Electronic Supplementary Material (ESI) for Nanoscale.

# 4. Experimental Section

Preparation of Perovskite Precursor : $CH_3NH_3I$ was synthesized in an ice bath for 2 hrs by reacting methylamine ($CH_3NH_2$, 33 wt% in ethanol from Sigma-Aldrich) with hydroiodic acid (HI, 57 wt% in water from Sigma-Aldrich). The white powders were precipitated by drying at 60 °C and washed for 3 times with diethyl ether (Sigma-Aldrich) before further dried out to be stored in nitrogen-filled glove-box. $CH_3$

$NH_3Cl$ was synthesized in the same way as $CH_3NH_3I$ by reacting methylamine with hydrochloric acid (HCl, 36.5–38 wt% in water from Sigma-Aldrich). $CH_3NH_3PbI_{3-x}Cl_x$ precursor solution was prepared by dissolving 0.88M lead chloride (99.999%, Sigma-Aldrich) and 2.64 M CH

$_3NH_3I$ in anhydrous N,N -Dimethylformamide (DMF, 99.8%, Sigma-Aldrich). Similarly, $CH_3NH_3PbI_3$ precursor solutions were prepared by dissolving 0.9 M lead iodide (99.999%, Sigma-Aldrich) and 0.9 M for 1:1, 1.35M for 1.5:1, 1.8 M for 2:1, 2.7 M $CH_3NH_3I$ for 3:1 in anhydrous DMF. The precursor solutions were filtered though a 0.2 µm PTFE filter before spin-coating.

Fabrication of Polymer/Perovskite/FTO Glass Sandwiched Structure Test Samples : The whole process was carried out in a nitrogen filled glovebox. $CH_3NH_3PbI_{3-x}Cl_x$ precursor solution was first spin-coated on a FTO glass. After drying over-night, a 40 mg/mL poly(methyl methacrylate) (PMMA, Mw of 120000, purchased from Sigma-Aldrich) solution in butyl acetate (anhydrous, 99%, Sigma-Aldrich) was then spin-coated on the perovskite film either before or after annealing.

**Fabrication of Planar Solar Cell Devices :** Solar cells were fabricated as follows: FTO (DHS-FTO22–15N, HeptaChroma) substrates were sequentially cleaned with deionized water, acetone, 2-propanol for 30 mins each, followed with oxygen plasma treatment for 1.5 mins. A compact$TiO_2$ hole-block layer was deposited on cleaned FTO by spin-coating a mildly acidic solution of titanium butoxide (97%, Sigma-Aldrich) in ethanol (consisting of 0.5 mL titanium butoxide and 50 μL 37% HCl solution in 6 ml ethanol) at 5000 rpm for 25s, and annealed at 500 °C for 45 min in an oven. Then $TiO_2$

coated FTO substrates were transferred into a nitrogen-filled glovebox and pre-heated at 100 °C for 10 min. After the substrates were cooled to room temperature, the perovskite precursor solution was spin-coated at 3000 r.p.m. for 60 s. After drying for more than 10 mins, the as spun films were annealed for 50 mins at 100 °C in the case of $CH_3NH_3PbI_{3-x}Cl_x$ and at 130 °C for 20 min (or 150 °C for 20 min) in the cases of $CH_3$

$NH_3I/PbI_2$ at molar ratios of 2:1 and 3:1. 30nm P3HT (Poly(3-hexylthiophene-2,5-diyl), LT-S909 from Lumtec.) hole transport layer was deposited on the annealed perovskite film by spin-coating 15 mg/ml P3HT solution in chlorobenzene at 3000 r.p.m. for 60 s. Finally, 100 nm Ag electrodes were thermally evaporated through a shadow mask under a vacuum of $1 \times 10^{-6}$ Torr to complete the device fabrication.

Characterizations : Morphology of the perovskite films were observed by HR-FESEM (FEI, Quanta 400). The elemental composition in the films was measured by EDX with StandardlessQuantification Model and by XPS (Thermo Fisher Scientific, ESCALAB 250). The crystalline structure for the perovskite films were identified by XRD (Rigaku, SmartLab). Thermal analyses for $CH_3NH_3I$ and $CH_3NH_3Cl$ powders were carried out by Thermogravimetric Analyzer (PerkinElmer, TGA 6) and DSC (PerkinElmer, TGA 6). Sample thicknesses were measured using an Alpha step 500 Surface profiler. The current density–voltage ( J – V ) curves were measured (Keithley Instruments, 2612 Series SourceMeter) under simulated AM 1.5 sunlight at 100 mW cm$^{-2}$ irradiance generated by an 94011A-ES Sol series Solar Simulator.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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$CH_3NH_3PbI_{3-x}Cl$

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**Supporting Information**

**2D/3D Perovskite Hybrids as Moisture-Tolerant and Efficient Light Absorbers for Solar Cells**

Chaoyan Ma,†[a] Chongqian Leng,†[a] Yixiong Ji,[a] Xingzhan Wei,[a] Kuan Sun,[b] Linlong Tang,[a] Jun Yang,[a] Wei Luo,[a] Chaolong Li,[a] Yunsheng Deng,[a] Shuanglong Feng,[a] Jun Shen,[a] Shirong Lu, ＊[a] Chunlei Du, ＊[a] and Haofei Shi＊[a]

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[b]*Key Laboratory of Low-grade Energy Utilization Technologies and Systems of the Ministry of Education of China, Chongqing, 400044, China; School of Power Engineering, Chongqing University, Chongqing, 400044, China.*

## Materials:

CAI was synthesized according to synthesis procedure of MAI.[1] All the other materials were purchased from commercial sources and used as received.

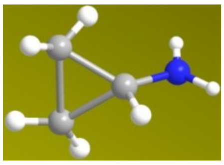

**Fig S1.** 3D molecular structures of cyclopropylamine, where N, C and H atoms are represented by balls in blue, grey and white, respectively.

## Experimental Section:

**Synthesis of CAI:** 9.5 ml hydriodic acid (57% in water, Aldrich) in ethanol (20.0 mL) and 5.0 ml cyclopropylamine (98%, Sigma Aldrich) were reacted in a round-bottom flask of 100 ml at 0 °C for 2 h with vigorously stirring. The pure products were gained after evaporation of reaction solvents and then recrystallization twice from ethanol and diethyl ether. Finally, the products were dried at 60°C in a vacuum oven for 24 h.

**Preparation and characterization of 2D perovksite ($CA_2PbI_4$) films:** A solution of 0.5 M PbI2 and 1.0 M CAI in cosolvent of dimethyl sulfoxide (DMSO) and γ-butyrolactone (GBL) (vol. ratio = 3:7) was prepared in a glove box. The solution was spin coated on substrates at 3000 rpm for 30 s , and the film was annealed at 100°C for 20 min to produce 2D perovksite CA2PbI4 films, which was further characterized by XRD.

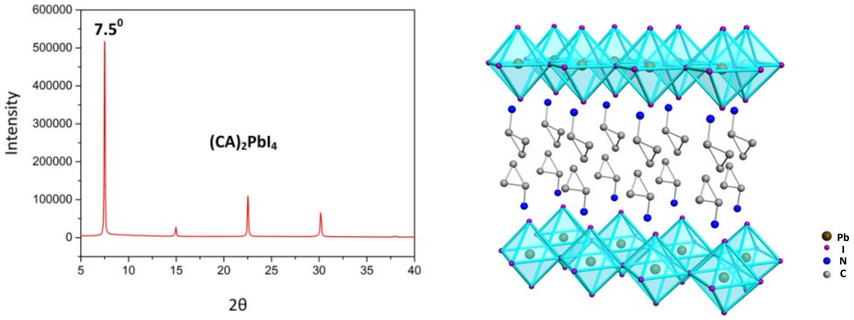

**Fig S2.** XRD pattern and crystal structure of the 2D perovskite $(CA)_2$ $PbI_4$ film

**Preparation of 2D/3D perovksite hybrid ($CA_2PbI_4/MAPbI_xCl_{3-x}$) films:** A solution of 0.14 M PbCl2, 1.26 M PbI2 and 1.3 M MAI in cosolvent of dimethyl sulfoxide (DMSO) and γ-butyrolactone (GBL) (vol. ratio = 3:7) was prepared in a glove box. The solution was spin coated on substrates at 1000 rpm for 20 s then 3500 rpm for 40 s to afford 3D perovksite ($MAPbI_xCl_{3-x}$) with slight excess of PbI2. At 45 s, dropping 900µl of anhydrous toluene and the film was annealed at 100°C for 20 min. After that, solutions of CAI with concentrations of 5 mg/ml, 10 mg/ml,20mg/ml and 30 mg/ml in anhydrous iso-propyl alcohol (IPA), were spin-coated on the prepared 3D perovksite at 3000 rpm for 30s and then annealed at 100°C for 20 min to produce 2D perovskite on the top through reaction of CAI with excess PbI2.

## Device Fabrication :

To fabricate the planar perovksite solar cells, a thin layer of PEDOT:PSS was coated on precleaned ITO glass. And then, the photoactive layers, including 2D/3D perovksite hybrids and homogenous 3D perovksite, were deposited as described above. On top of the perovskite layer, a PCBM layer of 20 nm was deposited. Next, rhodamine 101 was spin coated with a concentration of 0.05 wt% in IPA at 1500 rpm. Following, a supper-thin LiF layer with thickness of 1.0 nm was then evaporated on it. Finally, thermal deposition of a 100 nm-thick Ag electrode completed the fabrication of devices.

## Device Characterization:

The current density–voltage (J–V) curves were measured by a solar simulator (XES-50S1, SAN-EI) at 100 mA $cm^{-2}$ illumination (AM 1.5G) with scan range of from +1.5 V to −0.2 V and scan rate of 0.1 V/s, ignoring the hysteresis behavior of conventional PSCs. The hysteresis behaviors of the 2D/3D perovskite hybrid based PSCs were investigated and covered in the Supporting Information. The illumination intensity was calibrated by a Si-reference cell certificated by JIS (Japanese Industrial Standards). The J–V curves of all devices were measured by an active area of 0.11 $cm^2$. The external quantum efficiency (EQE) was measured by a power source (QE-LXE 75W Xenon lamp, Enli Technology Co., Ltd.) with a monochromator of QE-M110. UV–vis absorption was measured using a TU-1950 (Beijing's general instrument co., LTD) Spectrophotometer. Steady state PL was carried out using a HITACHI F-7000 Spectrofluorometer. XRD measurements were performed at room temperature with a PANalytical - X'Pert³ Powder diffractometer operating in Bragg–Brentano scanning mode, with angular resolution of 0.01°and Cu-K radiation (0.154056 nm wavelength). SEM images were measured by using JSM-7800F. The contact angle test was performed on the Kruss system (Model DSA-10). The thickness of films was tested by Alpha-step IQ system.

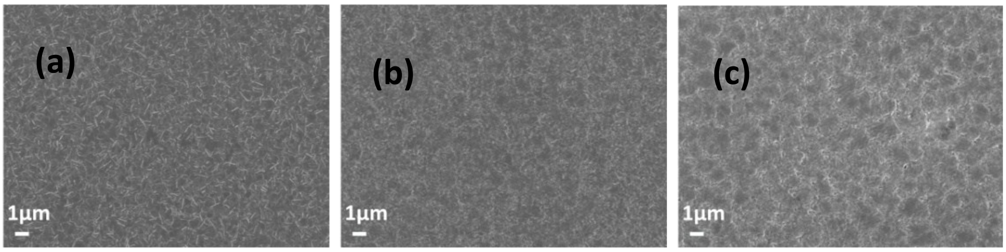

**Fig. S3.** Top-view SEM images of 2D/3D perovskite hybrid films on top of PEDOT:PSS deposited by different concentration of CAI: (a) 5mg/ml ,(b) 20mg/ml and (c) 30mg/ml.

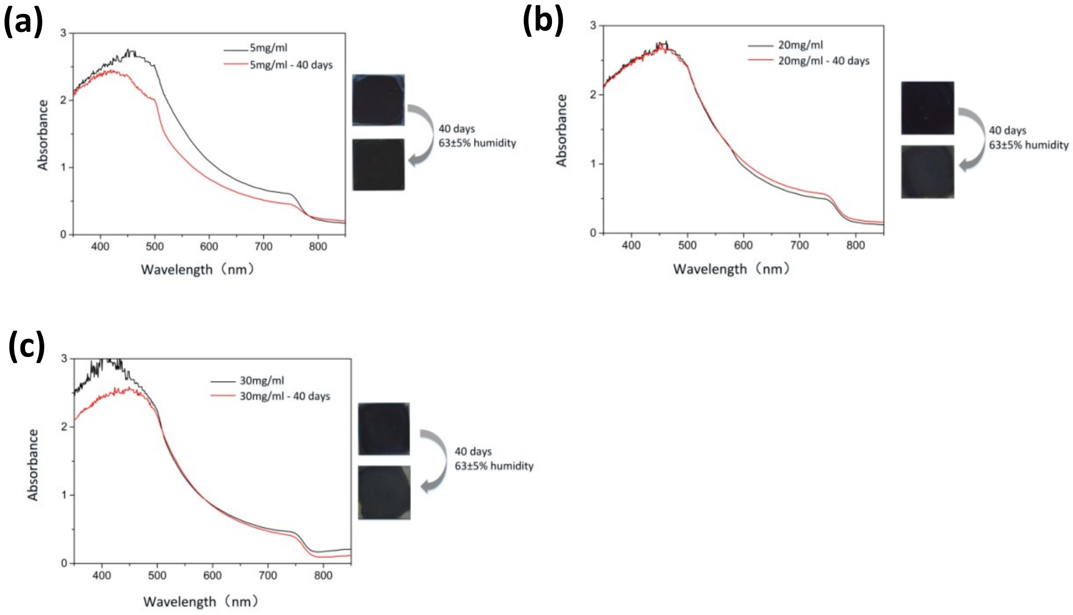

**Fig. S4.** UV-vis spectra of 2D/3D perovskite hybrid films freshly prepared with different concentration of CAI: (a) 5mg/ml, (b) 20mg/ml ,(c) 30mg/ml, and the same films after exposing to ambient air for 40 days. On the right are images of 2D/3D perovskite hybrid films before and after exposure to ambient air.

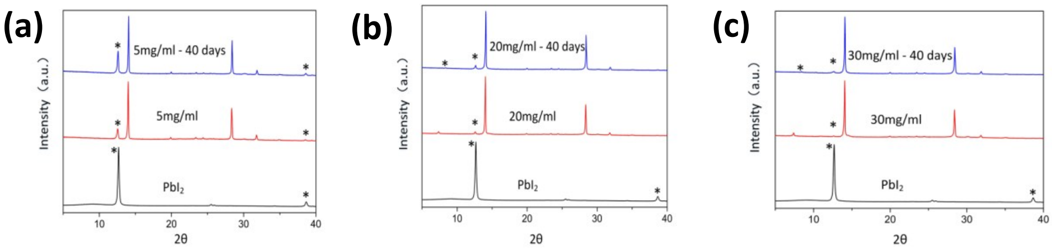

**Fig. S5.** XRD patterns of fresh and aged (after 40 days) 2D/3D perovskite hybrid films fabricated with different concentration of CAI: (a) 5mg/ml, (b) 20mg/ml, (c) 30mg/ml.

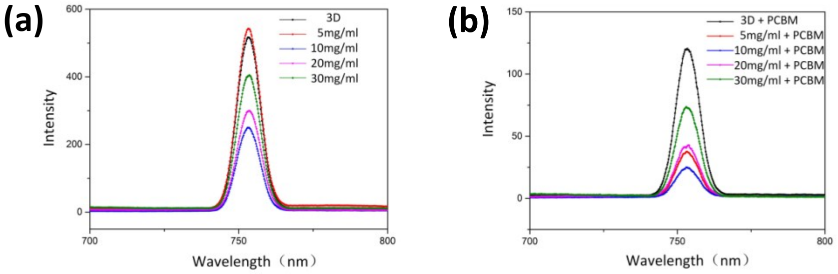

**Fig. S6**. Photoluminescence spectra of (a) 3D perovskite and 2D/3D perovskite hybrids , (b)3D perovskite / PCBM and (2D/3D perovskite hybrids )/ PCBM.

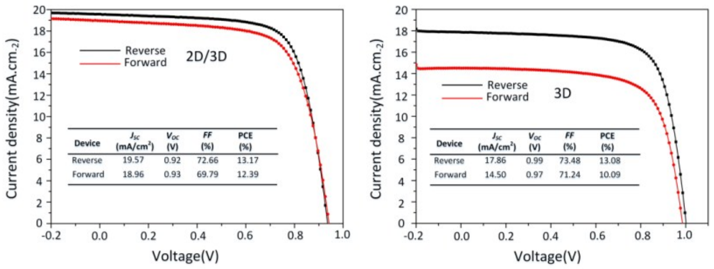

**Fig. S7.** Typical J-V curves for 2D/3D device (10 mg/ml CAI) and 3D only device with reverse and forward scans.

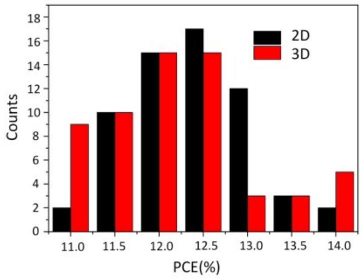

**Fig. S8.** Histogram of statistical PCEs counted from sixty 2D/3D perovskite devices (Red) and sixty 3D perovskite devices (Black).

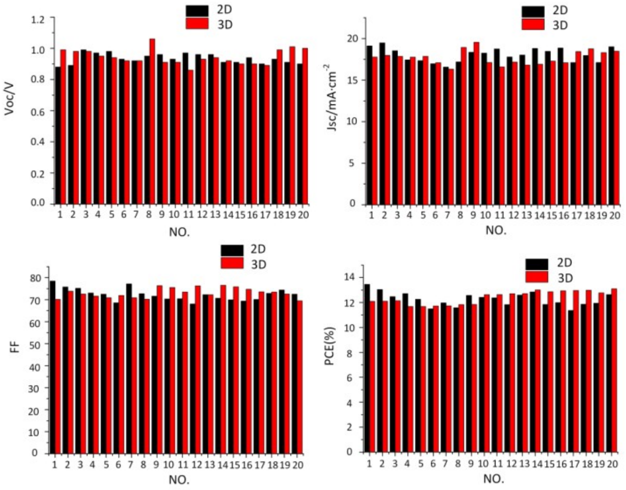

**Fig. S9.** Contrastive distribution (histograms) of the $J_{sc}$, $V_{oc}$, FF and PCE for selected twenty 2D/3D perovskite devices (Red) and twenty 3D perovskite devices (Black).

**Reference:**

SEM

images were measured using an Olympus

DP72 BH-2 (BHTU) and a

Philips XL30 FE

1. D. H. Cao, C. C. Stoumpos, O. K. Farha, J. T. Hupp and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2015, **137**, 7843-7850.