## **Supporting Information**

## Influence of the Stoichiometry of tin-based 2D/3D Perovskite active layer on Solar Cells performances

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**Figure S1.** XRD patterns of (a) a PEA<sub>0.08</sub>FA<sub>0.6</sub>SnI<sub>3</sub>film with hexagonal SnI<sub>2</sub> ( $\beta$ -SnI<sub>2</sub>) peaks at 12.7°, 25.6°, and 38.8°, (b) a PEA<sub>0.08</sub>FA<sub>0.7</sub>SnI<sub>3</sub> film with  $\beta$ -SnI<sub>2</sub> peaks at 12.7° and 25.6° and (c) a PEA<sub>0.08</sub>FA<sub>0.8</sub>SnI<sub>3</sub> film with  $\beta$ -SnI<sub>2</sub> peaks at 12.7° and 25.6 as well <sup>[1]</sup>.



Figure S2. GIWAXS patterns of  $PEA_{0.08}FA_{(x)}SnI_3$  films. The images were recorded using an incident angle of 0.25°.



**Figure S3.** The line-cut data in (a) in-plane  $(q_z)$  and (b) out-of-plane  $(q_y)$  of the GIWAXS images of the PEA<sub>0.08</sub>FA<sub>x</sub>SnI<sub>3</sub> films with X-ray incident angle of 0.25°, respectively.



Figure S4. SEM images of the  $PEA_{0.08}FA_xSnI_3$  films: (a) x=0.7, (b) x=0.85, (c) x=0.92, (d) x=1.0, (e) x=1.1, (f) the magnified image of x=1.1 sample.



Figure S5. Normalized PL spectra of PEA<sub>0.08</sub>FA<sub>(x)</sub>SnI<sub>3</sub> films.



**Figure S6.** Absorbance of  $PEA_{0.08}FA_{(x)}SnI_3$  films (a) with an incident light wavelength from 350 nm to 1000 nm and (b) from 700 nm to 900 nm. Note: the absorbance spectra in the short wavelength region (<600 nm) are saturated.





**Figure S7.** Mott-Schottky analysis of perovskite solar cells of different stoichiometry. (a-h)  $C^{-2}$  as a function of bias voltage. (i) carrier concentration as deriveved from Mott-Schottky analysis for the different samples.



**Figure S8.** Statistics for  $V_{OC}$ ,  $J_{SC}$ , FF and PCE of devices with an active area of 0.04 cm<sup>2</sup>. Note that: for the 0.70 M composition 8 samples were measured, for the 0.95 M composition 9 samples, and for the 1.20 M composition also 9 samples were measured. The graph includes the values from Table 1.



**Figure S9.** Statistics for  $V_{OC}$ ,  $J_{SC}$ , FF and PCE of devices with an active area of 0.09 cm<sup>2</sup>. Note that: for the 0.70 M composition 8 samples were measured, for the 0.95 M composition 9 samples, and also for the 1.20 M composition 9 samples were measured.



**Figure S10.** Statistics for  $V_{OC}$ ,  $J_{SC}$ , FF and PCE of devices using different 2D/3D films with an active area of 0.25 cm<sup>2</sup>. Note that: for the 0.70 M composition 8 samples were measured, for the 0.95 M composition 9 samples, and also for the 1.20 M composition 9 samples were measured.



Figure S11. IPCE measurements of ITO/PEDOT:PSS/ PEA<sub>0.08</sub>FA<sub>(x)</sub>SnI<sub>3</sub>/C60/BCP/Al devices.



Figure 12. Variation of the  $V_{OC_{2}}$  J<sub>SC\_{2</sub> FF and PCE of devices using different 2D/3D films vs time they have been exposed to air.

References:

[1] V. S. Kostko, O. V Kostko, G. I. Makovetskii and K. I. Yanushkevich, *Phys. status solidi*, 2002, **229**, 1349–1352.