Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Supplementary Information

## Long-term Stable and Highly Efficient of Perovskite Solar Cells with Formamidinium Chloride (FACl) Additive

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**Figure S1.** Optical photograph of perovskite films with different concentrations of FACl under 100℃annealing.

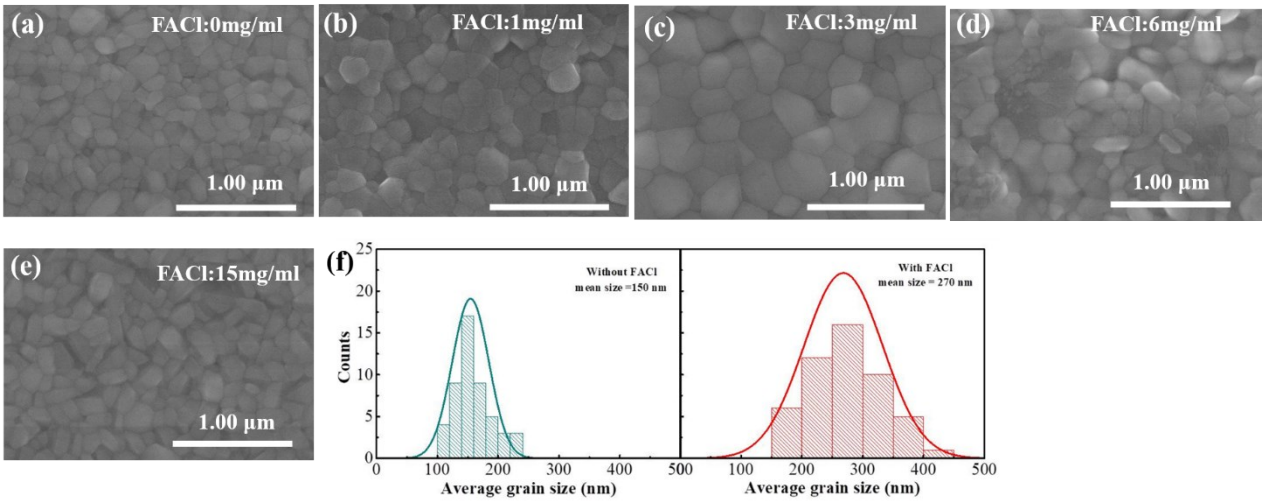


**Figure S2.** (a)-(e) SEM of perovskite films with different concentrations of FACl under 100 ℃annealing, (f) the grain size distribution histograms of perovskite film without and with 3mg/ml FACl

**Table S1.** Time constants related to the fast ($\tau_1$) and slow ($\tau_2$) decays extracted from time-resolved PL spectroscopy of $FA_{0.85}MA_{0.15}PbI_xBr_{3-x}$ films.

| | $\tau_1$ (ns) | $\tau_2$ (ns) |
|---|---|---|
| pristine | 25.6 | 36.7 |
| FACl(3mg/ml) | 227.8 | 356.2 |

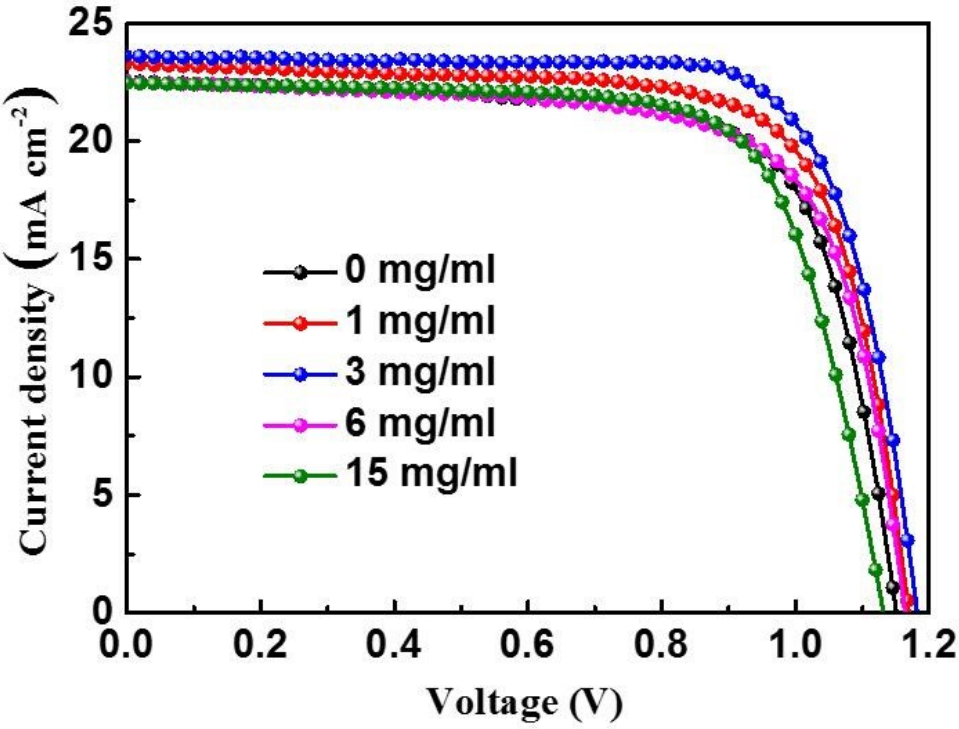


**Figure S3.** *J–V* curves of PSCs with different concentrations of FACl additive in perovskite precursor solutions under AM 1.5G illumination of 100 mW $cm^{-2}$

**Table S2**. Photovoltaics parameters of perovskite solar cells with different concentrations (mg/ml) of FACl additive in perovskite precursor solutions measured under standard 1 sun irradiation (reverse scan)

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|---|---|---|---|---|
| 0 | 1.15±0.02(1.152) | 22.41±0.52 (22.53) | 68.35±3.31 (71.79) | 17.10±1.55 (18.60) [a] |
| 1mg/ml | 1.16±0.08 (1.169) | 22.83±0.42 (23.28) | 71.12±3.26 (73.07) | 18.52±1.28 (19.88) [a] |
| 3mg/ml | 1.18±0.03 (1.183) | 23.26±0.45 (23.63) | 74.15±2.31 (75.21) | 20.46±0.55 (21.02) [a] |
| 6mg/ml | 1.16±0.04 (1.163) | 22.46±0.43 (22.51) | 69.26±2.78 (71.20) | 17.71±0.92 (18.63) [a] |
| 15mg/ml | 1.13±0.03 (1.136) | 22.38±0.52 (22.47) | 68.16±3.12 (70.67) | 16.56±1.48 (18.04) [a] |

[a]Numbers in parentheses show the champion device parameters.

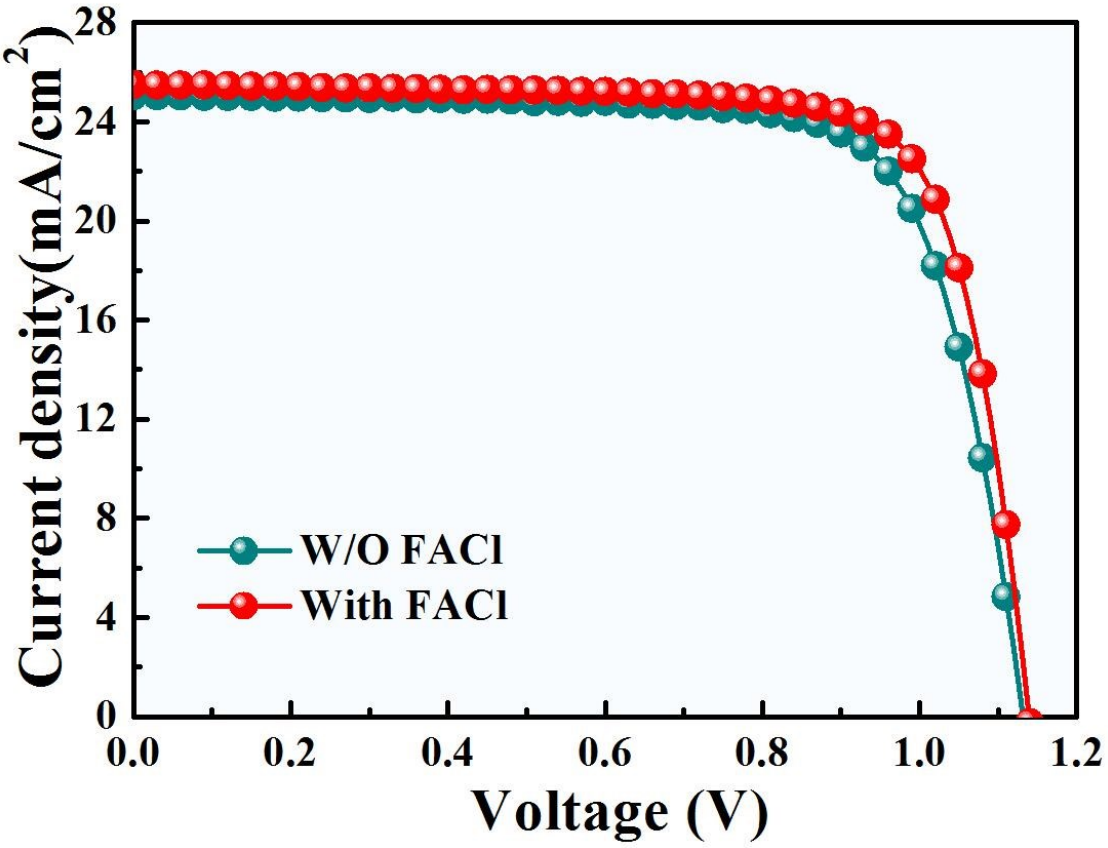


**Figure S4.** J–V curves for the planar perovskite solar cells with and without FACl. ($Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})_3$-based PSCs).

**Table S3** Photovoltaics parameters (best) of $Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})_3$-based PSCs with and without FACl

| **Sample** | $V_{oc}$ **(V)** | $J_{sc}$ **(mA/cm$^2$)** | **FF (%)** | **PCE (%)** |
|---|---|---|---|---|
| Without FACl | 1.132 | 25.05 | 75.36 | 21.37 |
| With FACl | 1.139 | 25.50 | 77.67 | 22.56 |

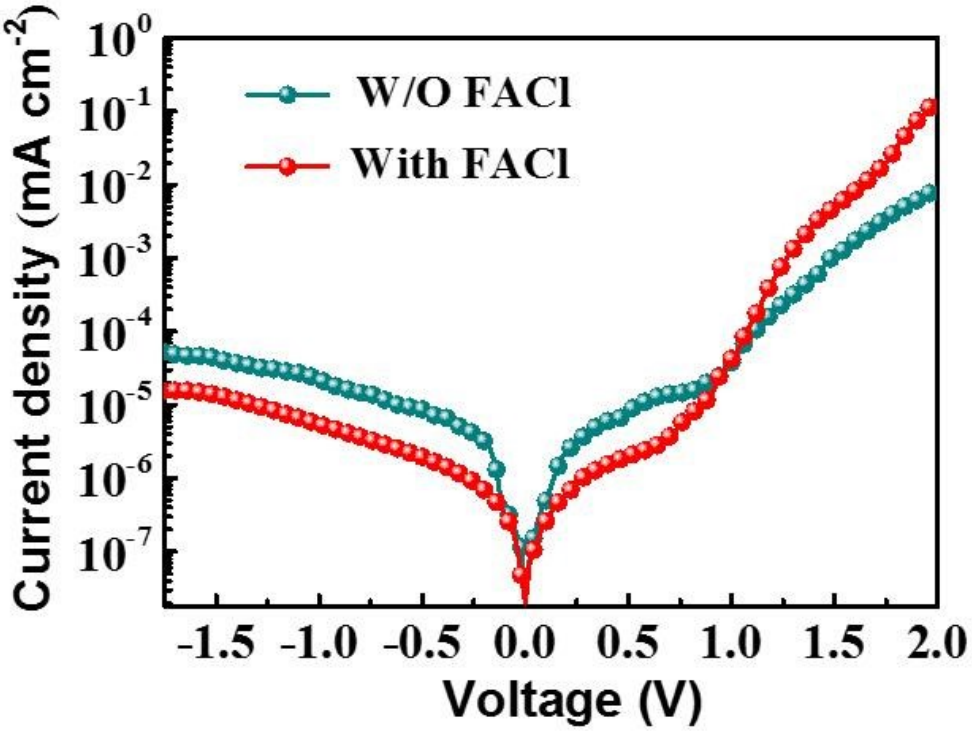


**Figure S5.** Dark current density of PSCs with and without FACl modification

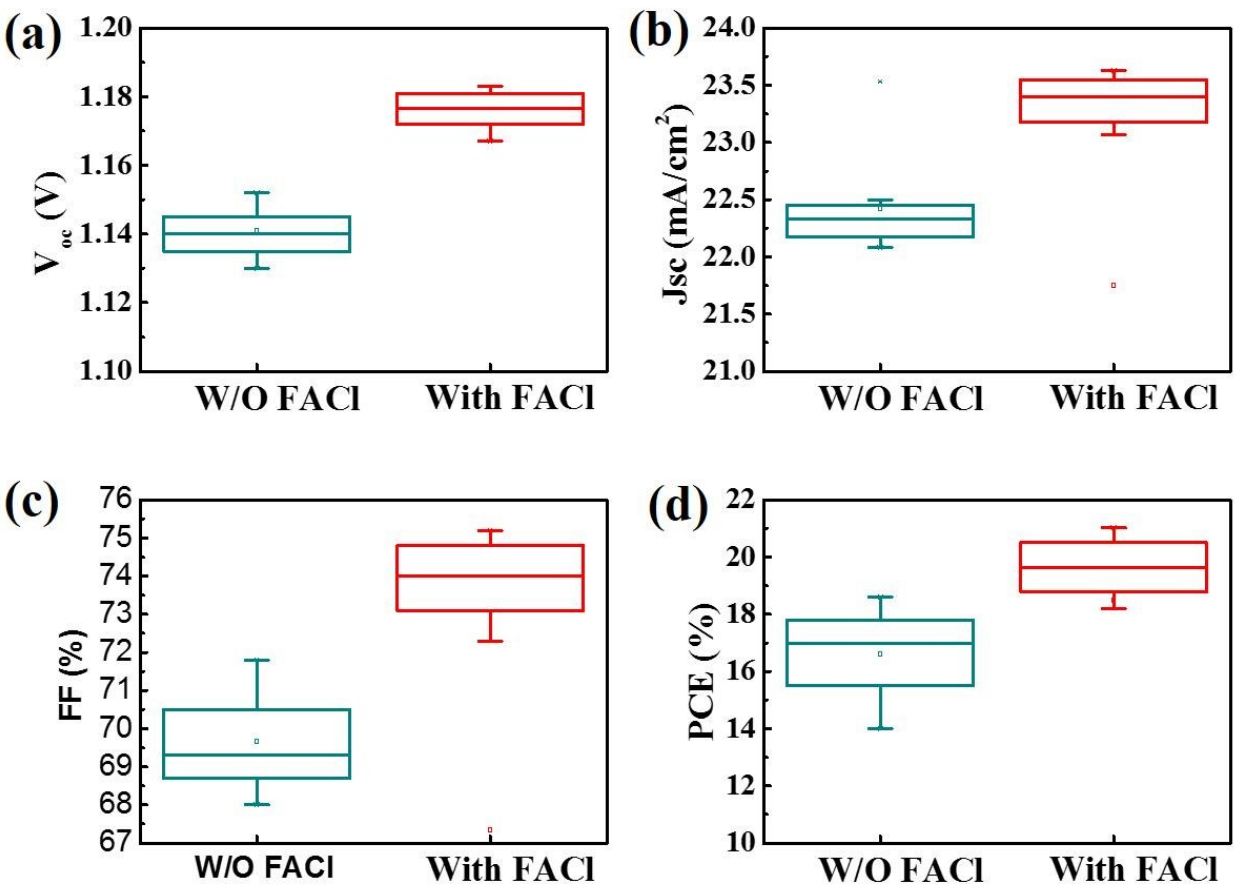


**Figure S6.** Comparison of the key photovoltaic parameters of the W/O FACl and With FACl of perovskite solar cells.

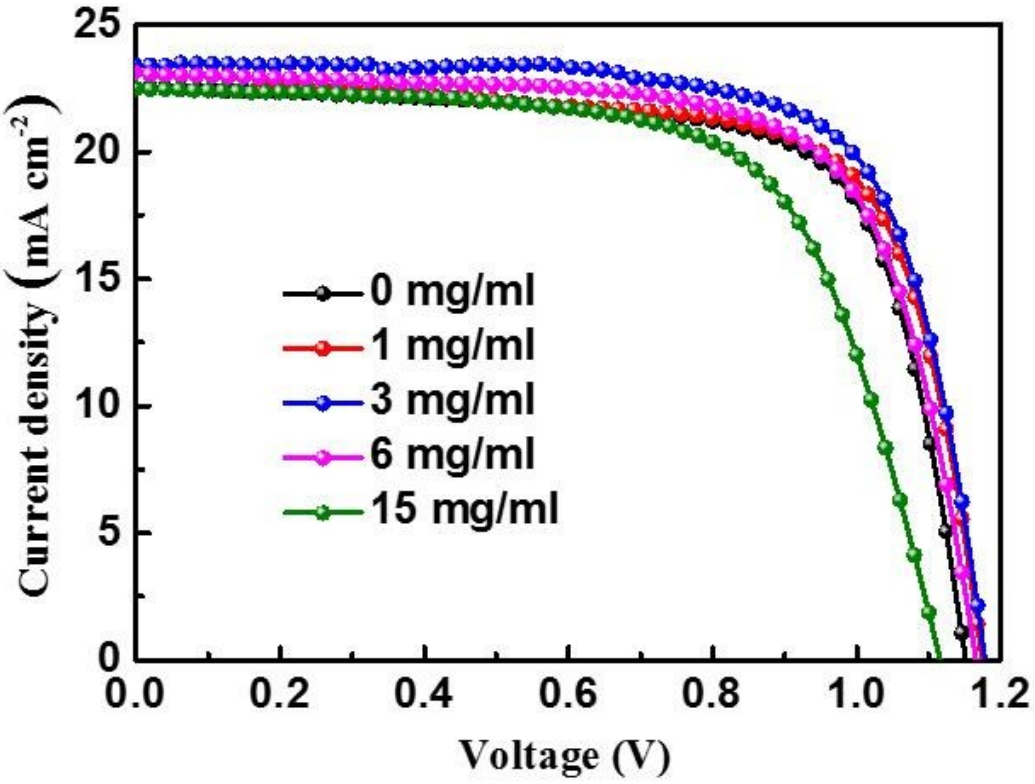


**Figure S7.** *J–V* curves of PSCs with different concerntrations of FABr additive in perovskite precursor solutions under AM 1.5G illumination of 100 mW $cm^{-2}$

**Table S4.** Photovoltaic parameters of PSCs with different quality (mg/ml) of FABr additive in perovskite precursor solutions.

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|---|---|---|---|---|
| 0 | 1.14±0.06 (1.150) | 22.12±0.46 (22.52) | 69.33±1.87 (71.84) | 17.22±1.56 (18.61) [a] |
| 1mg/ml | 1.17±0.02 (1.173) | 22.65±0.37 (23.19) | 69.27±1.76 (70.07) | 18.15±1.13 (19.07) [a] |
| 3mg/ml | 1.17±0.05 (1.178) | 23.13±0.32 (23.41) | 70.42±1.15 (72.51) | 19.32±1.57 (19.99) [a] |
| 6mg/ml | 1.16±0.03 (1.165) | 22.88±0.56 (23.27) | 68.81±2.12 (70.41) | 18.36±1.85 (19.10) [a] |
| 15mg/ml | 1.12±0.02 (1.120) | 22.21±0.33 (22.51) | 63.56±2.36 (65.81) | 15.06±1.53 (16.59) [a] |

[a]Numbers in parentheses show the champion device parameters.

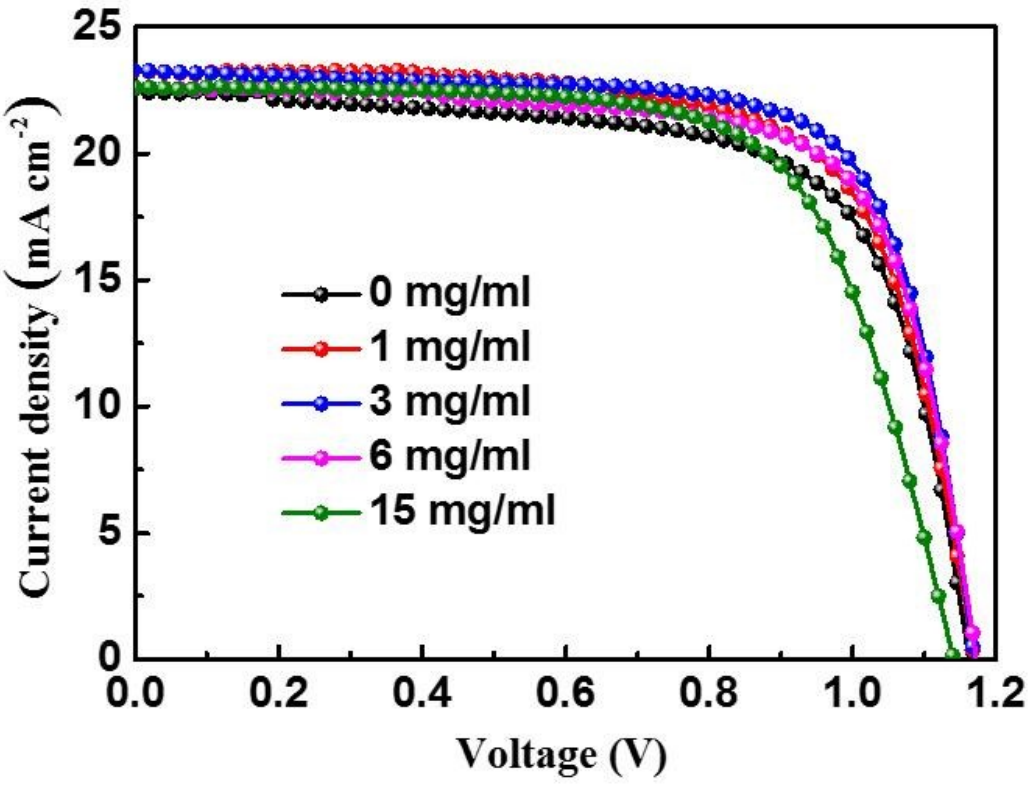


**Figure S8.** *J–V* curves of PSCs with different concerntration of FAI additive in perovskite precursor solutions under AM 1.5G illumination of 100 mW $cm^{-2}$

**Table S5.** Photovoltaic parameters of PSCs with different quality (mg/ml) of FAI additive in perovskite precursor solutions.

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|---|---|---|---|---|
| 0 | 1.15±0.08(1.161) | 22.12±0.35 (22.42) | 68.35±1.78 (70.12) | 17.25±1.67 (18.25)[a] |
| 1mg/ml | 1.16±0.07 (1.168) | 22.76±0.78 (23.25) | 68.47±1.52 (70.25) | 18.21±1.11 (19.07)[a] |
| 3mg/ml | 1.16±0.08 (1.168) | 23.09±0.32 (23.28) | 72.16±1.17 (73.07) | 19.16±0.62 (19.86)[a] |
| 6mg/ml | 1.15±0.08 (1.160) | 22.56±0.62 (23.02) | 69.53±1.37 (70.36) | 17.31±1.35 (18.78)[a] |
| 15mg/ml | 1.14±0.08 (1.146) | 22.12±0.55 (22.60) | 67.26±1.25 (68.02) | 16.12±1.68 (17.62)[a] |

[a]Numbers in parentheses show the champion device parameters.

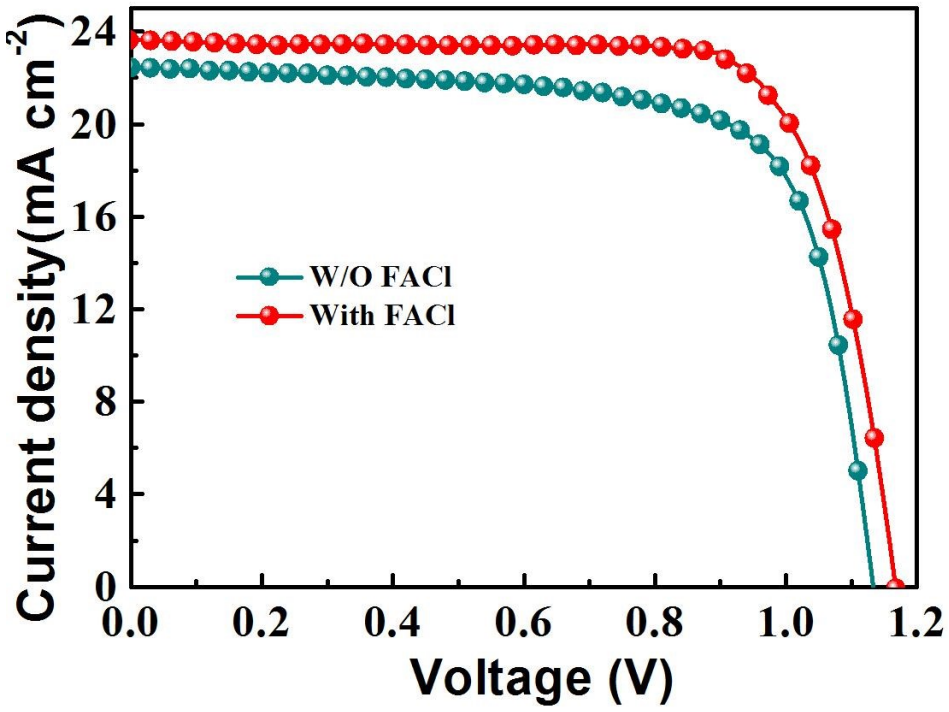


**Figure S9.** *J–V* curves of PSCs with different concerntration (0mg/mL and 3mg/mL) of FACl additive in excessive $PbI_2$ perovskite precursor solutions under AM 1.5G illumination of 100 mW $cm^{-2}$

**Table S6.** Photovoltaic parameters of PSCs with different concerntration (0mg/mL and 3mg/mL) of FACl additive in excessive $PbI_2$ perovskite precursor solutions.

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|---|---|---|---|---|
| 0 | 1.121±0.07 (1.133) | 22.12±0.32 (22.46) | 71.12±1.32 (72.21) | 17.57±1.12 (18.38)[a] |
| 3mg/mL | 1.170±0.05 (1.172) | 23.35±0.26 (23.62) | 75.26±0.58 (75.53) | 20.55±0.43 (20.91)[a] |

[a]Numbers in parentheses show the champion device parameters.