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


*Supporting information*

# Defect Tolerant Perovskite Solar Cells from Blade coated Non-Toxic Solvents

**Zhuoneng Bi,[1,2] Xabier Rodríguez-Martínez,[3] Clara Aranda,[1] Enrique Pascual San José,[3] Alejandro R. Goñi,[3,4] Mariano Campoy-Quiles,[3*] Xueqing Xu,[2*] Antonio Guerrero[1*]**

[1] Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain
[2] Key Laboratory of Renewable Energy, Guangdong Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China
[3] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain
[4] ICREA, Passeig Lluís Companys 23, 08010 Barcelona, Spain

Email: xuxq@ms.giec.ac.cn, *mcampoy@icmab.es*; *aguerrer@uji.es*
3 September 2018

## Film optimization and spin coated devices

Doctor blade deposition conditions were optimized to reach rapid kinetic supersaturation regime during film formation and to ensure the fast evaporation of DMSO. Due to the unlimited number of possible variations, we adopted a high throughput screening method. First, we tested the solubility limits for solutions containing $PbI_2$:MAI (1:1, molar ratio) and GBL:DMSO volume ratios between 1:7 to 4:1. The saturation of the solution was observed at concentration values between ~1.3 M and ~1.0 M, respectively. Films were deposited on FTO glasses by doctor blade and the optical quality of the films was evaluated by either naked eye or by measuring the absorption spectra of the most promising films. The presence of pinholes in the perovskite films is typically observed as scattering in transmission mode beyond 800 nm, which can be further confirmed by using an integrating sphere.[1] The temperature of the hotplate and the speed of the blade was systematically modified. The substrate is heated to the maximum temperature allowed by the doctor blade setup (150 °C) and using a blade speed of 1 mm/s with a fixed gap of 150 μm (see methods section for further information).

Optimized devices are prepared by the doctor blade process in the dry box as described in the main text. In ambient formation of chemical defects that can be monitored by absorbance measurements (Figure 2c). This defects are recombination centers that reduce the photocurrent that can be extracted and reduces de FF. Alternatively, for spin coating devices we have previously developed a method that avoids formation of these species even for spin coating under ambient conditions.[2] Using this knowledge we can prepare devices by spin coating with absorbance profile comparable to those prepared by doctor blade.

## Photovoltaic performance for optimization experiments

Different GBL:DMSO ratios were tested and found that a balance between the two solvents was essential to provide adequate morphology. When using DMSO with a low concentration with respect to GBL (8:2), the perovskite immediately crystallizes having not enough additive to generate the $PbI_2$:MAI:DMSO intermediate complex. As a result, the perovskite crystallizes too fast leading to a large proportion of pinholes. Under these conditions, small $V_{oc}$ and fill factors (FF) are obtained: 861 mV and 65%, respectively.

**Table SI1:** Summary of performance parameter conditions of best solvent ratio formulations.

| Conditions | **GBL:DMSO** | $J_{sc}$ **(mA/cm$^2$)** | $V_{oc}$ **(mV)** | ***FF*** **(%)** | ***PCE*** **(%)** |
|---|---|---|---|---|---|
| Ambient | 8 : 2 | 17.99 | 861 | 65 | 10.16 |
| | 7 : 3 | 21.67 | 984 | 71 | 15.12 |
| | 6 : 4 | 20.62 | 1010 | 75 | 15.63 |

## Microcopy analysis

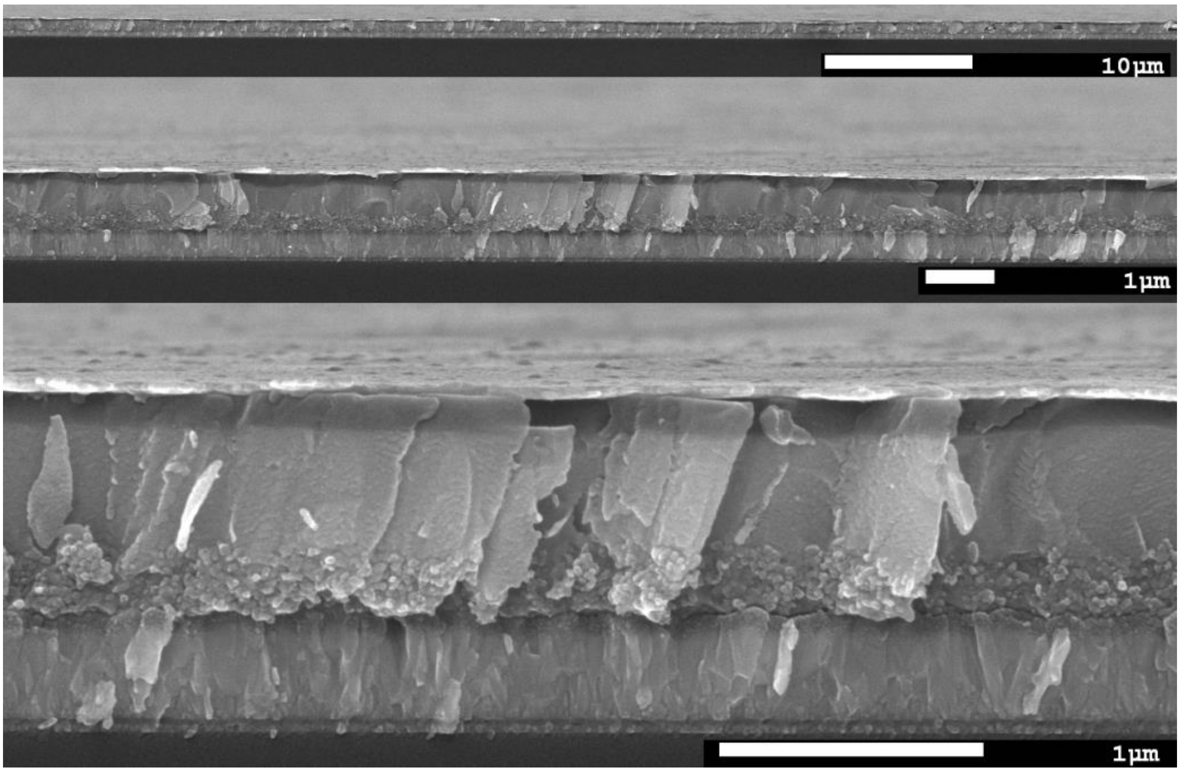


**Figure SI1:** Cross-Section SEM images of complete device at different magnifications.

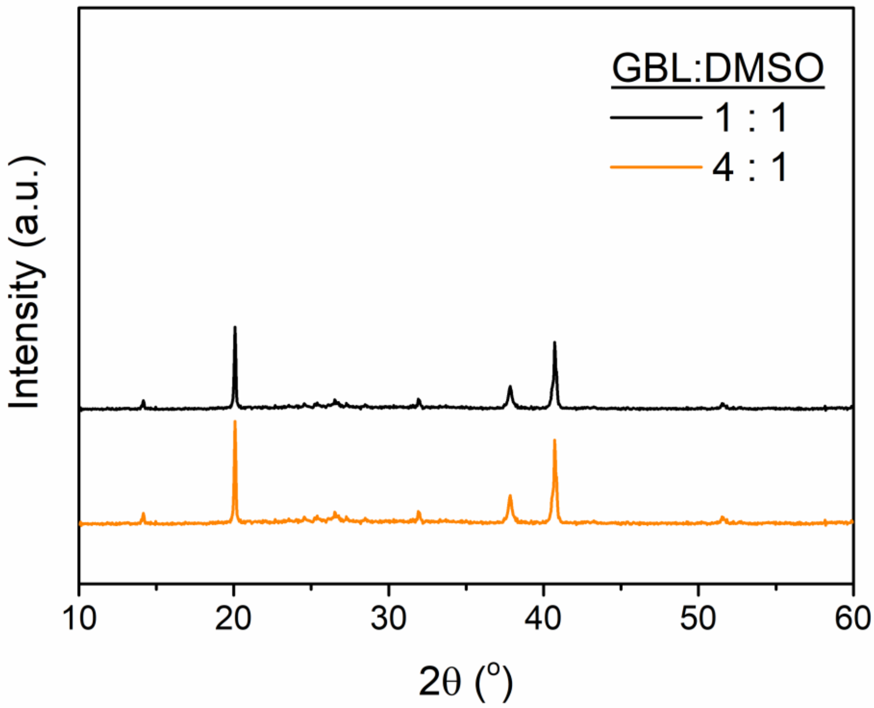


**Figure SI2:** XRD diffraction patterns of perovskite films deposited by doctor blade on Glass/FTO/$TiO_2$-cp/$TiO_2$-ms under different solvent formulations at a concentration 1.2

M.

## Presence of chemical defects as detected by absorbance measurements

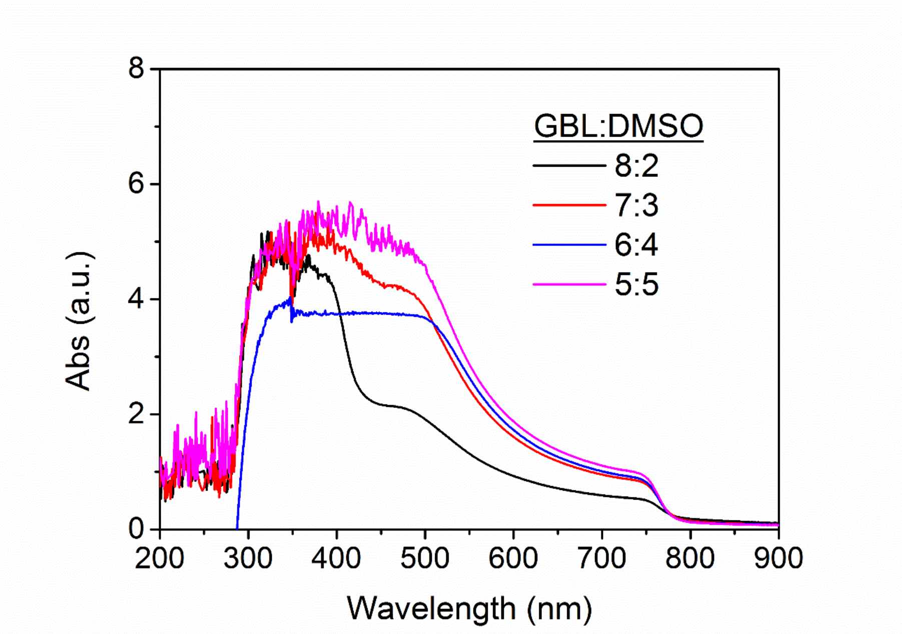


**Figure SI3:** Absorbance spectra of films fabricated in as a function of the GBL:DMSO volume ratio. Presence of undercoordinated lead species appear in the region 300-450 nm as reported previously.[3]

## PL analysis of small spherulites

We used polarized source and analyser 0-0 and 90-90 to evaluate if any potential anisotropic structure (at RT MAPI is tetragonal, but bond-wise it is almost as if it was cubic-which makes anisotropy very small if at all). No difference between vertical and horizontal polarization as observed in Figure SI3. The graph below shows the dichroic ratio calculated by dividing the two measurements (images) above. The fact that it is almost featureless indicates no preferential radial orientation.

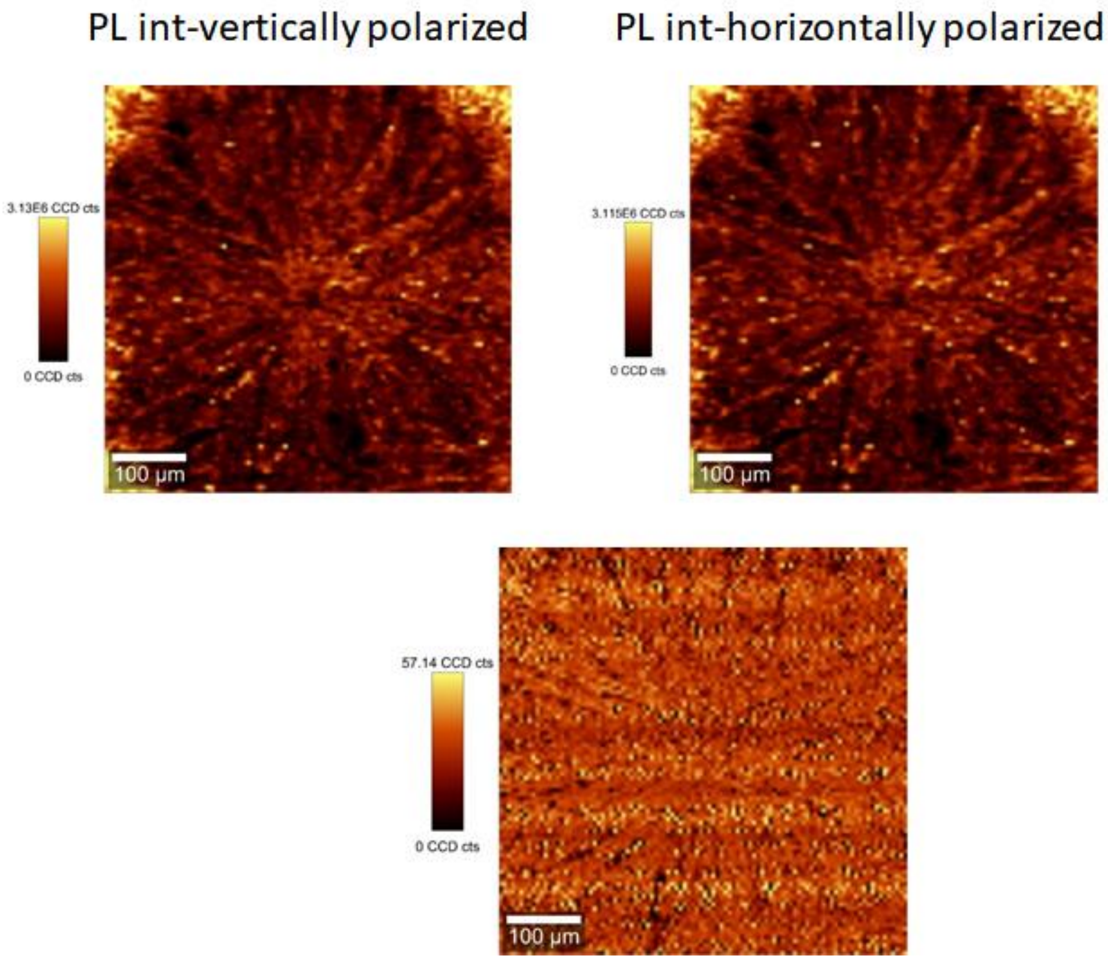


**Figure SI4:** PL analysis using vertical and horizontal polarizers.

## PL analysis of small spherulites

The behavior described for large spherulites is reproduced in the smaller size spherulites (Fig. SI4). If at all, it may look as though PL shifts are less pronounced in these smaller spherulites.

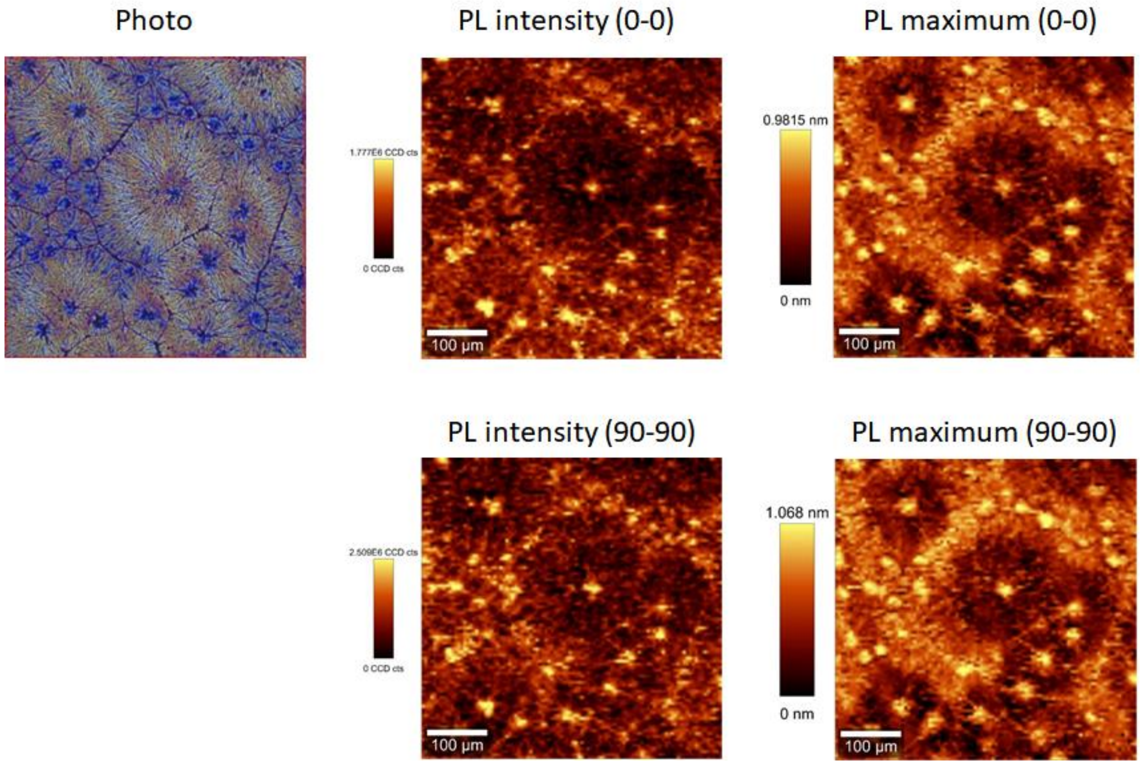


**Figure SI5:** PL analysis of spherulites with diameter in the order of 10-100 µm.

**Stability**

Stability measurements following adequate protocols have not been carried out due to the lack of adequate equipment to promote degradation under well controlled conditions.[4] However, we can state that in general devices were as stable as spin coated devices. Figure SI5 shows representative *J-V* curves of a device measured fresh (PCE= 17.26 %) and after storage (PCE= 16.82 %) during 50 days under nitrogen and 6 days under ambient for transportation from Spain to China.

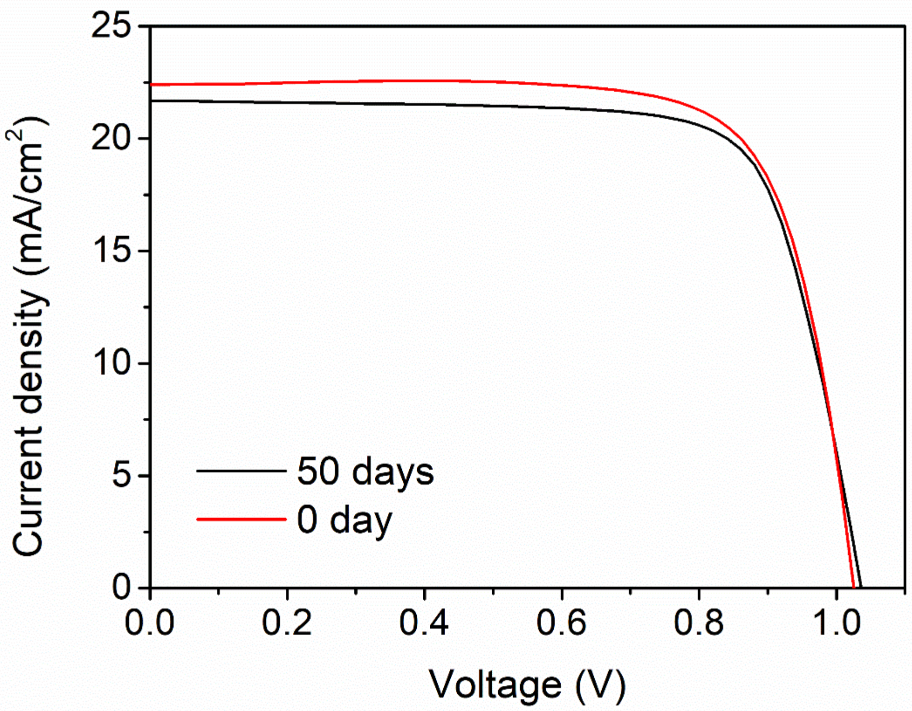


**Figure SI6:** Representative J-V curves of doctor bladed devices measured fresh and after storage during 50 days under nitrogen and 6 days under ambient.

EQE of a device fabricated by doctor blade is shown in Figure was measured and integrated current. Integrated current of 21.1 mA/cm2 can be calculated from the measurement which is within a 5 % of the values obtained during the J-V measurements.

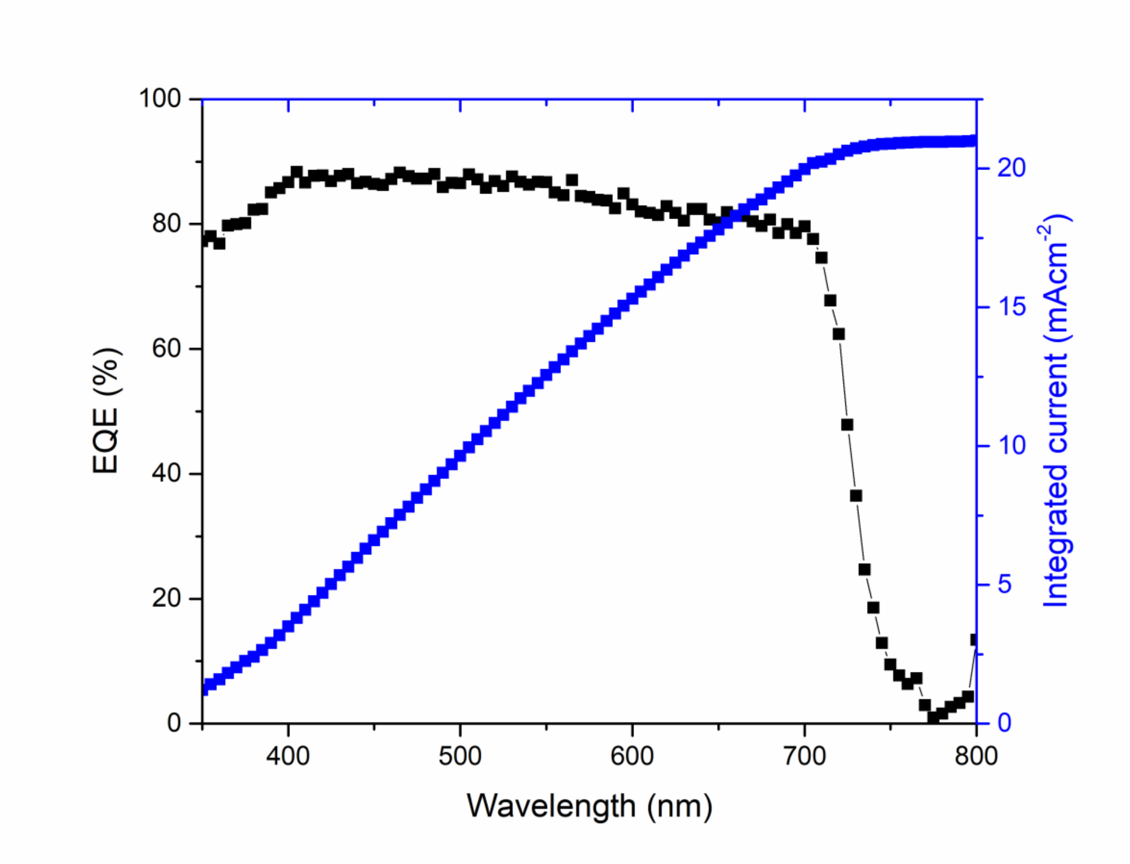


**Figure SI7:** EQE of a device fabricated by doctor blade.

**References**

1. Tian, Y.; Scheblykin, I. G., Artifacts in Absorption Measurements of Organometal Halide Perovskite Materials: What Are the Real Spectra? *J. Phys. Chem. Lett.* **2015**, *6*, 3466-3470.

2. Aranda, C.; Cristobal, C.; Shooshtari, L.; Li, C.; Huettner, S.; Guerrero, A., Formation criteria of high efficiency perovskite solar cells under ambient conditions. *Sustainable Energy & Fuels* **2017**, *1*, 540 - 547.

3. Rahimnejad, S.; Kovalenko, A.; Martí-Forés, S.; Aranda, C.; Guerrero, A., Coordination Chemistry Dictates the Structural Defects in Lead Halide Perovskites. *ChemPhysChem* **2016**, *17*, 2795.

4. Saliba, M.; Stolterfoht, M.; Wolff, C. M.; Neher, D.; Abate, A., Measuring

Aging Stability of Perovskite Solar Cells. *Joule* **2018**, *2*, 1019-1024.