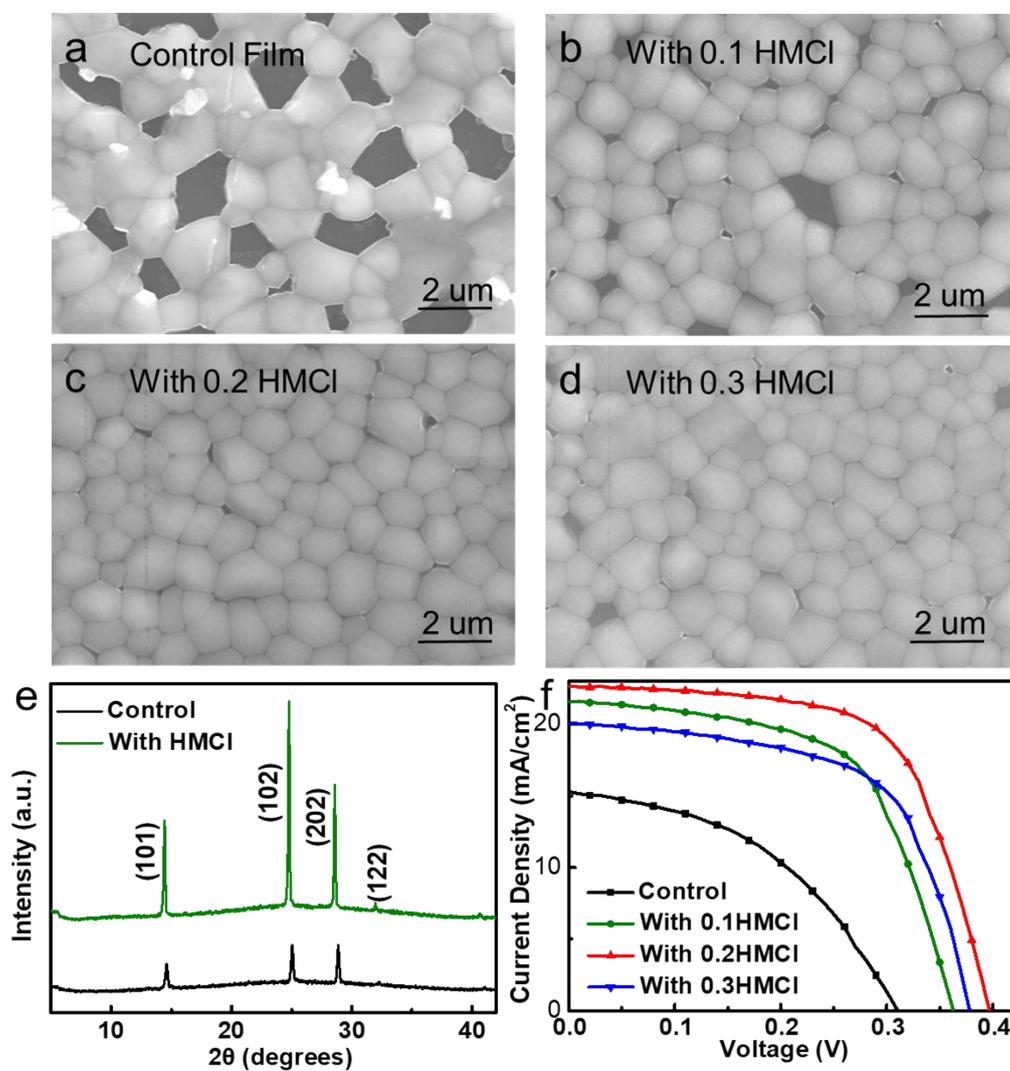
**Fig. S4.** Images of  $\text{FASnI}_3$  solution. (a) The  $\text{FASnI}_3$  solution added with  $\text{SnF}_2$ . (b) The solution exposed in air for 4 h. The oxidized precursor solution after adding HMCl and shaking for (c) 10 s and (d) 1 min.



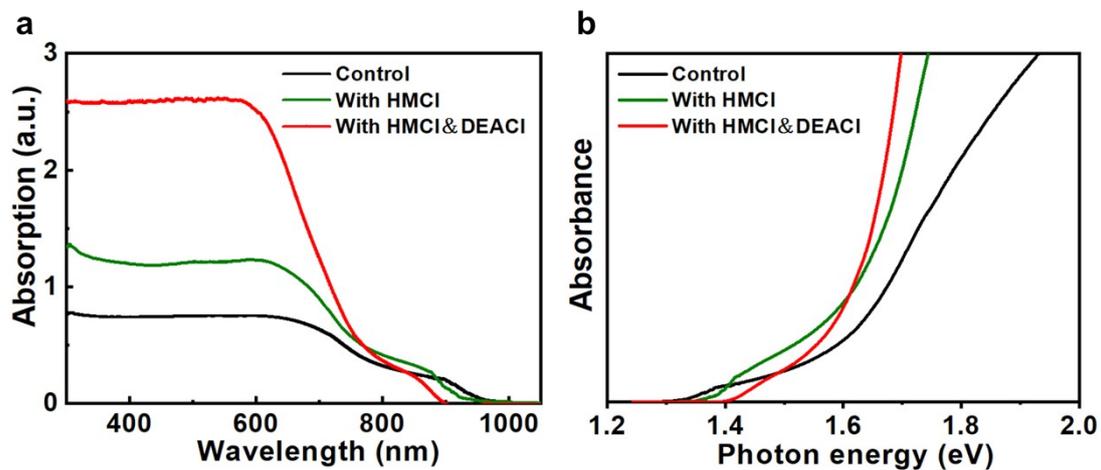
**Fig. S5.** 3D schematic diagram of the transformation of  $\text{FASnI}_3$  crystal in air environment.



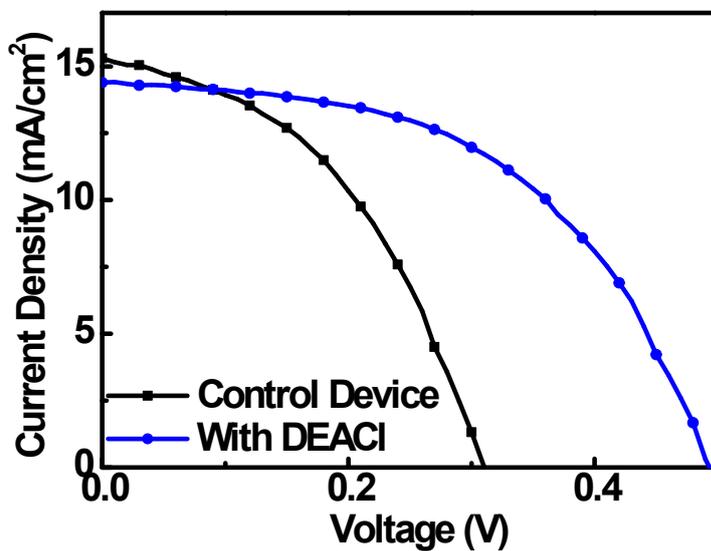
**Fig. S6.** XPS Sn 3d spectra of corresponding films (a) without additives, (b) with addition of 20% HMC1, and (c) with addition of 20% HMC1 and 20% DEAC1. The two peaks deconvoluted from the measured spectra at 486.5 and 487.5 eV are associated with  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ , respectively. The etching time is 30 s.



**Fig. S7.** SEM images of the Sn-based perovskite films with different amounts of HMCl. (a) without HMCl. (b) with 10% HMCl added. (c) with 20% HMCl added. (d) with 30% HMCl added. (e) XRD patterns of the Sn-based films, the control film (FASnI<sub>3</sub> film with 0.1M SnF<sub>2</sub>), and the film with 0.2M HMCl added. (f) *J-V* curves of Sn-based devices containing different amounts of HMCl.



**Fig. S8.** (a) Absorption spectrum of the different films. (b) Tauc plot of Sn-based perovskite films with different additive (Photo energy are 1.33eV, 1.36 eV, 1.42 eV, respectively).



**Fig. S9.** *J-V* curves of Sn-based devices with and without DEACl.

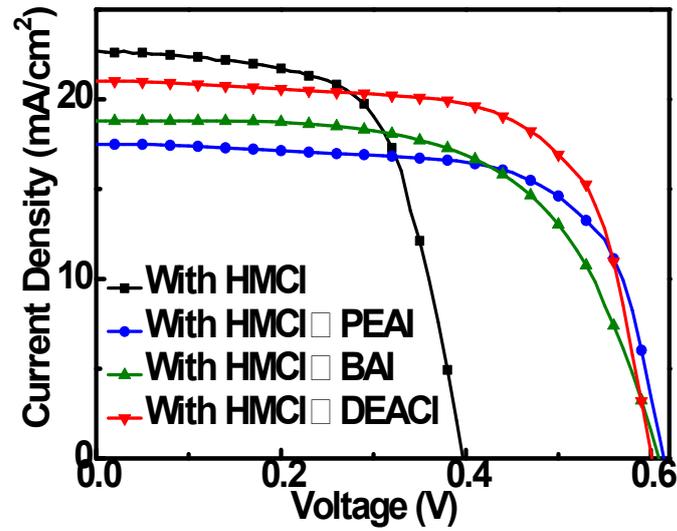


Fig. S10.  $J$ - $V$  curves of Sn-based devices containing HMCl with different large cations additive.

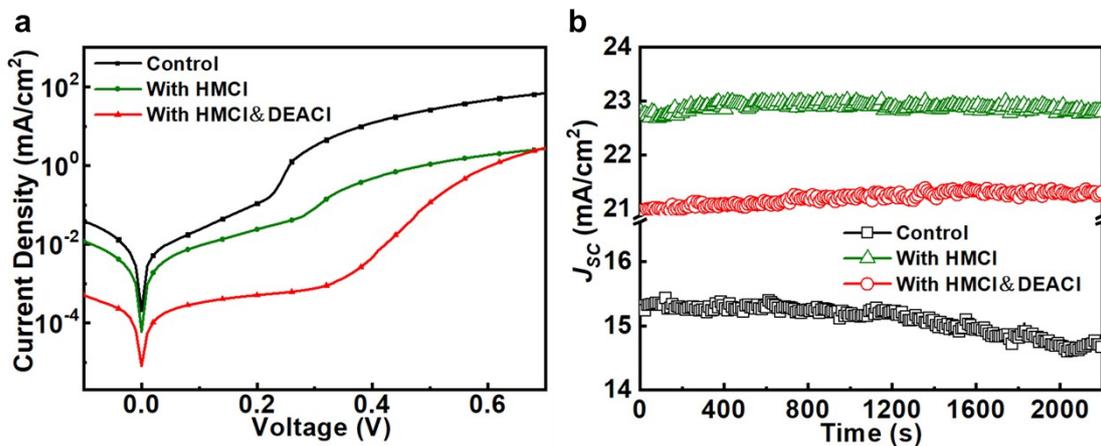


Fig. S11. (a) Dark  $J$ - $V$  curves of the control, with addition of HMCl, and with addition of HMCl and DEACl devices (b)  $J_{sc}$ - $T$  curves of the device with different additives under 1.5 G irradiation.

**Table S1.** The development of 2D tin-based perovskites in recent years

Year	Structure	Author	Journal	PCE (%)
2017	2D based BA <sup>+</sup>	Mercouri G. Kanatzidis	<i>ACS Energy Lett.</i>	2.37
2017	2D based PEA <sup>+</sup>	Zhijun Ning	<i>JACS</i>	5.94
2018	2D-3D hybrid	Maria Antonietta Loi	<i>Adv. Energy Mater.</i>	9
2018	2D-3D hybrid	Zhijun Ning	<i>Joule</i>	9.41
2019	2D based AVA <sup>+</sup>	Mingjian Yuan	<i>Adv. Funct. Mater.</i>	8.71
2020	2D based BA <sup>+</sup>	Mingzhen Liu	<i>ACS Energy Lett.</i>	4.04
2021	3D	Zhijun Ning	<i>J. Am. Chem. Soc</i>	14.6
2021	2D-3D	Zhubing He	<i>Adv. Mater.</i>	14.8
2022	2D based DEA <sup>+</sup>	This work	--	9.47

**Table S2.** Device parameters of Sn-based perovskite films adding with different content HMCl.

Sample	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
Control	15.3	0.31	48.28	2.29
10% HMCl	21.6	0.362	62.02	4.85
20% HMCl	22.7	0.396	66.22	5.95
30% HMCl	20.11	0.378	61.30	4.66

**Table S3.** Fitted TRPL parameters of Sn-based perovskite film with different additives.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)
Control	2.14	7.43
With HMCl	5.21	9.67
With HMCl&DEACl	7.92	16.32

**Table S4.** Device parameters of Sn-based perovskite solar cells with and without adding DEACl.

Sample	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
Control	15.3	0.31	48.28	2.29
With DEACl	14.39	0.493	51.71	3.67

**Table S5.** The corresponding parameters of trap concentration and carrier mobility of perovskite films with different additives.

Sample	$V_{TFL}$ (V)	$N_{trap}$ (cm <sup>-3</sup> )	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> S <sup>-1</sup> )
Control Film	0.321	$6.44 \times 10^{15}$	$1.2524 \times 10^{-4}$
With HMCl	0.0912	$1.242 \times 10^{15}$	$1.0043 \times 10^{-3}$
With HMCl&DEACl	0.0644	$1.126 \times 10^{15}$	$4.4581 \times 10^{-3}$

**Table S6.** The electrostatic potential (ESP) parameters of DEA<sup>+</sup>, BA<sup>+</sup> and PEA<sup>+</sup> calculated by density functional theory (EFT).

Sample	MPI (eV)	Volume (Å)	Minima ESP (eV)	Maxima ESP (eV)
DEA <sup>+</sup>	4.61911	123.61614	3.571654	6.511710
BA <sup>+</sup>	4.46498	123.81487	2.477844	6.933499
PEA <sup>+</sup>	3.86253	173.53287	1.907838	6.851608