## **Electronic Supplementary Information**

## Solution-processable antimony-based light-absorbing materials beyond lead halide perovskites

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## **Experimental section**

Aqueous hydroiodic acid (HI) (57 wt.% in water), methylamine (CH<sub>3</sub>NH<sub>2</sub>, 40 wt.% in water), Sbl<sub>3</sub> (99.998%), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), CsI (99.999%), and diethyl ether were purchased from Alfa Aesar and used without further purification. MAI was purchased from Lumitech, Taiwan. Poly(3,4-ethylenedioxythiophene):poly(p-styrene sulfonate) (PEDOT:PSS. Clevios P) was bought from Heraeus (Germany).

**Device fabrication:** Solar cell: Indium tin oxide (ITO)–coated glass substrates (<10  $\Omega$  sq<sup>-1</sup>, RiTdisplay) were cleaned through sonication, once in detergent (20 min) and then twice in deionized (DI) water (20 min each), and dried under N<sub>2</sub> gas. The substrates were treated with ultraviolet (UV)/ozone for 15 min to clean the surfaces and also to improve the surface adhesion. PEDOT:PSS was spin-coated (4000 rpm, 60 s) onto the ITO surfaces, followed by annealing (130 °C, 30 min). The substrates were transferred to a glove box for deposition of the perovskite active layer through a single-step spin-coating method. The MA<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> material was prepared from different molar ratio of SbI<sub>3</sub> and MAI in the DMF. The Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> material was prepared from different molar ratio of SbI<sub>3</sub> and CsI in the mixed DMF: DMSO (1:3) solvent. All solutions were kept on a hot plate at 70 °C overnight. Different volumes of HI was added before 60 min of spin coating in the precursor solution, and kept at room temperature. Solution was spin-coated (6000 rpm) onto PEDOT:PSS and annealed directly at 70 °C

for MA<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> and 150 °C for Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> for 30 min. A solution (20 mg/mL) of [6,6]-phenyl-C71-butyric acid methyl ester (PCBM) in chlorobenzene (CB) and was spin-coated (4000 rpm, 40 s) onto the perovskite layer, followed by annealing at 100 °C for 30 min. The device was completed through sequential thermal evaporation of C60 (30 nm), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 7 nm), and an aluminum electrode (100 nm) through a shadow mask under vacuum (pressure: 1 x 10<sup>-6</sup> torr). The active area of each device was 10 mm<sup>2</sup>.

**Characterization:** XRD patterns were recorded at room temperature using a Bruker D8 X-ray diffractometer (20 range: 5–80°; step size: 0.008°) equipped with a diffracted beam monochromator set for Cu K $\alpha$  radiation ( $\lambda$  = 1.54056 Å). SEM images were recorded using an FEI Nova 200 scanning electron microscope (15 kV). Glass substrates spin-coated with PEDOT:PSS were used for XRD measurements; ITO substrates spin-coated with PEDOT:PSS were used for recording SEM images. Absorption spectra of the films were measured using a Jacobs V-670 UV–Vis spectrophotometer. XPS was performed at room temperature using a PHI 5000 Versa Probe (ULVAC-PHI) apparatus equipped with an Al K $\alpha$  X-ray source (1486.6 eV). UPS was used to measure the valance band using He I emission (21.2 eV, ~50 W) as the source of ultra-violet light, and the take-off angle was 90°. EQE spectra were recorded under short-circuit conditions. Devices were encapsulated before they were removed for EQE measurement. The light source was a 75 W Xe lamp (Enlitech, QE-R3011); the light output from the monochromator was focused on the photovoltaic cell being tested (DC mode). The devices were illuminated inside a glove box by the Xe lamp, which functioned as a solar simulator (Thermal Oriel 1000 W) providing a simulated AM 1.5 spectrum (100 mW cm<sup>-2</sup>). The light intensity was calibrated using a mono-silicon photodiode with a KG-5 color filter (Hamamatsu).



Figure S1 UV–Vis absorbance spectra of devices incorporating (a)  $MA_3Sb_2I_9$  and (b)  $Cs_3Sb_2I_9$  films prepared at various molar ratios. (c) Tauc plot of  $SbI_3$ ,  $MA_3Sb_2I_9$ ,  $HI-MA_3Sb_2I_9$ ,  $Cs_3Sb_2I_9$  and  $HI-Cs_3Sb_2I_9$  thin films, respectively. (d) Photograph of  $MA_3Sb_2I_9$  and  $Cs_3Sb_2I_9$  film with and without HI additive.

In figure S1 (a), variation in the absorption intensity was observed for different ratio of SbI<sub>3</sub>:MAI due to different thickness of MA<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> perovskite films. Thickness of perovskite films were measured as 90, 120 and 155 nm for 0.4:1, 0.5:1 and 0.6:1, respectively. Best device performance was observed only at 0.5:1 (SbI<sub>3</sub>:MAI) ratio. In case of Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub>, perovskite films thickness were 60, 110 and 135 nm for 0.1:1, 0.2:1 and 0.3:1, respectively, and best device performance was observed only at 0.2:1 (SbI<sub>3</sub>:CsI) ratio.



Figure S2 UV-Visible absorbance spectrum of Sbl<sub>3</sub> thin film spin coated on glass/PEDOT:PSS substrate.



Figure S3 (a) Whole UPS spectra of Sb-based perovskite materials with and without addition of HI and (b) corresponding energy band diagram; Cross-sectional SEM images of (c)  $MA_3Sb_2I_9$  and (d)  $Cs_3Sb_2I_9$  device.



Figure S4 XRD pattern of Sb-based perovskite materials with different concentration of HI additives (a) MA<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> and (b) Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> perovskites.



Figure S5 XPS spectra of  $MA_3Sb_2I_9$ ,  $Cs_3Sb_2I_9$  perovskite films with and without HI additive prepared on glass substrates: (a) Sb 3d, (b) I 3d5, (c) Cs 3d, (d) C 1s, and (e) N 1s.



Figure S6 SEM images of Sb-based perovskite films, prepared at various molar ratios, deposited on PEDOT:PSS substrates; (a–c) SbI<sub>3</sub>:MAI (0.4:1, 0.5:1, 0.6:1); (d–f) SbI3:CsI (0.1:1, 0.2:1, 0.3:1).

Figure S6 displays SEM topographic images of films prepared using different precursor ratios for the various cations. The formation of microstructures is clearly evident for all three ratios of Sbl<sub>3</sub>:MAI (0.4:1, 0.5:1, 0.6:1) [Figures S6(a–c)]. In the case of the 0.4:1 ratio, the microstructures did not cover the PEDOT:PSS substrate completely and were not particularly uniform in size and shape. For the 0.5:1 ratio, the film covered the substrate well and the microstructures were arranged in a uniform manner and parallel to the substrate direction. For the 0.6:1 ratio, however, the microstructures were arranged randomly, increasing the roughness of the sample relative to that of the 0.5:1 sample. In the case of the Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> perovskite film [Figures S6(d–f)], the film prepared at a 0.2:1 molar ratio featured film coverage and uniformity superior to those obtained at the other two ratios, presumably beneficial for charge generation and transportation.



Figure S7 SEM images of  $MA_3Sb_2I_9$  perovskite thin film with different concentration of HI additives; (a) 10 µl/ml, (b) 20 µl/ml, (c) 30 µl/ml and (d) 40 µl/ml. Scale bar 4 µm.



Figure S8 SEM images of  $Cs_3Sb_2I_9$  perovskite thin film with different concentration of HI additives; (a) 5  $\mu$ l/ml, (b) 10  $\mu$ l/ml and (c) 20  $\mu$ l/ml. Scale bar 4  $\mu$ m.

When HI is added into  $MA_3Sb_2I_9$  perovskite precursor solution, the crystallinity and surface morphology improves as the volume of HI is increased upto 30 µl/ml. This has a positive effect on the device performance of the HI-MA\_3Sb\_2I\_9 based perovskite solar cells, thus increasing the power conversion efficiency. For HI concentrations > 30 µl/ml, the crystallinity was reduced but the enhanced film quality was retained. However, this leads to decreased device performance for volumes of HI > 30 µl/ml (Figure S7). In case of Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> based perovskite films, the pores on the surface were reduced and the film quality was enhanced with the addition of HI (5 µl/ml), which also increased the device performance. For addition of HI > 5 µl/ml (Figure S8), we observed a negative effect on the film quality leading to distortion of surface structures which also led to decreased device performance.



Figure S9. J-V characteristics of devices incorporating (a)  $MA_3Sb_2I_9$  and (b)  $Cs_3Sb_2I_9$  prepared at various molar ratios.

Table S1. D	evice performance	e parameters of s	olar cells	incorporating	Sb-based	perovskites	prepared
at various r	nolar ratios.						

Perovskite	Molar ratio	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
Sbl <sub>3</sub> :MAI	0.4:1	0.34	1.39	42.31	0.20
	0.5:1	0.62	3.41	43.99	0.93
	0.6:1	0.54	1.98	44.89	0.48
Sbl <sub>3</sub> :Csl	0.1:1	0.33	1.12	45.99	0.17
	0.2:1	0.62	2.11	46.63	0.61
	0.3:1	0.40	1.13	46.46	0.21



Figure S10. J-V characteristics of Sb-based perovskite devices with different concentration of HI additives; a)  $MA_3Sb_2I_9$  and (b)  $Cs_3Sb_2I_9$ .

Table S2. Device performance parameters of solar cells incorporating Sb-based perovskites prepared at various molar ratios.

Perovskite	HI concentration	<i>V</i> <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
	(µl/ml)				
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	10	0.52	4.74	51.93	1.28
	20	0.62	4.88	50.90	1.54
	30	0.62	5.41	60.52	2.03
	40	0.60	5.69	52.43	1.79
Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	5	0.60	2.91	48.11	0.84
	10	0.38	2.50	47.37	0.45
	20	0.35	1.93	45.89	0.31

Table S3. Summary of reported photovoltaic performance parameters of Sb- based perovskite solar cells.

Device structure	V <sub>oc</sub> (V)	J <sub>sc</sub>	FF (%)	PCE	Reference
		(mA cm <sup>-2</sup> )		(%)	
FTO/TiO <sub>2</sub> /Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> /PTAA/Au	0.307	-	-	-	S1
ITO/PEDOT:PSS/(CH <sub>3</sub> NH <sub>3</sub> ) <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> /	0.896	1.0	55	0.49	S2
PCBM/ZnO/Al					
FTO/TiO <sub>2</sub> /meso-	0.55	2.11	56.97	0.66	S3
TiO <sub>2</sub> /Rb <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> /poly-TPD/Au					
ITO/PEDOT:PSS/(NH <sub>4</sub> ) <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> /	1.03	1.15	42.9	0.51	S4
PCBM/AI					
ITO/PEDOT:PSS/MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> /	0.62	5.41	60.82	2.04	Current
PCBM/C <sub>60</sub> /BCP/AI					study
ITO/PEDOT:PSS/Cs <sub>3</sub> Sb <sub>2</sub> l <sub>9</sub> /	0.60	2.91	48.11	0.84	
PCBM/C <sub>60</sub> /BCP/AI					



Figure S11 *J*–*V* characteristics of champion perovskites/PC<sub>71</sub>BM planar heterojunction solar devices by influence of scanning direction on the performance of solar cells (a)  $MA_3Sb_2I_9$  and (b)  $Cs_3Sb_2I_9$  perovskite materials with HI additives.

Lead iodide perovskite solar cells often reveal hysteresis in their J-V curves with respect to the scan direction and rate, due to charge accumulation or dielectric polarization resulting from the ferroelectric characteristics of the perovskite materials.[S5, S6] To investigate the hysteresis behavior of our Sb-based perovskite devices, we measured their J-V characteristics over various scan directions. These devices exhibited negligible hysteresis (Figure S11 a, b). To obtain more quantitative information about J-V hysteresis, we estimated the hysteresis index (HI) using following equation:[S7]

$$Hysteresis index = \frac{JRev(0.8 Voc) - JFor(0.8 Voc)}{JRev(0.8 Voc)}$$

where  $J_{\text{Rev}}$  (0.8 $V_{\text{oc}}$ ) and  $J_{\text{For}}$  (0.8 $V_{\text{oc}}$ ) represent the photocurrent densities at 80% of the value of  $V_{\text{oc}}$  for the reverse and forward scans, respectively. Hysteresis index of less than 0.1 represents a system without significant hysteresis; a value of greater than 0.1 represents a system exhibiting hysteresis. The hysteresis index of our devices based on MA<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> and Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> with HI additive were 0.0177 and 0.693, respectively. Thus, these MA<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> perovskite material exhibited negligible hysteresis and Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> have very low hysteresis, which would be beneficial when using them as light harvesting layers in photovoltaic applications.



Figure S12 Normalized power conversion efficiency degradation curve over time for different perovskite devices.

## References

- [S1] B. Saparov, F. Hong, J.-P. Sun, H.-S. Duan, W. Meng, S. Cameron, I. G. Hill, Y. Yan and D. B.
  Mitzi, *Chem. Mater.*, **2015**, 27, 5622-5632.
- [S2] J.-C. Hebig, I. Kühn, J. Flohre and T. Kirchartz, ACS Energy Lett., **2016**, 1, 309-314.
- P. C. Harikesh, H. K. Mulmudi, B. Ghosh, T. W. Goh, Y. T. Teng, K. Thirumal, M. Lockrey, K.
  Weber, T. M. Koh, S. Li, S. Mhaisalkar and N. Mathews, *Chem. Mater.*, 2016, 28, 7496-7504.
- [S4] C. Zuo, L. Ding, Angew. Chem. Int. Ed., 2017, DOI: 10.1002/anie.201702265.
- [S5] S. Meloni, T. Moehl, W. Tress, M. Franckevicius, M. Saliba, Y. H. Lee, P. Gao, M. K. Nazeeruddin, S. M. Zakeeruddin, U. Rothlisberger and M. Graetzel, *Nat. Commun.*, 2016, 7, doi:10.1038/ncomms10334.
- [S6] H. J. Snaith, A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, S. D. Stranks, J. T.-W.
  Wang, K. Wojciechowski and W. Zhang, J. Phys. Chem. Lett., 2014, 5, 1511-1515.
- [S7] H.-S. Kim and N.-G. Park, J. Phys. Chem. Lett., 2014, 5, 2927-2934.