

# **Supporting information**

## **Reproducible Planar Heterojunction Solar Cells Based on One-Step Solution-Processed Methylammonium Lead Halide Perovskites**

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## REAGENTS

Lead chloride ( $\text{PbCl}_2$ , 98%, Sigma-Aldrich, CAS no.7758-95-4, product no. 268690)

Lead iodide ( $\text{PbI}_2$ , 99%, Sigma-Aldrich, CAS no. 10101-63-0, product no.211168)

Lead acetate trihydrate ( $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ , 99.999% trace metals basis, Sigma-Aldrich, CAS no. 6080-56-4, product no. 316512)

Titanium isopropoxide (99.999% trace metals basis, Sigma-Aldrich, CAS no. 546-68-9, product no. 377996)

Methylamine iodide (MAI, Dyesol)

2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene

(spiro-MeOTAD, Borun New Material Technology Co., Ltd)

[6,6]-phenyl C61-butyric acid methyl ester (PCBM, >99.5%, SOLENNE BV)

Fullerene ( $\text{C}_{60}$ , 99.9%, Argos organics)

Bathocuproine (BCP, sublimed grade, 99.99% trace metals basis, Sigma-Aldrich, CAS no. 4733-39-5, product no. 699152)

4-*tert*-butylpyridine (tBP, Sigma-Aldrich, CAS no. 3978-81-2, product no.142379)

Bis (trifluoromethanesulfonyl)imide lithium salt (Li-TFSI, 99.95% trace metals basis, Sigma-Aldrich, CAS no. 90076-65-6, product no. 544094)

Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, *CLEVIOS*<sup>TM</sup> P VP Al 4083, Heraeus)

Hypophosphorous acid solution (HPA, 50 wt% in water, Sigma-Aldrich, CAS no. 6303-21-5, product no. 214906)

Hydrochloric acid (HCl, 37%, Sigma-Aldrich, CAS no.7647-01-0, product no. 320331)

*N,N*-dimethylformamide (DMF, 99.8%, anhydrous, Sigma-Aldrich, CAS no. 68-12-2, product no. 227056)

Chlorobenzene (CB, 99.8%, anhydrous, Sigma-Aldrich, CAS no. 108-90-7, product no. 284513)

1,2-Dichlorobenzene (DCB, 99%, anhydrous, Sigma-Aldrich, CAS no. 95-50-1, product no. 240664)

Toluene (99.8%, anhydrous, Sigma-Aldrich, CAS no. 108-88-3, product no. 244511)

2-Propanol (IPA, 99.5%, anhydrous, Sigma-Aldrich, CAS no. 67-63-0, product no. 278475)

Ethanol (99.5%, anhydrous, Sigma-Aldrich, CAS no. 64-17-5, product no. 459836)

Acetic anhydride (99%, Sigma-Aldrich, CAS no. 108-24-7, product no. 320102)

Hellmanex detergent (Sigma-Aldrich, product no. Z805939)

## **PROCEDURE**

### **1. Preparation of substrates**

#### **Etching and cleaning of substrates**

##### **■ FTO substrates**

FTO-coated glass sheets (TEC7, Pilkington) were etched with zinc powder (Zinc powder; Alfa aesar) and 2 M aqueous HCl solution to obtain required electrode pattern. Usually, we use 1g of zinc powder and 10 mL HCl solution for 10 cm<sup>2</sup> FTO glass with our stripe etching line patterned by 19 mm acetate film tape (3M scotch tape). The FTO substrates were sequentially washed with 2% Hellmanex in water, deionized water, acetone, ethanol and iso-propanol in sonication bath for 10-15 min, followed by O<sub>2</sub> plasma cleaning for 10 min.

##### **■ ITO substrates**

The patterned ITO substrates were purchased from Huayu Tech, Shenzhen, China with the size of 28×28 mm, the thickness is 1.1 mm and the square resistance is less than 10 Ω. The ITO substrates were first cleaned with 2% Hellmanex in water, and then were ultrasonically cleaned with deionized water, acetone, ethanol and iso-propanol for 10min, respectively. Before spin-coating, the substrates were treated with O<sub>2</sub> plasma for 10 min.

## **2. Preparation and deposition of compact TiO<sub>2</sub>, fullerene and PEDOT:PSS layer**

### ■ TiO<sub>2</sub> layer

The TiO<sub>2</sub> precursor was prepared by dropping tetra-titanium isopropoxide solution (155  $\mu$ L in 1.25 mL ethanol) into a solution of 15  $\mu$ L of aqueous HCl solution (2 M) in 1.25 mL ethanol. The solution was then filtered twice with 0.2  $\mu$ m PTFE filter in dry-air filled dry box (~17% humidity) to remove dusts and large TiO<sub>x</sub> particles. The TiO<sub>2</sub> coated FTO substrate was then heated to 150 °C for 10 min, 300 °C for 20 min then ramp up to 500 °C for 20 min. The obtained TiO<sub>2</sub> compact layers were further treated with 20 mM TiCl<sub>4</sub> solution at 70 °C for 60 min and then sintered at 450 °C for 30 min.

### ■ Fullerene layer

We dissolve C<sub>60</sub> in 1,2-dichlorobenzene at a concentration of 10 mg/ml. The solution was stirred overnight at room temperature and spin-coated on FTO substrates (TEC 15) at 1500 rpm for 60 s, yielding in a film thickness of ~ 30 nm. The as-deposited films were then annealed at 55 °C for 5 minutes to remove the solvent.

### ■ PEDOT:PSS layer

The as received PEDOT:PSS solution was first diluted with methanol (1:2, v/v). The diluted solution was spin-coated in air on a cleaned ITO substrate at 4000 rpm for 40s, followed by annealing at 150 °C for 10 min.

## **3. Deposition of perovskite films**

### **3MAI:PbCl<sub>2</sub> precursor**

#### ■ Preparation of 3MAI: PbCl<sub>2</sub> precursor

We generally prepare PbCl<sub>2</sub> precursor solution by mixing 387.5 mg MAI and 225.8 mg PbCl<sub>2</sub> in 1.231 mL anhydrous DMF under magnetic stirring (~1000 rpm) at room temperature for 12 h. We first dissolve MAI in DMF and then PbCl<sub>2</sub> was added into the MAI/DMF solution. In general, PbCl<sub>2</sub> dissolves sparingly in DMF and we always observe cloudy solution at the beginning. The precursor becomes to a clear light yellow color after stirring for 8-10 h. The perovskite solution was filtered with 0.45

$\mu\text{m}$  PTFE filter to remove possible dust.

■ Deposition of  $\text{PbCl}_2$  precursor on compact  $\text{TiO}_2$  and fullerene layer

For toluene-assisted deposition, the perovskite precursor (100  $\mu\text{L}$  per 2.5  $\text{cm}^2$  substrate) was spun on a clean substrate with a consecutive two-step spin-coating process at 1200 rpm for 25 s and 2000 rpm for 12 s under controlled relative humidity (~15%). 350  $\mu\text{L}$  of toluene was slowly and continuously dropped onto the pre-crystallized perovskite film after ~5 s of the second step spin program. We observed reddish pink color during toluene quenching, and then the color of perovskite film became yellowish after spin-coating. The perovskite films were dried at room temperature for 15 min and the color changed to dark reddish-brown. The films were then annealed at 70  $^{\circ}\text{C}$  for 15 min on a hotplate in the dry box and then quickly transferred to a preheated oven at 100  $^{\circ}\text{C}$  for 90 min. Finally, the samples were annealed at 120  $^{\circ}\text{C}$  for 15 min in drybox.

For perovskite deposition on fullerene compact layer,  $\text{PbCl}_2$  precursor solution with a concentration of 38 wt% was made by dissolving MAI and  $\text{PbCl}_2$  with 3:1 molar ratio in anhydrous DMF. The precursor solution was coated onto C60 compact layers by a consecutive two-step spin-coating process at 1300 rpm for 25 sec and 3000 rpm for 15 sec under low humidity (< 17% at R.T.) in drybox. Directly after spin-coating, the perovskite films were dried by air blowing for 30 sec. The obtained perovskite films were subsequently dried at R.T. for 15 min and then 70  $^{\circ}\text{C}$  for 15 min on a hot plate. Afterwards, the films were transferred to an oven for further annealing at 100  $^{\circ}\text{C}$  for 120 min then ramp up to 120  $^{\circ}\text{C}$  for 15 min.

**Table S1. Key parameters need to be optimized for the 3MAI:PbCl<sub>2</sub> precursor**

Key parameters	Range	Optimal parameters
Humidity	10~30 %	15%
Concentration precursor	35-40 wt%	38 wt%
Toluene volume	300-500 $\mu$ L	350 $\mu$ L
Air blowing time	20-60 s	30 s
First-step spin-coating	1200-2000 r.p.m/15s-30s	1200 r.p.m/25s
Second-step spin-coating	2000-4000 r.p.m/10s-20s	2000 r.p.m/12s
Drying @ RT (temp/time)	18-25 °C/10-20 min	20°C/15 min
Drying @ 70°C (temp/time)	60-75 °C/5-30 min	70 °C/15 min
First-step annealing	90-105 °C/60 -150 min	100 °C/90min
Second-step annealing	110-130 °C/7-20 min	120°C/15 min

**Pb(Ac)<sub>2</sub>·3H<sub>2</sub>O precursor****■ Preparation of Pb(Ac)<sub>2</sub>·3H<sub>2</sub>O precursor**

To prepare 30 wt% standard Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O precursor solution, the MAI (450.6 mg) was weighed in the glovebox and dissolved in the DMF (2 mL) first. PbAc<sub>2</sub>·3H<sub>2</sub>O (358.6 mg) weighed outside was then added in the MAI/DMF solution. Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O is suggested to be stored outside the glovebox to avoid dehydration, only the necessary amount is transferred into the glovebox when needed. After all the chemicals were completely dissolved, HPA solution (3  $\mu$ l for 1ml precursor solution) was added into the clear precursor solution obtained above outside and then shake on a lab dancer for 2 min to homogenize the solution. 4.5  $\mu$ L/1mL HPA was added in 42 wt% precursor (0.8 M Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O and 2.4 M MAI) used for inverted planar solar cells.

**■ Dehydration of Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O**

For the dehydration of Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O, acetic anhydride and Pb(Ac)<sub>2</sub>·3H<sub>2</sub>O with 3:1 molar ratio was mixed in a flask and heated to 90°C. To ensure totally elimination of the water, a little excess acetic anhydride was used. After reaction for 30 min under

stirring, the solution was distilled off at 40 °C under low vacuum with a rotary evaporator. Completely dehydrated Pb(Ac)<sub>2</sub> can be obtained after drying the obtained white powder in a vacuum oven at 50 °C overnight.

■ Spin-coating of Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O precursor

We used 30 wt% and 42 wt% precursor solution for conventional and inverted planar solar cells, respectively. 100 µL precursor solution was spread on top of each substrate. The spin-coating process was carried out at 2000 r.p.m for 45s with a ramp time of 6s. (Note: we always block the top hole of the lid for spin-coating on PEDOT:PSS substrates). After proper drying process (10 min drying on TiO<sub>2</sub> and no drying on PEDOT:PSS layer), the samples were then annealed at preheated hot plate (100 °C) for 5 min to obtain perovskite films.

**Table S2. Key parameters need to be optimized for deposition of the Pb(Ac<sub>2</sub>)·3H<sub>2</sub>O precursor**

Key parameters	Range	Optimal parameters
Concentration	20-45 wt%	30 wt% for the n-i-p structure and 42 wt% for the p-i-n structure
HPA concentration	2-10 µL/ 1mL	3 µL/ 1mL for the 30 wt% precursor and 4.5µL/ 1mL for the 42 wt% precursor.
Spin-coating speed/time	2000-4000 r.p.m/45s-60s	2000 r.p.m/45s
Ramp time	3-12s	8 s
Drying after spincoating	RT for 0-15 min	0 min for PEDOT: PSS and 10 min for TiO <sub>2</sub>
Annealing temperature/time	90-120 °C/3 min-15 min	100 °C/5 min

#### 4. Preparation and deposition of the top hole and electron transport layers

■ Deposition of spiro-OMeTAD

7 wt% spiro-OMeTAD in chlorobenzene was stirred at 90 °C for 15 min. Additives of

4-tert-butylpyridine (tBP) and lithium bis (trifluoromethanesulfonyl)imide (Li-TFSI) were then sequentially added into the solution with a molar ratio of 80% and 30% with respect to spiro-OMeTAD. The spiro-OMeTAD hole-transporting layer was deposited in drybox by spin-coating of 80  $\mu\text{L}$  solution on the substrate at 2000 r.p.m for 45 s. The devices were put in a desiccator overnight in order to dry out the solvent and oxidize the spiro-OMeTAD.

#### ■ Deposition of PCBM and BCP

Both the PCBM (20 mg/mL in chlorobenzene) and BCP solution (0.5 mg/mL in IPA) was prepared in glovebox. The PCBM solution was stirred at 50  $^{\circ}\text{C}$  overnight and filtered with 0.22  $\mu\text{m}$  PTFE filter before use. Due to the low solubility of BCP in IPA, the solution was heated at 100  $^{\circ}\text{C}$  under stirring for 1-2 h.

The PCBM solution was dynamically spin-coated on top of perovskite film at a speed of 1800 r.p.m for 40 s. All of the PCBM coated samples were annealing at 100  $^{\circ}\text{C}$  for 10 min after spin-coating. After cooling down to room temperature, BCP solution was dynamically spin-coated on the top at a speed of 4000 r.p.m (5s ramp) for 30 s.

### **5. Deposition of Electrodes and solar cells characterization**

#### ■ Deposition of electrodes

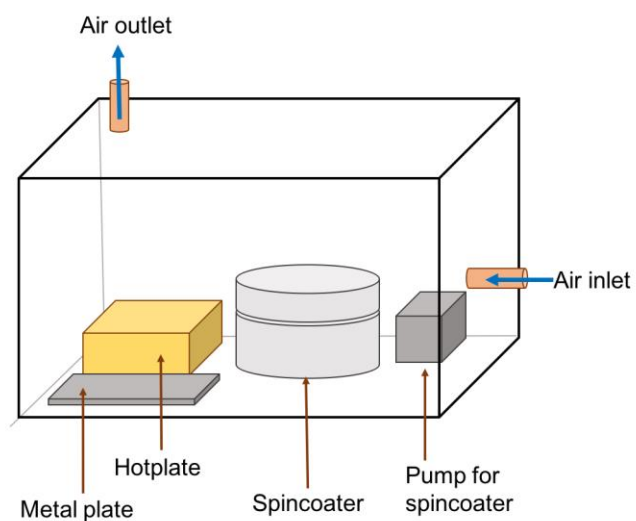
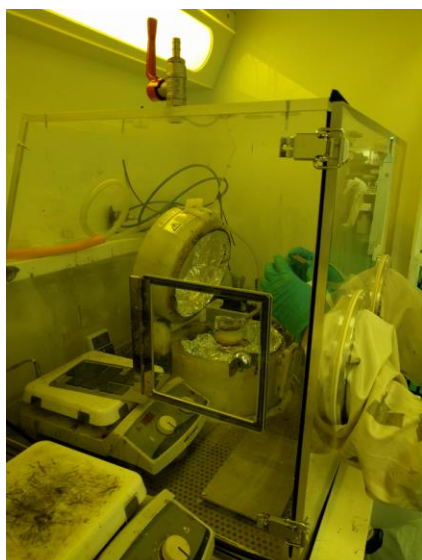
100 nm silver electrodes were thermally evaporated under vacuum of  $\sim 5 \times 10^{-6}$  Torr, at a rate of 0.1-0.2 nm  $\text{s}^{-1}$ . Note that the temperature of the vacuum chamber should be controlled under 40  $^{\circ}\text{C}$  during the evaporation of metal electrode, a higher temperature will cause possible degradation of perovskite films.

#### ■ Test of the devices

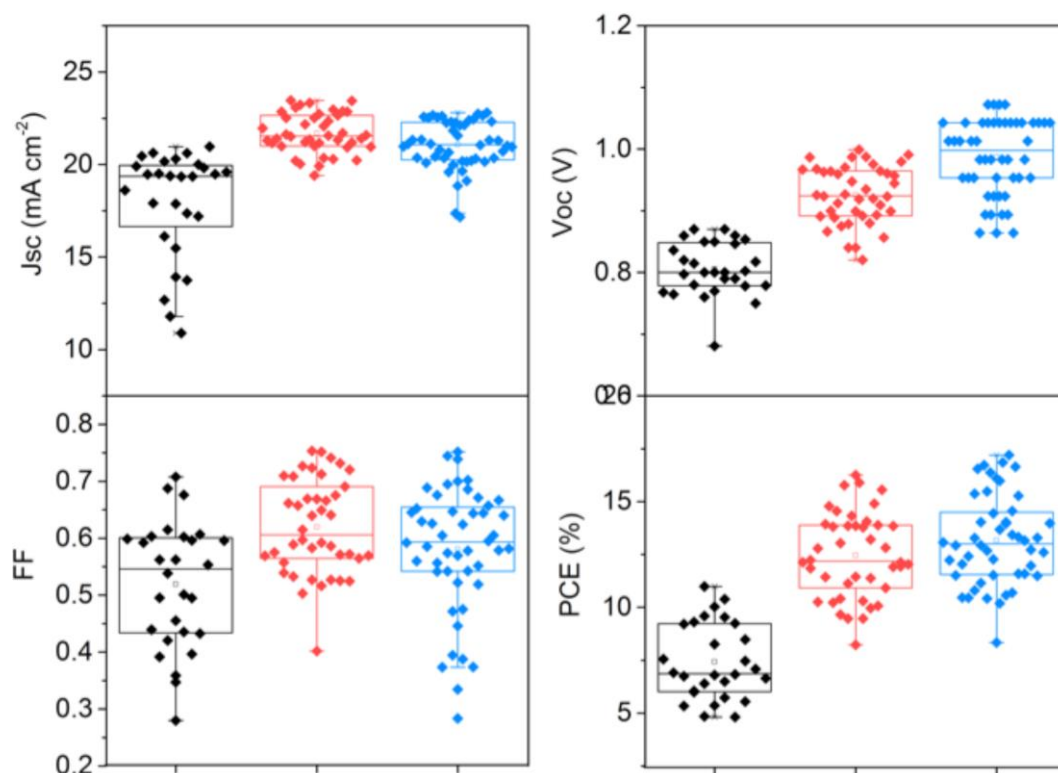
The current density–voltage (J-V) curves were measured (2400 Series SourceMeter, Keithley Instruments) under simulated AM 1.5 sunlight at 100  $\text{mW cm}^{-2}$  irradiance generated by an Abet Class AAB sun 2000 simulator, with the intensity calibrated with an NREL calibrated KG5 filtered Si reference cell. The mismatch factor was calculated to be less than 1%. The solar cells were masked with a metal aperture to define the active area, typically 9.19  $\text{mm}^2$  and measured in a light-tight sample holder



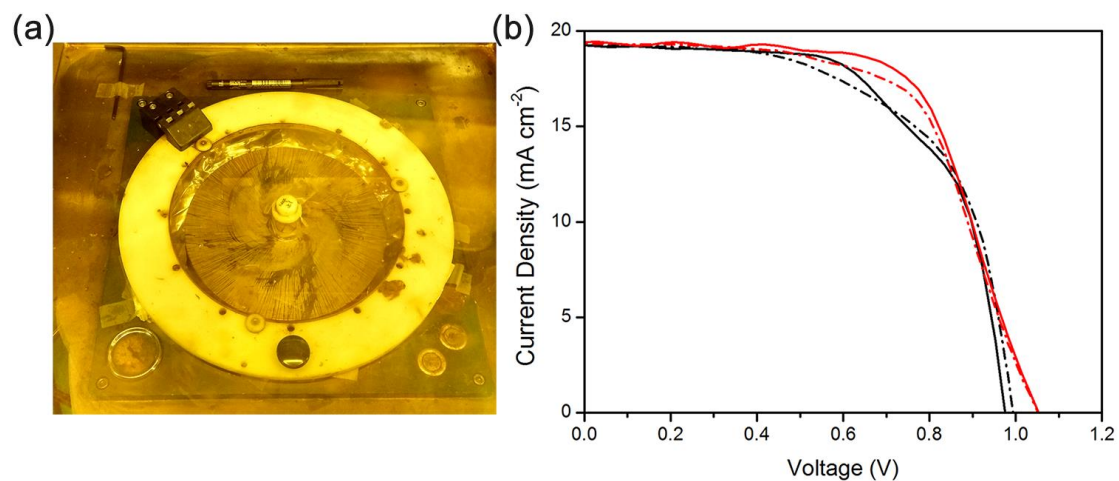
to minimize any edge effects and ensure that the reference cell and test cell are located in the same spot under the solar simulator during measurement.



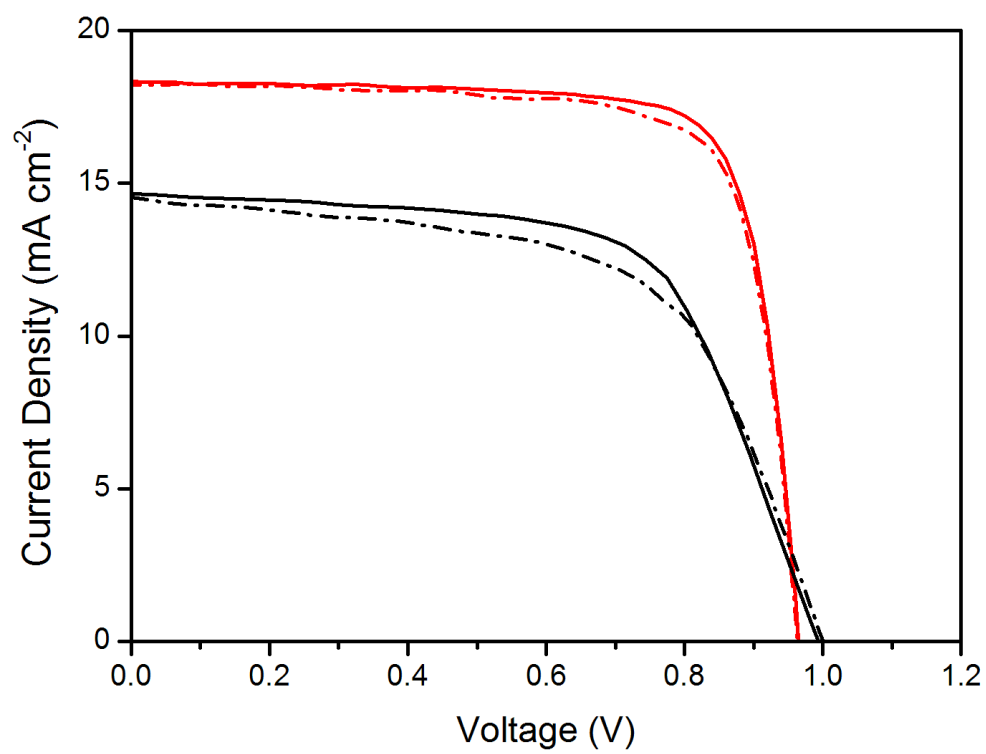
**Figure S1.** The photograph and design of the dry-box used in our cleanroom.



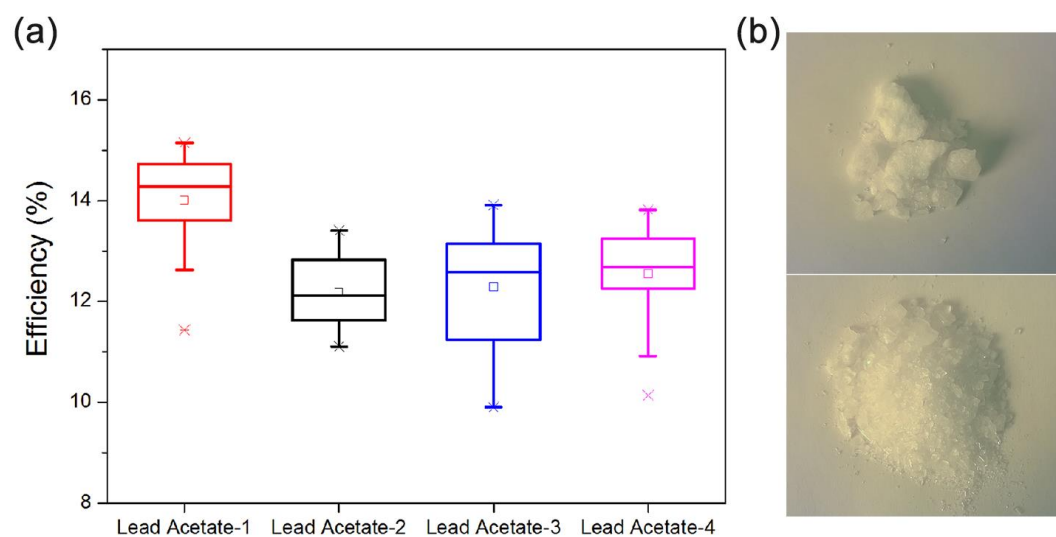
**Figure S2.** Photovoltaic performance characteristics of devices fabricated with perovskite films deposited from the  $\text{PbCl}_2$  precursor using conventional (black), antisolvent-drenching (red), and air-drying (blue) assisted deposition processes, respectively.



**Figure S3.** (a) Top view photograph of the spin-coater used in our glovebox, hole of the lid is blocked with a Telfon plug. (b) Two abnormal J-V curves of devices fabricate with the top hole open. J-V curves measured from forward bias (FB) to short-circuit (SC) (dash line) and back again (solid line) exhibit large hysteresis.



**Figure S4.** J-V curves of inverted devices with (red) or without (black) thermal annealing treatment for the PCBM layer.



**Figure S5.** (b) Device performance of inverted solar cells fabricated from  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  purchased from Sigma-Aldrich with the same product no. but in different bottles. (c) Photographs of different  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  crystals from the same bottle.