Electronic supplementary information for the manuscript:

Hydrazinium-assisted stabilisation of methylammonium tin iodide for leadfree perovskite solar cells

Sergey Tsarev,^a Aleksandra G. Boldyreva^a, Sergey Yu. Luchkin^a, Moneim Elshobaki^a, Mikhail I. Afanasov^c, Keith .J. Stevenson^a and Pavel. A. Troshin^{a,b}

a. Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Nobel St. 3, Moscow 143026, Russian Federation

b. The Institute for Problems of Chemical Physics of the Russian Academy of Sciences, Semenov Prospect

1, Chernogolovka 141432, Russian Federation.

c. Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1-3, Moscow, Russian Federation

Contents:

Figure S1. Illustration of <i>d</i> 001 peak shift of the MA _(1-x) HA _x SnI ₃ diffraction patterns in13.5 -14.7°2Theta region.	2
Figure S2. J-V curves and corresponding photovoltaic parameters of the top MA _{0.8} HA _{0.2} SnI ₃ solar cell scanned in forward (black colour) and reverse (red colour) directions at 10mV/sec scanning rate	3
Figure S3 . IV curves of the top MA _{0.8} HA _{0.2} SnI ₃ solar cell after storing under inert atmosphere for 2 and 5 days	4
Figure S4. Mössbauer spectra of MASnI ₃ (top) and MA _{0.8} HA _{0.2} SnI ₃ (bottom) powders	4
Table S1 . Photovoltaic parameters of the top MA _{0.8} HA _{0.2} SnI ₃ solar cell after storing under an inert atmosphere for 2 and 5 days	5
Table S2. Photovoltaic parameters of published solar cells configurations based on MASnI ₃ absorber layer	6



Figure S1.J-V curves and corresponding photovoltaic parameters of the top MA_{0.8}HA_{0.2}Snl₃solar cell scanned in forward (black colour) and reverse (red colour) directions at 10mV/sec scanning rate



Figure S2. Illustration of *d*001 peak shift of the $MA_{(1-x)}HA_xSnI_3$ diffraction patterns in13.5 -14.7°2Theta region. The values of lattice constants *a* were estimated from the positions of *d*001 peaks.



Figure S3. IV curves of the top $MA_{0.8}HA_{0.2}SnI_3$ solar cell after storing in an inert atmosphere for 2 and 5 days

Table S1. Photovoltaic parameters of the top $MA_{0.8}HA_{0.2}SnI_3solar$ cell after storing in a glovebox for 2 and 5 days

Storage time	Voc, V	J _{sc} mA/cm ²	FF ,%	PCE , %
fresh	0.38	14.1	49	2.6
2days	0.49	9.0	53	2.35
5 days	0.46	9.0	56	2.34



Figure S4. Mössbauer spectra of MASnI₃ (top) and MA_{0.8}HA_{0.2}SnI₃ (bottom) powders

Table S2. Photovoltaic parameters of published solar cells configurations based on MASnI₃ absorber layer

Solar cell configuration	Voc (top), V	J _{sc} (top) mA/cm²	FF (top),%	PCE (Top), %	Stability
FTO/TiO ₂ c/TiO ₂ mp/MASnI ₃ /Spiro- OMFTAD/Au (top device only) ¹	0.88	16.8	42	6.4	No data
FTO/TiO ₂ c/TiO ₂ mp/MASnI ₃ /Spiro- OMETAD/Au ²	0.68±0.03	16.3±0.71	48±3	5.23±0.18	80% PCE retained within 12 hour of storage under nitrogen
FTO/TiO2c/TiO2mp/{en}MASnI3/PTAA/Au3	0.373 ± 0.019	23.03 ± 1.67	61.20 ± 3.52	5.26 ± 0.47	15 minutes under air exposure
$FTO/TiO_2c/TiO_2mp/{en}MASnI_3$ (hydrazine vapour)/PTAA/Au (top device only) ³	0.428	24.28	63.72	6.63	No data
$FTO/TiO_2c/TiO_2mp/MASnI_3$ (hydrazine vapour)/PTAA(TPFB)/Au (top device only) ⁴	0.377	19.92	51.73	3.89	No data
FTO/TiO ₂ c/TiO ₂ mp/MASnI ₃ /PTAA/Au ⁵	0.217 ±0.043 (0.273)	15.1 ± 3.08 (17.36)	34.8 ± 2.81 (39.1)	1.16 ± 0.42 (1.86)	No data
FTO/TiO₂c/TiO₂mp/MASnI₃/Au (top device only) ⁶	(0.320)	(21.4)	(46)	(3.15)	Stable over 300 sec of measurement
ITO/PEDOT:PSS/Poly-TPD/MASnl ₃ (CVD)/C60/BCP/Ag ⁷	(0.377)	(12.1)	(36.6)	(1.7)	No data
ITO/PEDOT:PSS/MASnl _s (LT_VASP)/C ₆₀ /BCP/ Ag ⁸	0.450±0.01	11.8±1.2	40±3	2.14±0.35	60% PCE after 200h of light exposure
ITO/PEDOT:PSS/HA _{0.2} MA _{0.8} SnI ₃ /PCBM/Ag (this work)	0.35 ±0.05 (0.38)	11.8±2.8 (14.1)	50±2 (49)	2.1±0.5 (2.6)	90% PCE after 5 days storage in a glovebox

References:

- 1 F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang and M. G. Kanatzidis, *Nat. Photonics*, 2014, **8**, 489–494.
- 2 N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A.-A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, A. Petrozza, L. M. Herz and H. J. Snaith, *Energy Environ. Sci.*, 2014, **7**, 3061–3068.
- W. Ke, C. C. Stoumpos, I. Spanopoulos, L. Mao, M. Chen, M. R. Wasielewski and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2017, **139**, 14800–14806.
- 4 T.-B. Song, T. Yokoyama, C. C. Stoumpos, J. L. Logsdon, D. H. Cao, M. R. Wasielewski, S. Aramaki and M. G. Kanatzidis, J. Am. Chem. Soc., 2016, **139**, 836-842.
- 5 T. Yokoyama, D. H. Cao, C. C. Stoumpos, T. Bin Song, Y. Sato, S. Aramaki and M. G. Kanatzidis, *J. Phys. Chem. Lett.*, 2016, **7**, 776–782.
- 6 F. Hao, C. C. Stoumpos, P. Guo, N. Zhou, T. J. Marks, R. P. H. Chang and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2015, **137**, 11445–11452.
- 7 Y. Yu, D. Zhao, C. R. Grice, W. Meng, C. Wang, W. Liao, A. J. Cimaroli, H. Zhang, K. Zhu and Y. Yan, *RSC Adv.*, 2016, **6**, 90248–90254.
- 8 T. Fujihara, S. Terakawa, T. Matsushima, C. Qin, M. Yahiro and C. Adachi, J. Mater. Chem. C, 2017, 5, 1121–1127.