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Supporting Information for

Elucidating the Role of Chlorine in Perovskite Solar Cells

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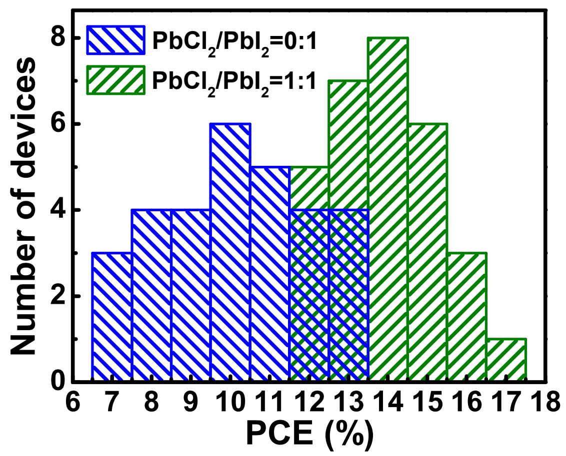

Fig. S1 Statistical histogram chart of device efficiency.

For each condition, 30 devices were fabricated, and an average PCE of ~10% and ~14% were achieved with a $PbCl_2/PbI_2$ mole ratio of 0:1 and 1:1, respectively.

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[†] Electronic Supplementary information (ESI) is available.

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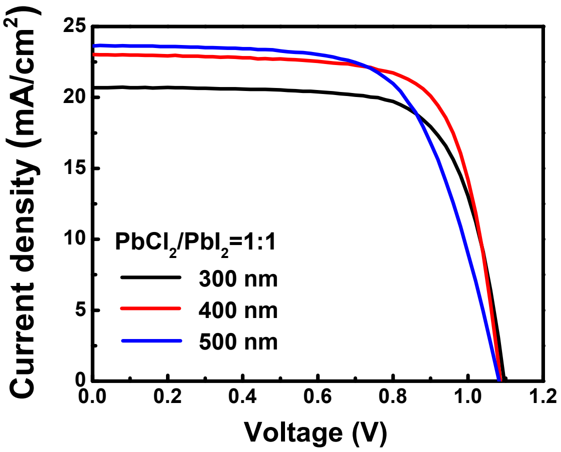

Fig. S2 *J-V* curves of devices with different thickness of perovskite absorption layer.

The thickness of perovskite absorption layer plays a key role on device efficiency. Thin layer leads to an insufficient light absorption, as well as relatively lower J_{SC}; Thick absorption layer guarantees sufficient light harvest; However, too thick layer will dramatically weaken the built-in-potential and limits the carrier transportation and collection. Hence, the thickness effect on device performance has been carefully studied and $PbCl_2/PbI_2$ mole ratio was fixed at 1:1. Finally, an optimized thickness of 400 nm has been adopted in the coming experiment. Table S1 lists the photovoltaic parameters of devices with different perovskite film thickness.

Table S1 Photovoltaic parameters of devices with different perovskite film thickness.

Different thickness	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF [%]	R_s [Ω cm^2]	R_{Sh} [Ω cm^2]	PCE [%]
300 nm	20.68	1.09	72.00	5.12	4732.18	16.22
400 nm	**23.02**	**1.09**	**72.21**	**4.26**	**5284.77**	**18.12**
500 nm	23.64	1.09	65.08	7.86	4828.09	16.77

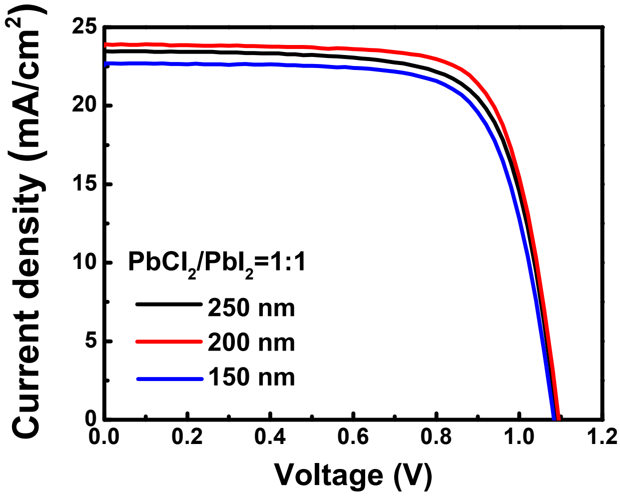

Fig. S3 *J-V* curves of devices with different thickness of Spiro-OMeTAD.

The thickness of Spiro-OMeTAD layer also plays a key role on device performance. Thick hole transporting layer (HTL) guarantees fully conformal coverage of beneath perovskite layer; However, too thick HTL will introduce parasitic resistance in device. Hence, the thickness of HTL was also carefully optimized. It has been found that device with a 200 nm-thick HTL exhibits the best performance. Finally, as shown in Table S2, device efficiency has been dramatically enhanced to as high as 19.41% by adjusting the thickness of perovskite and HTL to 400 nm and 200 nm, respectively.

Table S2 Photovoltaic parameters of devices with different thickness of Spiro-OMeTAD.

Different thickness	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	R_s [Ω cm^2]	R_{Sh} [Ω cm^2]	PCE [%]
250 nm	23.48	1.09	72.17	4.52	4935.66	18.47
200 nm	**23.80**	**1.09**	**75.16**	**4.37**	**3193.70**	**19.41**
150 nm	22.68	1.09	71.99	4.92	2141.10	17.80

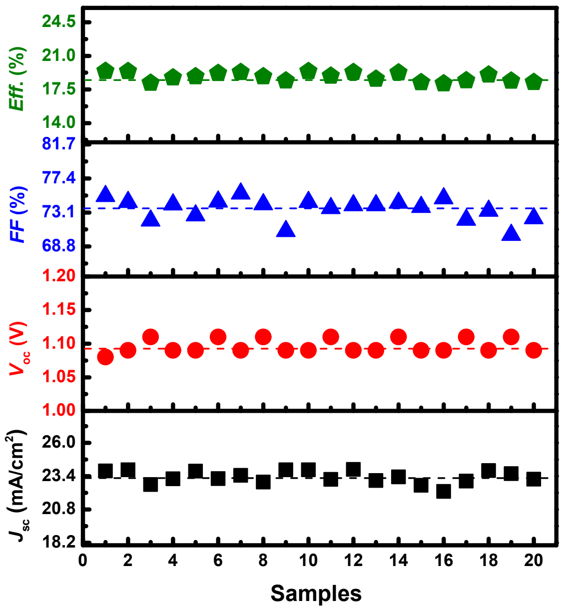

Fig. S4 Statistical distributions of the device parameters obtained in 20 devices fabricated with optimized conditions.

Reproducibility of optimized device was also verified by fabricating more than 20 devices with same process, and an average PCE, *FF*, V_{OC} and J_{SC} of 18.81%, 73.52%, 1.09 V, and 23.31 mA cm^{-2} have been achieved, respectively.

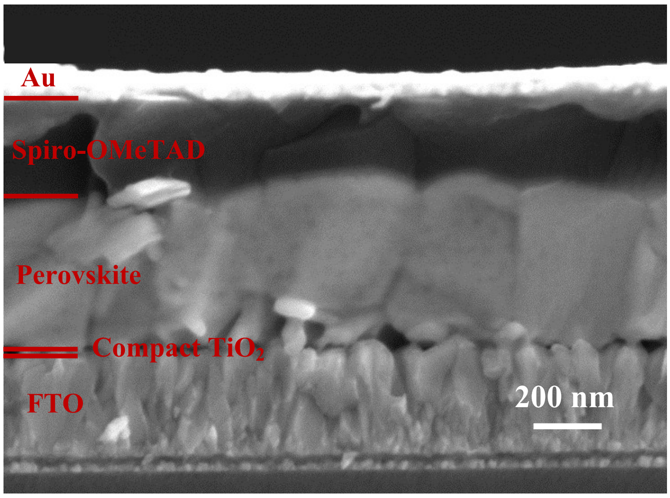

Fig. S5 Typical cross-sectional SEM image of device.

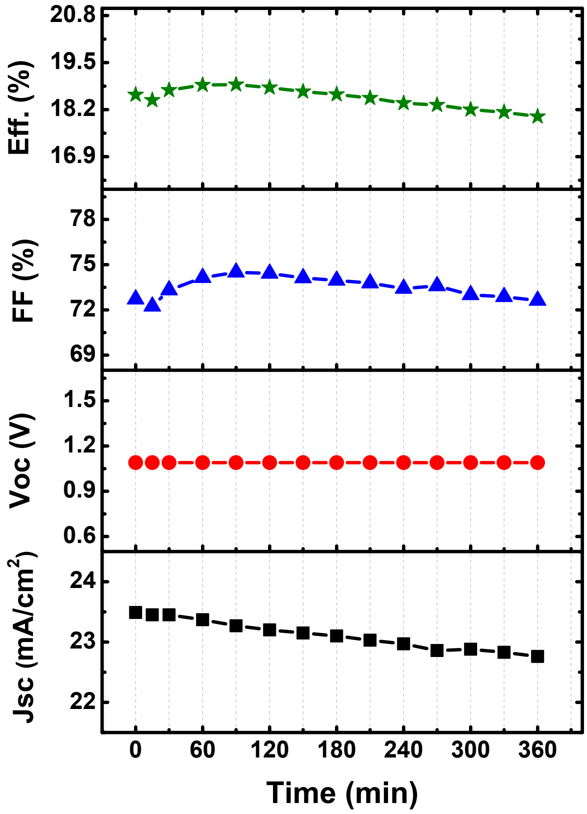

Fig. S6 Device parameters evolution under continuous AM 1.5G light illumination.

Device V_{OC} keeps almost stable, while J_{SC} degrades slowly under continuous light exposure; *FF* increases slightly at the first 120-min light illumination, and then keeps almost stable. As a result, only a 4.5% efficiency deterioration has been observed after 6-hours AM 1.5G exposure, indicating a relatively good stability.