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### Paper:

Lakhiani, H., Dunlop, T., De Rossi, F., Dimitrov, S., Kerremans, R., Charbonneau, C., Watson, T., Barbé, J. & Tsoi, W. (2019). Variations of Infiltration and Electronic Contact in Mesoscopic Perovskite Solar Cells Revealed by High Resolution MultiMapping Techniques. *Advanced Functional Materials*, 1900885

<http://dx.doi.org/10.1002/adfm.201900885>

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# Variations of infiltration and electronic contact in mesoscopic perovskite solar cells revealed by high-resolution multi-mapping techniques

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ABSTRACT A combination of high-resolution mapping techniques were developed to probe the homogeneity and defects of mesoscopic perovskite solar cells. Three types of cells using a one-step infiltration process with methylammonium lead iodide (MAPbI<sub>3</sub>) or 5-ammoniumvaleric acid-MAPbI<sub>3</sub> solutions, or two-step process with MAPbI<sub>3</sub> solution were investigated. The correlation between photoluminescence, photocurrent, electroluminescence and Raman maps gives a detailed understanding of the different infiltration mechanisms, electronic contact at interfaces and effect on local photocurrent for the cells. One-step MAPbI<sub>3</sub> cell has very limited infiltration of the perovskite solution which results in poor device performance. High loading of the mesopores of the TiO<sub>2</sub> and ZrO<sub>2</sub> scaffold is observed when using 5-ammoniumvaleric acid, but some micrometer-sized non-infiltrated areas remain due to dense carbon flakes hindering perovskite infiltration. The two-step cell has a complex morphology with features having either beneficial or detrimental effects on the local photocurrent. Our results provide key insights to achieve better infiltration and homogeneity of the perovskite film in mesoporous devices but can also serve further work on planar devices to develop efficient extraction layers. Besides, this multi-mapping approach allows the correlation of the local photo-physical properties of full perovskite devices, which would be challenging to obtain by other techniques.

KEYWORDS: mesoscopic perovskite solar cells, photocurrent, photoluminescence, Raman, electroluminescence, mapping, infiltration, electronic contact.

Carbon-based hole-conductor-free mesoscopic perovskite solar cells (C-PSCs) have emerged as one of the most promising perovskite solar cell architectures, in terms of low cost of materials, ease of manufacture and long-term stability,<sup>[1],[2]</sup> as well as environmental impact/carbon footprint.<sup>[3]</sup> Consisting of an all-printable triple mesoscopic stack, *i.e.* titania (TiO<sub>2</sub>) scaffold, insulating layer (either ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) and carbon-based back electrode, lab scale C-PSCs have achieved 15.9% PCE for a methylammonium lead iodide (MAPbI<sub>3</sub>) perovskite chemically modified by adding SrCl<sub>2</sub>,<sup>[4]</sup> and 17% PCE when a triple cation

1 perovskite is used as the absorber.<sup>[5]</sup> While still lagging behind other types of PSCs, in terms of efficiency (record PCE for  
2 mesoporous TiO<sub>2</sub>-based PSCs with organic HTM and evaporated metal electrode is over 22%),<sup>[6],[7]</sup> C-PSCs have demonstrated  
3 unprecedented long-term stability: over 1 year under continuous AM1.5 illumination and over 1000 hours under different conditions  
4 of illumination and external stresses, even for un-encapsulated cells.<sup>[8],[9]</sup> Large area modules have been reported by different  
5 groups, with PCE over 10% on 10 x 10 cm<sup>2</sup> substrates,<sup>[9],[10],[11],[12]</sup> and around 6% for A4 sized modules.<sup>[13]</sup> In addition, the lack  
6 of expensive metal cathode<sup>[14]</sup> and organic HTM,<sup>[15]</sup> use of abundant materials, easy printing processes and low capital cost  
7 equipment also account for simpler and cheaper manufacturing process, paving the way for C-PSCs to move quickly from the lab  
8 to the market.

9 Unlike spin-coating, perovskite precursors solutions are infiltrated into the mesoporous triple stack with little waste of material,  
10 via drop casting, ink-jet printing or automatized dispensing.<sup>[16]</sup> When using DMF or DMF:DMSO as solvents, a good infiltration  
11 of the thick stack (usually >10 μm) is achieved for both one-step<sup>[17]</sup> and two-step deposition.<sup>[18]</sup> However, for large scale production  
12 it is critical to replace DMF with less toxic solvent such as gamma-Butyrolactone (GBL). It was shown that when using GBL  
13 solvent, 5-ammonium valeric acid iodide (AVAI) should be added to the MAPbI<sub>3</sub>-GBL precursors solution to improve the  
14 wettability and induce better pore filling.<sup>[1]</sup> Furthermore, AVAI promotes the formation of a characteristic multi-dimensional  
15 2D/3D perovskite junction, responsible for the remarkable long-term stability of this type of cells.<sup>[9]</sup> Beside solvents, processing  
16 variables, such as temperature and humidity, can affect the infiltration throughout such a thick structure, potentially resulting in  
17 local variations in the perovskite crystallisation that might be levelled up and hindered when assessing the device via J-V  
18 measurements.

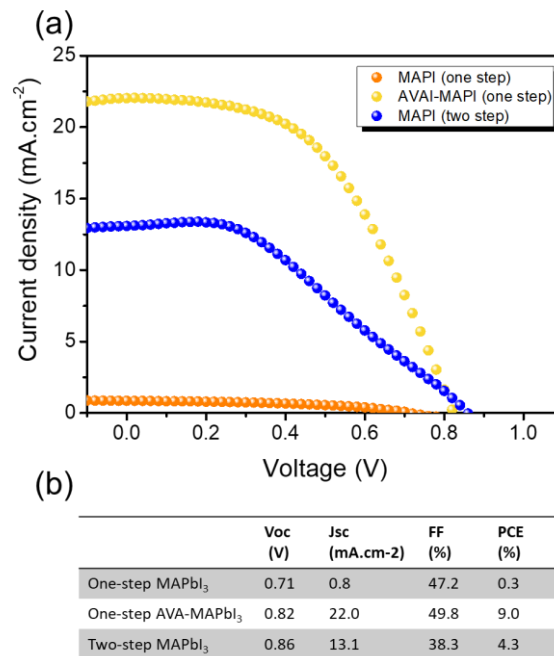
19 In this work, we developed advanced multi-mapping techniques to spatially investigate the device uniformity and defects in C-  
20 PSCs based on different infiltration processes using GBL solvent: one-step process with MAPbI<sub>3</sub>-GBL or AVAI-MAPbI<sub>3</sub>-GBL  
21 precursors solutions, or two-step process with MAPbI<sub>3</sub>-GBL precursors solution. Recently, researchers have probed spatial  
22 variations in local photoluminescence and photocurrent of planar inverted-type PSCs and suggested variability in contact to the  
23 active layer, which causes local carrier extraction heterogeneity and eventually impacts the device performance.<sup>[19],[20]</sup> However,  
24 to our knowledge, no such study has been carried out on mesoscopic PSCs in which the contact properties between the perovskite  
25 layer and the extraction layers might be radically different due to the mesoporous structure of the device itself and the infiltration  
26 process used in this case. Here, for the first time photoluminescence (PL), electroluminescence (EL), Raman and photocurrent  
27 maps are acquired on the same area with high resolution. On the contrary to imaging techniques,<sup>[21]</sup> these maps are spectrally and  
28 spatially resolved which means that the PL, EL and Raman spectra are acquired for each data point. Hence, information such as PL  
29 and EL peak width and position, and Raman maps for selected peaks can be extracted from these data, which allows not only to  
30 gain information about spatial heterogeneities but also to identify the nature of the observed features. The PL intensity alone can  
31 be complex to interpret in a full device structure as competing mechanisms such as charges quenching and non-radiative  
32 recombination may happen simultaneously. However, using complementary techniques such as PL, EL and photocurrent mapping  
33 allows to gain better understanding of mesopore filling by the perovskite solution and electronic coupling with the extraction layer.  
34 These techniques are carried out on full devices in a non-destructive way so that they provide a relatively simple inspection tool  
35 which allows to correlate the overall PV performance to the device defects and homogeneity.

## 36 **RESULTS AND DISCUSSION**

### 37 **Current voltage characteristics**

38 The performance of the mesoscopic perovskite solar cells prepared using different solutions and deposition processes were first  
39 characterized under 1 sun AM1.5g illumination and the results are shown in Figure 1. It is important to consider that the

1 performance of this type of cells depends on the masked area exposed to light during the J-V measurements, due to the poor  
 2 conductivity of the carbon top electrode which limits the fill factor:<sup>[18]</sup> the smaller the masked area, the higher the FF and PCE. The  
 3 1 cm<sup>2</sup> active area was masked to 0.5 cm<sup>2</sup> to have more realistic measurements of the device operation. A striking difference in  
 4 performance was observed between the cells infiltrated via one-step deposition with MAPbI<sub>3</sub> and AVAI-MAPbI<sub>3</sub>: the one-step  
 5 MAPbI<sub>3</sub> delivers just 0.3% PCE due to very poor J<sub>sc</sub> value, whereas the one-step AVAI-MAPbI<sub>3</sub> has 9.0% PCE. Although this  
 6 value is lower than PSCs using the conventional architecture, it is in line with the values reported for C-PSCs.<sup>[18]</sup> To obtain higher  
 7 efficiencies without using AVAI, a two-step infiltration method is preferable: a PbI<sub>2</sub> solution in DMF is infiltrated into the  
 8 mesoscopic stack, which is then immersed in a MAI solution in IPA to promote the conversion to MAPbI<sub>3</sub>.<sup>[18],[16]</sup> However, the  
 9 two-step MAPbI<sub>3</sub> cell is not as efficient as the one-step AVAI-MAPbI<sub>3</sub> (4.3% vs 9.0% PCE and J<sub>sc</sub> of 13.1 vs 22.0 mA.cm<sup>-2</sup>,  
 10 respectively), which is mostly due to smaller fill factor and J<sub>sc</sub>.



11  
 12 **Figure. 1** (a) J-V curves under 1 sun AM1.5G illumination of mesoscopic perovskite solar cells fabricated using one-step MAPbI<sub>3</sub>,  
 13 one-step AVAI-MAPbI<sub>3</sub> and two-step MAPbI<sub>3</sub> processes. (b) PV parameters measured for the three types of cells.

#### 14 High-resolution multi-mapping

15 In order to understand the significant variations in performance of the different types of cells under solar spectrum, the cells were  
 16 characterized under nitrogen atmosphere by high-resolution photoluminescence, photocurrent, electroluminescence and Raman  
 17 mapping on 500 x 500 μm and 20 x 20 μm areas using a Renishaw InVia confocal Raman microscope. All maps and optical images  
 18 were taken from the substrate side. For PL, photocurrent and Raman maps, a 532 nm laser is transmitted through the  
 19 glass/FTO/compact TiO<sub>2</sub> layer before being absorbed within the perovskite infiltrated in the mesoporous structure. The calculated  
 20 excitons generation profile in C-PSCs at 532 nm is shown in Figure S1. Assuming that perovskite has fully infiltrated the  
 21 mesoporous structure, more than 93% of carriers are generated in the perovskite within the mp-TiO<sub>2</sub> layer. While the PL and  
 22 photocurrent techniques will give evidences on the variations in charges extraction/electronic coupling between the perovskite and  
 23 the mp-TiO<sub>2</sub> extraction layer, Raman spectroscopy will provide us with a direct experimental assay of perovskite infiltration.  
 24 Indeed, if perovskite has not fully infiltrated the mp-TiO<sub>2</sub>, enhanced mp-TiO<sub>2</sub> Raman signal will be measured in this case. Hence,

1 PL/photocurrent and Raman mapping are complementary and allow to discriminate between the effects of lower electronic contact  
2 at the interface and poor perovskite infiltration. For EL map, an electrical bias is applied between the carbon and FTO electrodes.  
3 The injection of charges at the different interfaces as well as the electrical properties of the different layers in the entire stack can  
4 influence the resulting map.

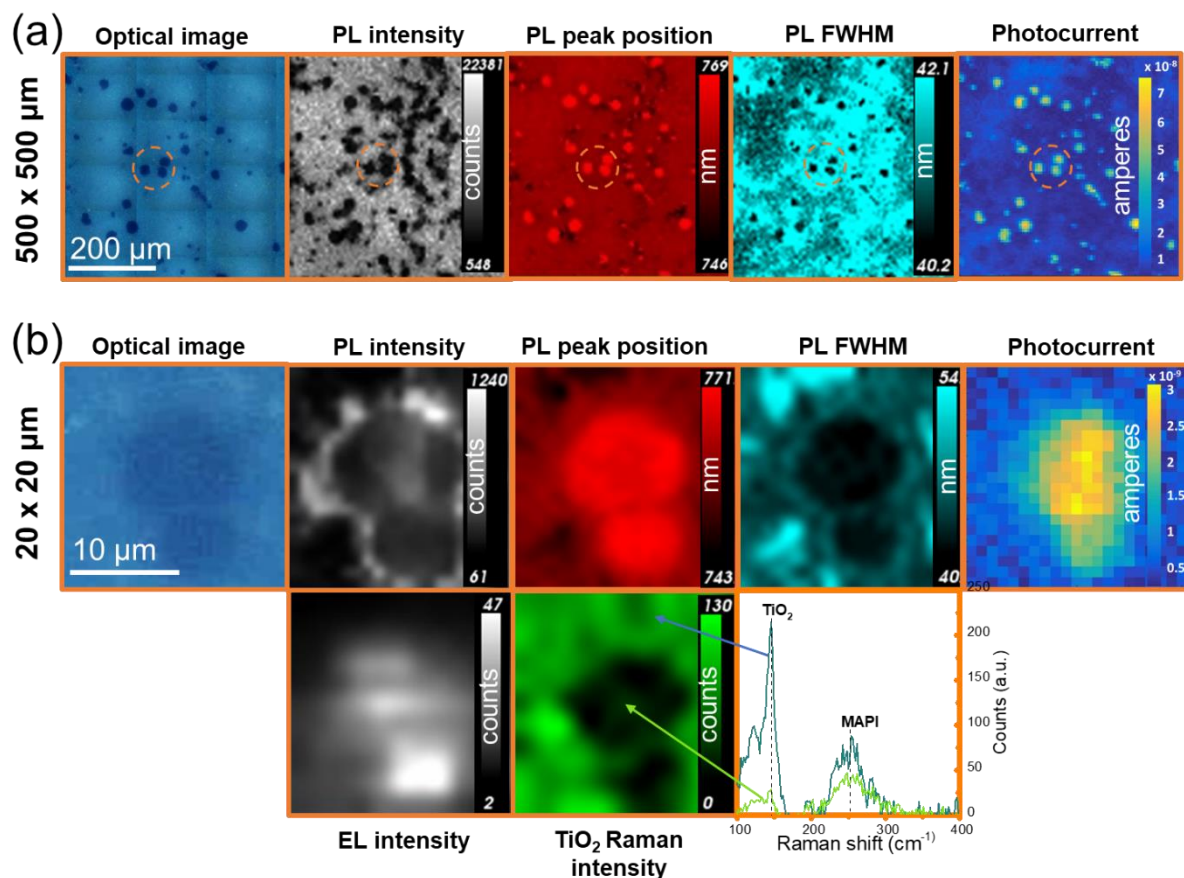
5 The complete set of maps for the cell prepared using one-step process with MAPbI<sub>3</sub> solution (without AVAD) is shown in Figure  
6 2. The 500 x 500 μm optical microscopy image in Figure 2a reveals a clearly non-uniform film with micrometre-sized dark circular  
7 features randomly distributed over the device (indicated by orange dashed circles). The PL intensity map spatially correlates well  
8 with the optical image and indicates that these features have lower PL intensity as compared to surrounding regions. The  
9 photocurrent map acquired simultaneously is in excellent agreement with the optical image and PL maps, and indicates a significant  
10 increase in photocurrent where the features are observed. This spatial correlation between low PL intensity and higher photocurrent  
11 can be explained by better charge extraction from these regions reducing the yield of radiative recombination in these areas and  
12 suggesting the presence of ‘hot’ spots with better electrical contact between the perovskite and mp-TiO<sub>2</sub>.

13 To study these hot spots further, we extended the capabilities of our mapping technique to detect changes in PL peak position and  
14 full width at half maximum (FWHM). In recent works, researchers have focused on PL intensity only<sup>[19],[22]</sup> but to our knowledge  
15 there is no such study showing variations in PL peak position and width in perovskite solar cells. The maps presented in Figure 2a  
16 reveal a clear red-shift and narrowing of the photoluminescence at the higher photocurrent ‘hot’ spots. We hypothesize that the  
17 better contact and electronic coupling between the perovskite active material and mp-TiO<sub>2</sub> ETL allows photogenerated electrons  
18 in the conduction band to be extracted at short circuit before they can recombine radiatively. This results in reduced band-to-band  
19 recombination flux and emission arising from slower charges, likely thermally-activated from shallow defects, as described in  
20 Figure S2. On the contrary, in regions of poor electrical contact, PL emission originates from higher energy band-to-band emission  
21 because charges extraction rates are slower than emission. This mechanism could also explain the narrower PL FWHM at the ‘hot’  
22 spots where the charge extraction flux is much higher than the emission, thus reducing the density of emissive charge carriers to  
23 those close in energy to the band edge. However, the photoluminescence line width is also an indication of the structural disorder  
24 present in the perovskite crystal.<sup>[23]</sup> Hence, we suggest that the perovskite crystals may have significantly less trap states at the high  
25 photocurrent regions, which could be explained by passivation of trap states at the perovskite surface in contact with the mp-TiO<sub>2</sub>  
26 ETL. We note that other samples using the same one-step infiltration process have been measured and showed similar optical and  
27 electronic properties, as shown in the 100 x 100 μm maps in Figure S5. This suggests that the observed non-uniformities are a result  
28 of the infiltration process itself and do not vary significantly from batch-to-batch.

29 From the large map, a region showing a typical ‘hot’ spot with lower PL intensity/higher photocurrent was selected to perform  
30 higher resolution 20x20 μm maps with 1 μm step size shown in Figure 2b. This feature is representative of the other features  
31 observed on the large map in Figure 2a, which have similar PL and photocurrent properties. Mapping smaller areas allows to obtain  
32 more detailed maps on specific features, but also enables acquiring the EL and Raman maps which are more difficult to perform  
33 on a large scale as they require longer acquisition time in order to obtain sufficient signal-to-noise ratio (which might also degrade  
34 the device). On the contrary to the PL map which lateral resolution is limited by the size of the laser beam exciting the sample, for  
35 the EL map photons are generated by an electrical bias which is applied to the entire cell. In this case, the resolution of the map is  
36 dependent on several factors such as the lens numerical aperture, slit size and CCD area. A trade-off between lateral resolution and  
37 signal intensity is necessary, which explains why the resolution of the EL map is rather low as compared to the other maps.  
38 However, from the EL intensity map, it is quite clear that the ‘hot’ spot has higher EL intensity than surrounding regions. This  
39 reveals better charge injection at these regions, in good agreement with charge quenching indicated by the PL and photocurrent  
40 maps.<sup>[21]</sup> Even if the PL, EL and photocurrent maps clearly demonstrate heterogeneities in local charges extraction/injection, these  
41 techniques only are not sufficient to reveal the role played by perovskite infiltration.<sup>[19]</sup> Hence, a Raman map was performed on

1 the same region. On the contrary to other mapping techniques used in this work, Raman is a chemical probe which gives direct  
2 information about the chemical phases present in the device, independently from electronic processes involved in the device  
3 structure. MAPbI<sub>3</sub> has a weak Raman signal and would require long acquisition time to get sufficient signal-to-noise ratio, which  
4 could be harmful for the cell.<sup>[24]</sup> Instead, it is more appropriate to display the more intense peak of anatase phase of TiO<sub>2</sub> at 144 cm<sup>-1</sup>  
5 as shown in Figure 2b.<sup>[25]</sup> Due to the high absorption coefficient of perovskite, MAPbI<sub>3</sub> has a “shielding” effect on the TiO<sub>2</sub> signal.  
6 The darker region at the centre of the map indicates that less TiO<sub>2</sub> is probed by the laser because perovskite material can absorb  
7 the laser before it penetrates deeper in the structure, as a result of better infiltration (single point spectra are shown in Figure 2b  
8 next to the Raman map). For comparison, the TiO<sub>2</sub> Raman map of an empty mesoporous stack (before perovskite infiltration)  
9 shown in Figure S3b along with a typical Raman spectrum extracted from this map indicates a rather uniform and intense signal  
10 from the mp-TiO<sub>2</sub> layer at 144 cm<sup>-1</sup> as there is no perovskite to block the penetration of the laser beam in the layer stack. Even if  
11 the mp-TiO<sub>2</sub> film may have some slight thickness variations as observed in Figure S3b, it cannot explain the signal variations  
12 shown in Figure 2b, which is almost one order of magnitude higher outside the dark spot than inside.

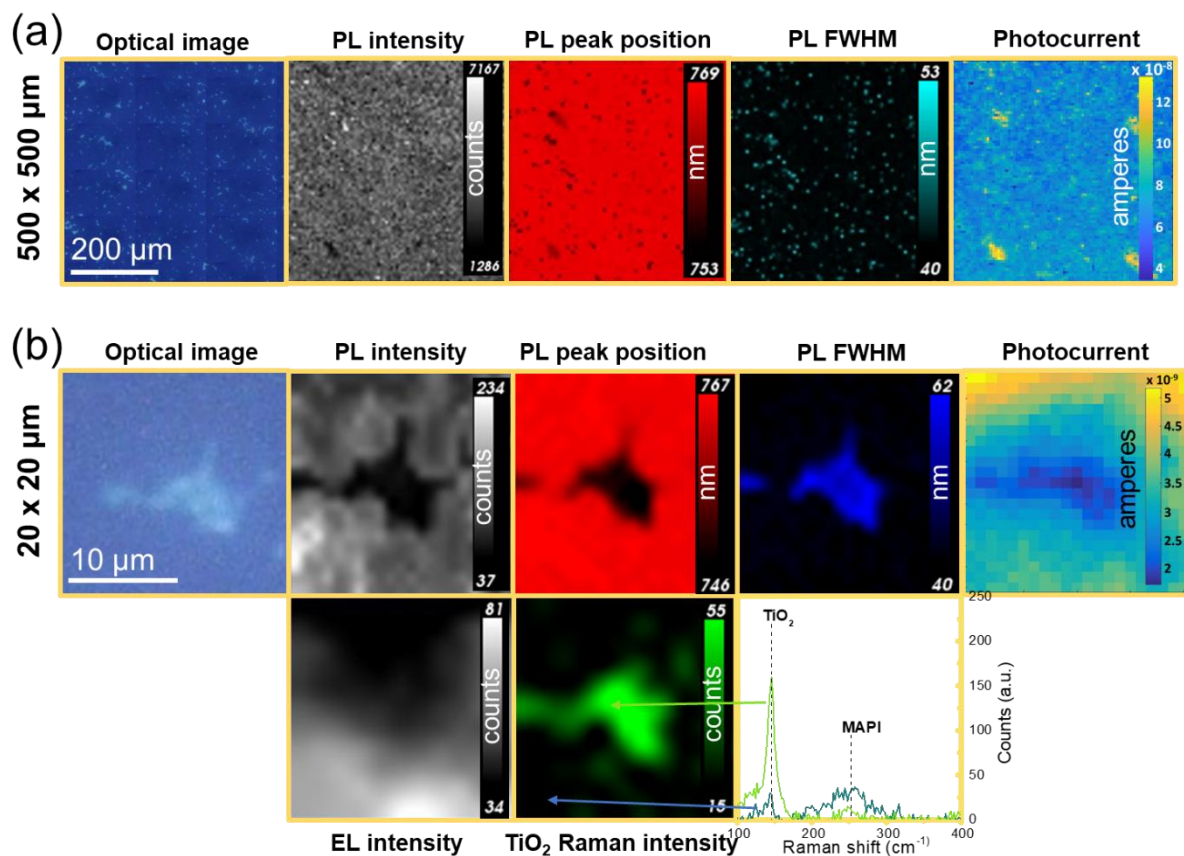
13 This therefore shows that all the different maps acquired on the perovskite solar cell using one-step MAPbI<sub>3</sub> infiltration process  
14 are consistent with poor infiltration of the layer stack. Only randomly dispersed micrometre-sized areas are well infiltrated with  
15 perovskite and provide sufficient electronic contact with the mp-TiO<sub>2</sub> to participate in the photocurrent delivered by the cell,  
16 whereas most of the cell is ineffective. This explains why the J<sub>sc</sub> measured for this cell is less than 1 mA.m<sup>-2</sup> as most of the incident  
17 light is not absorbed in the perovskite within the mp-TiO<sub>2</sub> layer but deeper in the layer stack (in ZrO<sub>2</sub> or carbon). In Figure S4, an  
18 optical image of the one-step MAPbI<sub>3</sub> device was processed to show a clear contrast between infiltrated and non-infiltrated areas.  
19 It was measured that well infiltrated regions represent around 4% of the whole device only. Hence, if the whole device was  
20 efficiently infiltrated, the J<sub>sc</sub> could be multiplied by 25 and reached up to 20 mA.cm<sup>-2</sup>, which is similar to the one-step AVAI-  
21 MAPbI<sub>3</sub> device.



1  
 2 **Figure. 2** High-resolution multi-mapping of mesoscopic solar cells fabricated from one-step MAPbI<sub>3</sub> solution process. (a) 500 x  
 3 500 μm optical microscopic image, PL peak intensity, PL peak position, PL full width at half maximum (FWHM) and photocurrent  
 4 maps (measured with 1.5 μW laser power). Dashed circles indicate well-infiltrated regions of high photocurrent with narrowed and  
 5 red-shifted PL. (b) 20 x 20 μm optical image, PL peak intensity, PL peak position, PL FWHM, photocurrent (measured with 0.3  
 6 μW laser power), electroluminescence intensity and Raman TiO<sub>2</sub> peak intensity maps measured across a typical feature. Raman  
 7 single point spectra between 100 cm<sup>-1</sup> and 400 cm<sup>-1</sup> measured on and off the feature are also shown.

8 Then, the same set of maps was acquired on the cell using a one-step infiltration process with AVAI-MAPbI<sub>3</sub> solution, as shown  
 9 in Figure 3. Although exact same mapping parameters were used, critically different results were obtained for this type of device.  
 10 At first glance, from the 500 x 500 μm optical microscopy image in Figure 3a the one-step AVAI-MAPbI<sub>3</sub> device looks much more  
 11 uniform than the one-step MAPbI<sub>3</sub> device described before. Small bright features can be observed, much smaller than the dark  
 12 features observed in Figure 2a. The PL maps shown in Figure 3a indicate that these features have lower PL peak intensity, lower  
 13 wavelength and higher width than the surrounding area. The photocurrent map indicates highly uniform photocurrent across the  
 14 device. However, it can be seen that four spots have significantly higher photocurrent as compared to the rest of the mapped area  
 15 (□120 nA against □70 nA). The distance of exactly 300 μm between these spots corresponds to the size of the mesh used to print  
 16 the carbon electrode by screen printing. We believe that the carbon is thinner at the mesh intersections, which could help to infiltrate  
 17 the perovskite solution, resulting in better charge extraction and reduced recombination. However, most of the device is uniform  
 18 so that higher resolution maps are needed to have detailed information about the inhomogeneities present in the layer stack. Figure  
 19 3b shows 20x20 μm optical image, PL, photocurrent, EL and TiO<sub>2</sub> Raman peak intensity maps taken around a typical bright feature.

1 It shows clear decrease in PL intensity, which also corresponds to a decrease in photocurrent and decrease in EL intensity. The  
 2 correlation low PL/low photocurrent/low EL is different from the results obtained with the one-step MAPbI<sub>3</sub> sample (low PL/high  
 3 photocurrent/high EL correlation) and can be explained by poor perovskite infiltration at these regions. Indeed, if the mp-TiO<sub>2</sub>  
 4 pores are not properly filled with perovskite phase, the reduced amount of perovskite material induces lower PL signal because of  
 5 scattering effect in the mp-TiO<sub>2</sub> structure, but also lower photocurrent and lower EL due to inefficient electron transport at the  
 6 perovskite/mp-TiO<sub>2</sub> interface. In good agreement with these results, the TiO<sub>2</sub> Raman map in Figure 3b also indicates higher TiO<sub>2</sub>  
 7 signal at the centre of the map because of the reduced amount of perovskite in this area. Based on the previous discussion, the PL  
 8 blue-shift and broadening at the defect location are also in good agreement with electrons in the conduction band not being  
 9 quenched because of inefficient contact with the mp-TiO<sub>2</sub> extraction layer. Hence, on the contrary to the one-step cell using MAPbI<sub>3</sub>  
 10 solution, the cell using AVAI-MAPbI<sub>3</sub> solution is much more uniform and displays excellent perovskite infiltration, which induces  
 11 efficient charge transport through the device. Although some areas of poor infiltration and reduced photocurrent remain, they  
 12 represent only 2% of the whole surface (Figure S4). We note that on the contrary to Figure 2a which shows that well-infiltrated  
 13 regions have circular shape, these areas of poor infiltration have random shape as observed in Figure 3b. The circular shape can be  
 14 explained by radial diffusion of the perovskite solution once in contact with the c-TiO<sub>2</sub> interface, while the random shape is  
 15 determined by the shape of the feature blocking perovskite infiltration (*i.e.* dense carbon flake as discussed later).



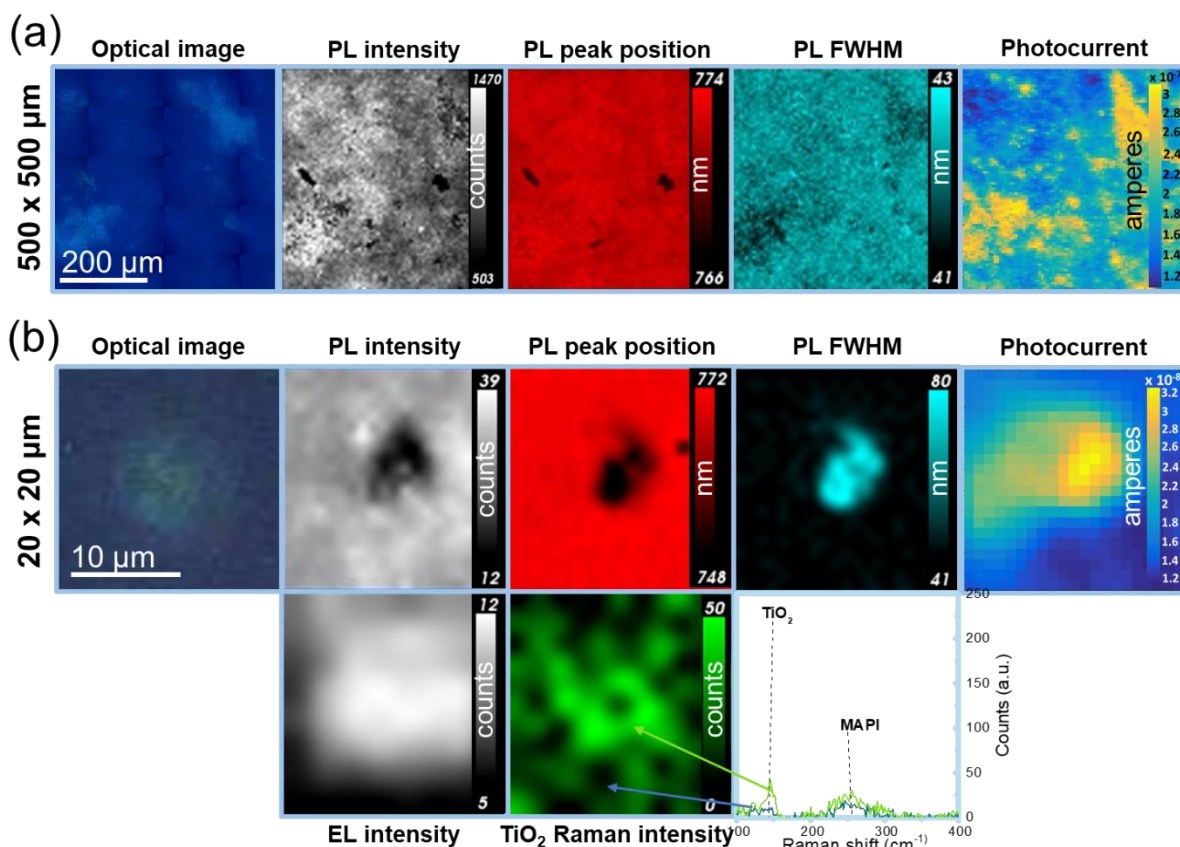
16

17 **Figure 3** High-resolution multi-mapping of mesoscopic solar cells fabricated from one-step AVAI-MAPbI<sub>3</sub> solution process. (a)  
 18 500 x 500 μm optical microscopic image, PL peak intensity, PL peak position, PL FWHM and photocurrent maps (measured with  
 19 1.5 μW laser power). (b) 20 x 20 μm optical image, PL peak intensity, PL peak position, PL FWHM, photocurrent (measured with



1 0.3  $\mu$ W laser power), electroluminescence intensity and Raman TiO<sub>2</sub> peak intensity maps measured across a typical feature. Raman  
2 single point spectra between 100 cm<sup>-1</sup> and 400 cm<sup>-1</sup> measured on and off the feature are also shown.

3 Finally, Figure 4 shows the set of maps acquired on the device using a two-step infiltration process. The 500 x 500  $\mu$ m optical  
4 microscopy image in Figure 4a shows a very different pattern from the two previous samples (vertical and horizontal lines are due  
5 to the microscope montage). The centre of the image is rather uniform but large bright areas are observed on the top-right and  
6 bottom left of the image. The PL intensity map shows large regions of higher PL intensity and some smaller features with lower  
7 PL intensity, which are not clearly seen on the microscopy image. The photocurrent map also reveals large variations in  
8 photocurrent, which do not clearly correlate with the PL map or microscopy image (higher resolution maps at three different  
9 locations are shown in Figure S8 in SI). In fact, on the contrary to both one-step devices for which the observed features are only  
10 related to infiltration mechanisms, the two-step device is more complex and has several types of features/defects across the mapped  
11 area with various PL/photocurrent correlations. Indeed, PbI<sub>2</sub> is first infiltrated within the structure which means that variations in  
12 PL and photocurrent might come from incomplete mesopores infiltration by the PbI<sub>2</sub> solution and/or non-uniform PbI<sub>2</sub> nucleation.  
13 Then, as PbI<sub>2</sub> reacts with MAI, another type of non-uniformity could originate from PbI<sub>2</sub> not being fully converted to MAPbI<sub>3</sub>  
14 during the dipping process. This is likely to happen considering the relatively thick layer stack (especially as the active perovskite  
15 is in the mp-TiO<sub>2</sub>, which means that MAI needs to infiltrate deep in the layer stack). In Figure 4b, high-resolution maps were taken  
16 around a feature having lower PL intensity, higher photocurrent and higher EL intensity. This feature is not representative of all  
17 features observed on the large map because several types of defects are formed for this sample but is interesting as it shows  
18 properties not observed for both one-step devices. This correlation can be ascribed to better charge quenching and injection at the  
19 interface but as the TiO<sub>2</sub> Raman map is rather uniform for the entire mapped area, it means that the observed feature is not due to  
20 infiltration inhomogeneity and should be explained by a different mechanism. In a previous work, we have shown that a very thin  
21 PbI<sub>2</sub> film can passivate the interface between the perovskite and extraction layers, which helps to extract charges and results in  
22 slightly higher photocurrent.<sup>[26]</sup> Here, the observed results can be explained similarly: some PbI<sub>2</sub> may not have fully converted to  
23 MAPbI<sub>3</sub> in the mp-TiO<sub>2</sub> layer close to the c-TiO<sub>2</sub> blocking layer, and could help to extract electrons as long as this residual PbI<sub>2</sub> is  
24 thin enough (too thick PbI<sub>2</sub> would induce higher series resistance and lower photocurrent). Hence, for the two-step device it is  
25 thought that the large variations observed in the PL and photocurrent maps with diverse correlations could be due to several distinct  
26 defects such as poor PbI<sub>2</sub> infiltration, non-uniform nucleation and incomplete conversion of the PbI<sub>2</sub>.



1  
 2 **Figure. 4** High-resolution multi-mapping of mesoscopic solar cells fabricated from two-step MAPbI<sub>3</sub> solution process. (a) 500 x  
 3 500 μm optical microscopic image, PL peak intensity, PL peak position, PL FWHM and photocurrent maps (measured with 1.5  
 4 μW laser power). (b) 20 x 20 μm optical image, PL peak intensity, PL peak position, PL FWHM, photocurrent (measured with 0.3  
 5 μW laser power), electroluminescence intensity and Raman TiO<sub>2</sub> peak intensity maps measured across a typical feature. Raman  
 6 single point spectra between 100 cm<sup>-1</sup> and 400 cm<sup>-1</sup> measured on and off the feature are also shown.

### 7 Cross-sectional scanning electron microscopy

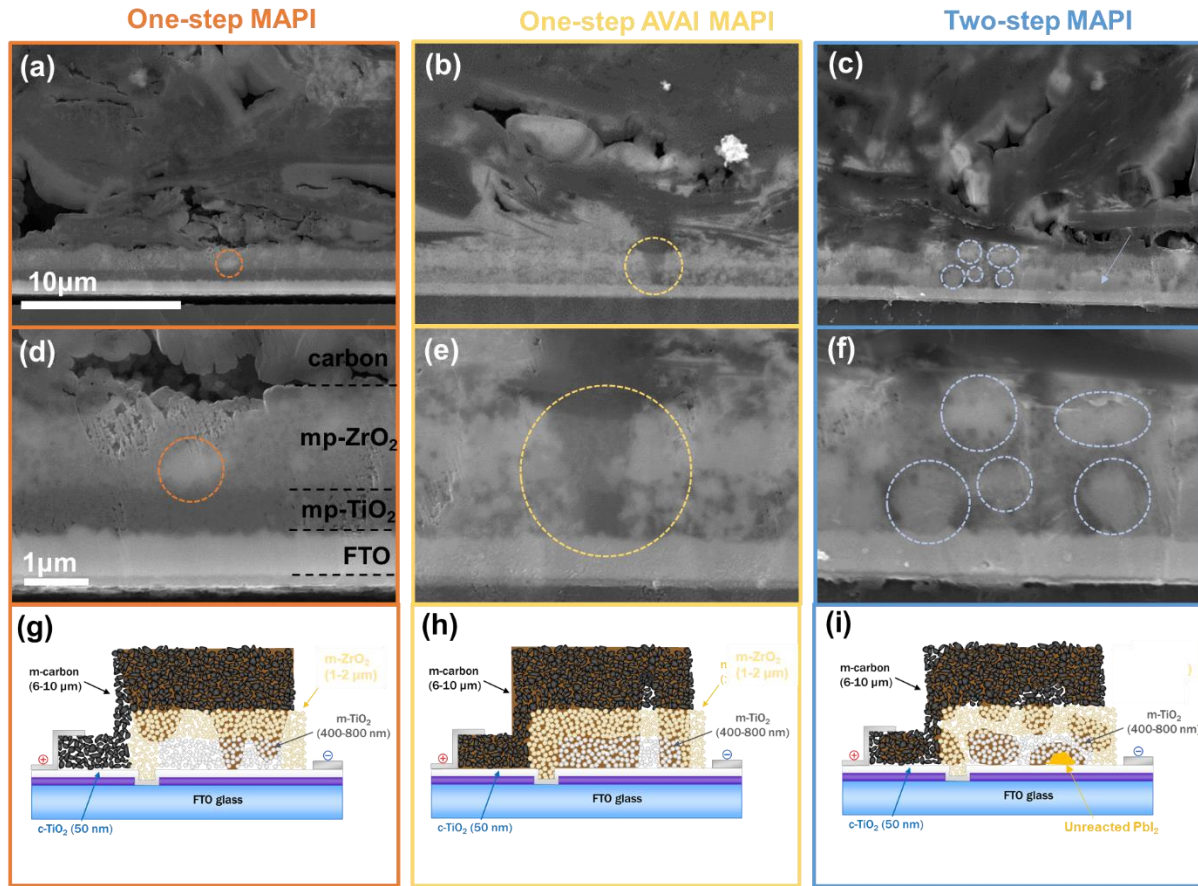
8 Cross-sectional scanning electron images for the three types of devices are presented in Figure 5a-g. This technique is  
 9 complimentary to the high-resolution maps as it shows the infiltration of perovskite not only close to the mp-TiO<sub>2</sub> interface but in  
 10 the entire depth of the mesoporous structure. Low and high magnification cross-sectional images of the one-step MAPbI<sub>3</sub> cell are  
 11 shown in Figure 5a and d, respectively. Elements with higher Z values have lower penetration of the secondary electrons (SE) and  
 12 an increased signal count. This results in an increased SE signal from the Pb-containing phases and eventually brighter appearing  
 13 areas, which allows the identification of infiltrated areas with higher perovskite concentrations in the mesoporous stack. The layer  
 14 stack FTO/mp-TiO<sub>2</sub>/mp-ZrO<sub>2</sub>/carbon is clearly observed and shows very poor perovskite infiltration for the one-step MAPbI<sub>3</sub>  
 15 device. In fact, perovskite can only be seen in a small portion of the ZrO<sub>2</sub> layer (indicated by the orange circle). These observations  
 16 do not imply that perovskite was not infiltrated in the mp-TiO<sub>2</sub> layer in some parts of the device, as observed in Figure 2, but there  
 17 is little chance to cut the sample exactly at these infiltrated areas and observe them on the cross-section. On the contrary, for the  
 18 one-step AVAI-MAPbI<sub>3</sub> cell shown in Figure 5b and e, most of the mp-TiO<sub>2</sub> and mp-ZrO<sub>2</sub> layers are homogeneously infiltrated by  
 19 the perovskite solution, in good agreement with the multi-mapping results. However, a “trench” is visible where the perovskite

1 didn't infiltrate the mesoporous layers. The fact that perovskite is also missing in the carbon layer just on top of the trench reveals  
2 that a dense carbon flake prevented the perovskite from infiltrating in the layer stack. Energy dispersive spectroscopy (EDS)  
3 mapping was realized on a selected area of the cross-section around one larger trench as shown in Figure S9 (some trenches can be  
4 up to 10  $\mu\text{m}$  in width, which correlates well with the maps in Figure 3b). As perovskite is identified by its Pb and I elements, it is  
5 clear that the perovskite is significantly reduced within the depth of the trench from the carbon to the mp-TiO<sub>2</sub> layer as Pb and I  
6 elements are much less present in the trench. The EDS mapping also indicates a higher carbon content just on top of the trench  
7 which confirms that a denser carbon flake is present and hinder perovskite infiltration.

8 The two-step device shown in Figure 5c and f has a more complex morphology. Here, both the mp-TiO<sub>2</sub> and mp-ZrO<sub>2</sub> layers are  
9 relatively well infiltrated with perovskite but it can be observed that perovskite doesn't form a continuous film, on the contrary to  
10 the one-step AVAI-MAPbI<sub>3</sub> cell. Instead, distinct perovskite grains are visible either in the mp-TiO<sub>2</sub> or mp-ZrO<sub>2</sub> layer (as indicated  
11 by the blue circles). This peculiar morphology is in excellent agreement with recent work which details the nucleation and growth  
12 mechanisms of sequential deposition, explained as follow:<sup>[27],[28]</sup> after the first infiltration step, PbI<sub>2</sub> forms a partly amorphous PbI<sub>2</sub>  
13 film with crystalline clusters having preferential (001) orientation along the substrate surface. Upon dipping into MAI, amorphous  
14 PbI<sub>2</sub> is transported to add to the crystalline clusters leaving areas devoid of PbI<sub>2</sub> around the clusters. Besides, due to Ostwald  
15 ripening, clusters of small size merge with the large clusters which grow further and convert to MAPbI<sub>3</sub>, starting from the surface  
16 of the clusters. This process results in localised crystals of MAPbI<sub>3</sub> with significantly reduced perovskite concentrations in the  
17 surrounding mesoporous lattice, which explains the discontinuous appearance of the MAPbI<sub>3</sub> film for the two-step device. From  
18 Figure 5c, it can also be seen some areas in the mp-TiO<sub>2</sub> which have more continuous MAPbI<sub>3</sub> film (indicated by blue arrow), while  
19 the ZrO<sub>2</sub> layer on top is depleted in MAPbI<sub>3</sub>. It is thought that PbI<sub>2</sub> clusters nucleate first at the bottom of the mesoporous structure,  
20 in contact with the c-TiO<sub>2</sub> blocking layer, and form PbI<sub>2</sub> platelets orientated along the substrate surface. As amorphous PbI<sub>2</sub> in the  
21 mp-ZrO<sub>2</sub> is transported to crystalline clusters in the mp-TiO<sub>2</sub>, it leaves an empty space in the ZrO<sub>2</sub> mesoporous layer where MAPbI<sub>3</sub>  
22 do not form. Finally, the presence of non-reacted PbI<sub>2</sub> at the bottom of the mp-TiO<sub>2</sub> layer cannot be unambiguously confirmed  
23 using EDS owing to the contribution from the perovskite to the EDS signal that could be detected using EDS. However, as MAI  
24 reacts preferentially at the surface of the PbI<sub>2</sub> clusters, it forms a compact MAPbI<sub>3</sub> layer which denies the MAI solution access to  
25 the underlying PbI<sub>2</sub> for conversion. This is then more likely that unreacted crystalline PbI<sub>2</sub> can be trapped at the bottom of the mp-  
26 TiO<sub>2</sub> layer, as explained by Ummadisingu and Grätzel in other work.<sup>[27]</sup>

27 The SEM cross-sectional observations are in excellent agreement with the results obtained with the mapping techniques and show  
28 dramatic differences in terms of perovskite infiltration, homogeneity and morphology, which are summarized in Figure 5g-i. It is  
29 clear that the one-step MAPbI<sub>3</sub> cell suffers from poor perovskite infiltration in the mesoporous structure, where only micrometre-  
30 sized areas are infiltrated all the way until the c-TiO<sub>2</sub> interface, which explains the very poor efficiency measured for this cell. On  
31 the contrary, the one-step AVAI-MAPbI<sub>3</sub> cell displays a highly uniform perovskite film in the mp-TiO<sub>2</sub> layer due to proper  
32 infiltration through the entire structure. This is consistent with results from Mei et al. who observed much denser filling of the TiO<sub>2</sub>  
33 pores with AVAI- MAPbI<sub>3</sub> as compared to MAPbI<sub>3</sub>.<sup>[1]</sup> This was explained by a templating action of the AVAI which affects the  
34 perovskite crystal nucleation and growth within the mesoporous TiO<sub>2</sub> scaffold. However, it is observed here that dense carbon  
35 flakes can prevent perovskite infiltration in some areas, which could affect light collection in these regions. Hence, it is thought  
36 that device fabrication process could be optimized to avoid such effect. The perovskite solution could be infiltrated directly in the  
37 mp-ZrO<sub>2</sub> and mp-TiO<sub>2</sub> layers without carbon, before depositing a top electrode at low temperature (using graphene for example).  
38 The mesoporous carbon layer formulation could also be modified to obtain a more uniform layer and avoid the formation of dense  
39 flakes. For the case of the two-step MAPbI<sub>3</sub> cell, the morphology of the perovskite layer is more complex. It is clear from the  
40 mapping correlations that several types of features are present with either beneficial or detrimental effects on the photocurrent. It

1 is thought that the mechanisms of sequential deposition should be better controlled to obtain more uniform nucleation of  $\text{PbI}_2$   
 2 clusters in the mp- $\text{TiO}_2$  and consecutive  $\text{MAPbI}_3$  growth.



3  
 4 **Figure. 5** High and low magnification cross-sectional secondary electron microscopy images of mesoscopic perovskite solar cells  
 5 based on (a, d) one-step  $\text{MAPbI}_3$ , (b, e) one-step AVAI- $\text{MAPbI}_3$  and (c, f) two-step  $\text{MAPbI}_3$ . Cartoon showing mesoscopic  
 6 perovskite solar cell structure and perovskite infiltration using (g) one-step  $\text{MAPbI}_3$ , (h) one-step AVAI- $\text{MAPbI}_3$  or (i) two-step  
 7  $\text{MAPbI}_3$  processes.

## 8 CONCLUSIONS

9 Combining high-resolution photoluminescence, electroluminescence, Raman and photocurrent mapping on the same area with  
 10 cross-sectional SEM measurements, this study provides unprecedented insights into infiltration mechanisms and electronic  
 11 transport properties in mesoscopic perovskite solar cells. We have demonstrated that when using one-step deposition process, 5-  
 12 ammonium valeric acid (AVAI) is key to induce better pore filling in the mesoporous structure. Without AVAI, only around 4%  
 13 of the cell's area is fully infiltrated and provides efficient electronic coupling with the  $\text{TiO}_2$  extraction layer, which explains the  
 14 poor device short-circuit current in this case. When AVAI is used, around 98% of the cell's area is effective in delivering  
 15 photocurrent, but dense microscale carbon flakes still prevent perovskite infiltration in some areas and induce current losses. Quite  
 16 differently, when using a two-step deposition process, a complex perovskite morphology is observed with isolated grains separated  
 17 by areas of low perovskite concentration, which forms a discontinuous network. This is ascribed to the intercalation of MAI between

1 crystalline  $\text{PbI}_2$  clusters, and then structural reorganisation into  $\text{MAPbI}_3$ . It is thought that small amount of non-reacted  $\text{PbI}_2$  is  
2 more likely to remain at the interface with the c- $\text{TiO}_2$  blocking layer which could improve photocurrent extraction at this interface.  
3 These results motivate further work to achieve better infiltration and homogeneity of the perovskite film in mesoporous devices.  
4 Besides, our results provide key insights that could also be applied to characterize devices with planar structure. Although  
5 infiltration mechanisms are not an issue for planar devices, variations in electronic contact at interfaces could be monitored using  
6 these multi-mapping techniques. This would allow to develop high-quality contacts that can extract photogenerated carriers more  
7 efficiently.

## 8 **METHODS AND EXPERIMENTAL SECTION**

### 9 **Cell preparation and testing**

10 FTO glass substrates (TEC7, XOP) were etched using a Rofin Nd:YVO4 laser (532 nm, speed of 150  $\text{mm}\cdot\text{s}^{-1}$ ), cleaned with  
11 Hellmanex solution in deionised water, washed with deionised water and rinsed in acetone and isopropanol, before being  $\text{O}_2$  plasma  
12 treated. A 50 nm-thick compact  $\text{TiO}_2$  layer was deposited via spray pyrolysis at 300°C from a solution of 10% titanium di-  
13 isopropoxide bis(acetylacetonate) (Sigma) in isopropanol. The mesoporous triple stack was obtained via screen printing of  
14 commercial pastes: first, the  $\text{TiO}_2$  layer (30 NRD Dyesol, diluted 1:1 by weight with terpineol), followed by sintering at 550°C for  
15 30 minutes; then the  $\text{ZrO}_2$  layer (ZT/SP Solaronix), sintered at 400°C for 30 minutes; finally, the carbon layer (Gwent Electronic  
16 Materials), sintered at 400°C for 30 minutes, as previously reported.<sup>[16],[13]</sup>

17 One-step  $\text{MAPbI}_3$ : an equimolar (0.952 M) solution of  $\text{PbI}_2$  (TCI Chemicals) and MAI (Dyesol) in GBL (Sigma) was prepared  
18 and stirred at 70°C until completely dissolved.<sup>[12]</sup> It was then infiltrated by drop casting onto the carbon electrode, left at room  
19 temperature for 10 min, then annealed in a fan oven at 50°C for 1 h.

20 One-step AVAI-  $\text{MAPbI}_3$ : The same 0.952 M solution of  $\text{PbI}_2$  and MAI in GBL was prepared and 5-ammonium valeric acid iodide  
21 (5-AVAI, Dyesol) was added to it in a 3% molar ratio between 5-AVAI and MAI. As for one-step  $\text{MAPbI}_3$ , the solution was drop  
22 casted, and the devices left at room temperature for 10 min before being annealed in a fan oven at 50°C for 1 h.

23 Two-step  $\text{MAPbI}_3$ : a 1.2 M  $\text{PbI}_2$  solution dissolved in N,N-dimethylformamide (DMF) at 70°C was used to infiltrate the  
24 mesoporous stack kept at 70°C on a hot plate; after 30 minutes, the cells were cooled down to RT and immersed in a 10 mg/ml  
25 MAI solution in IPA for 30 min at room temperature and then annealed for 10 min in a fan oven at 100°C.<sup>[18]</sup>

26 Silver paint was applied to the contacts prior to measurements and the 1  $\text{cm}^2$  active area was masked to 0.49  $\text{cm}^2$  using laser-cut  
27 black adhesive masks. Current density - voltage (JV) measurements were carried out using a class AAA solar simulator (Newport  
28 Oriel Sol3A) under 1 sun illumination conditions, calibrated against a KG5 filtered silicon reference cell (Newport Oriel 91150-  
29 KG5), and a Keithley 2400 source meter. The devices were scanned from  $V_{oc}$  to  $J_{sc}$  and *vice versa* at a scan rate of 130  $\text{mV}\cdot\text{s}^{-1}$ .

### 30 **High-resolution multi-mapping**

31 Multi-mapping measurements were carried out using a Renishaw InVia confocal Raman microscope in backscattering  
32 configuration by measuring the samples through the glass substrates. All measurements were performed under nitrogen atmosphere  
33 in an electrical chamber (LTS420E, Linkam Scientific Instrument) mounted directly to a X-Y scanning stage (100 nm minimum  
34 step size). Utilising the scanning stage, maps are produced with individual spectra at each region. All measurements were conducted  
35 with a 50x objective lens (NA = 0.50). For Photoluminescence, photocurrent and Raman maps, a 532 nm laser excitation source  
36 was used (spot size  $\approx$  1  $\mu\text{m}$ ). PL and photocurrent (laser beam-induced current) data were acquired simultaneously at short circuit:

1 excitation parameters of 1.5  $\mu\text{W}$  laser power ( $1.5 \times 10^5 \text{ mW.cm}^{-2}$ ) and 50 ms were used for the large photoluminescence-  
2 photocurrent maps ( $500 \times 500 \mu\text{m}$ ), whereas 0.3  $\mu\text{W}$  laser power ( $3 \times 10^4 \text{ mW.cm}^{-2}$ ) and 100 ms acquisition time were used for the  
3 high-resolution maps ( $20 \times 20 \mu\text{m}$ ). To acquire the photocurrent, the device electrodes were connected to a lock-in amplifier  
4 (Stanford Research SR830) with a chopper cutting the laser beam at 134 Hz. Raman spectra were acquired using a laser power of  
5 0.3 mW with an acquisition time of 5 s, whilst individual spectra were acquired in 10 seconds. A source-meter unit (Keithley 236)  
6 was used to apply an electrical bias for electroluminescence maps. A bias voltage of 3 V to 5 V and acquisition time of 5 s to 10 s  
7 were used to obtain sufficient signal-to-noise ratios. Due to ion migration effect during the EL measurements, 200 seconds were  
8 left following the application of the electrical bias before the mapping was started to allow the current to reach equilibrium.

### 9 **Scanning electron microscopy**

10 Cross sections were prepared after glass cutting using a Hitachi IM4000 Plus Ar broad beam ion miller with a probe current of 4kV  
11 for 1.5 hours. Samples were mounted onto a conductive holder and coated in 5nm Pt to provide conductivity for the glass substrate.  
12 Imaging was undertaken on a Jeol JSM-7800F Field Emission SEM at 15kV using secondary electron imaging, with EDS detector  
13 from Oxford Instruments.

## 14 15 **SUPPORTING INFORMATION**

16 Available: carrier generation profile at 532 nm, Schematic carrier dynamic processes in regions of bad and good electronic  
17 contact with mp-TiO<sub>2</sub>, PL and Raman maps of an empty mp-TiO<sub>2</sub>/mp-ZrO<sub>2</sub>/mp-carbon stack (before perovskite infiltration),  
18 contrasted optical images for the one-step MAPbI<sub>3</sub> and one-step AVAI-MAPbI<sub>3</sub> C-PSCs, optical microscopy image, PL intensity  
19 and photocurrent maps of the two-step MAPbI<sub>3</sub> cell taken at 3 different regions, SEM-EDS cross-sectional maps of a one-step  
20 AVAI-MAPbI<sub>3</sub> mesoscopic perovskite solar cell. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### 24 **Author Contributions**

25 The manuscript was written through contributions of all authors. All authors have given approval to the final version of the  
26 manuscript.

## 27 **CONFLICTS OF INTEREST**

28 There are no conflicts to declare.

## 29 **ACKNOWLEDGEMENTS**

1 We would like to acknowledge Renishaw plc, the M2A funding from the European Social Fund through the Welsh Government,  
2 Supergen Solar Challenge (EP/M025020/1), the assistance provided by the Swansea University College of Engineering AIM  
3 facility, which was funded in part by the EPSRC (EP/M028267/1), the European Regional Development Fund through the Welsh  
4 Government (80708) and the Ser Solar project via Welsh Government.

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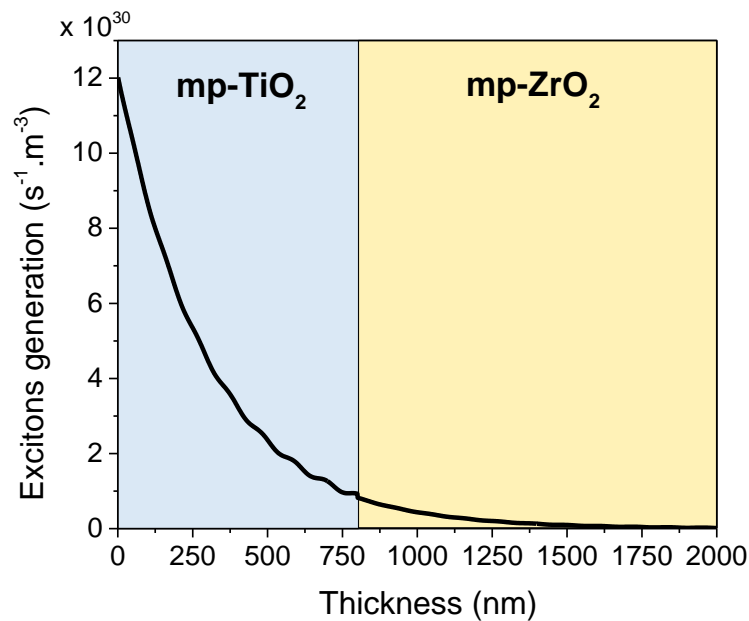


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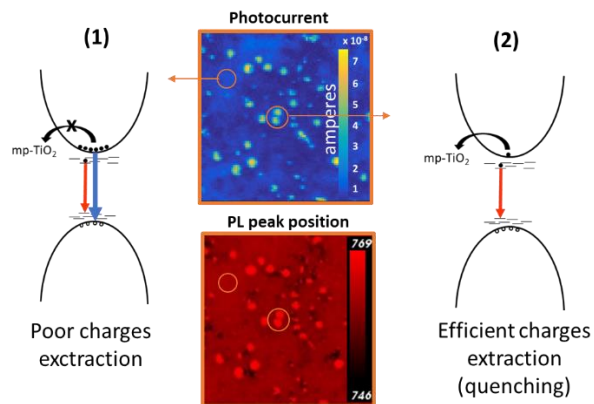
## Supporting Information



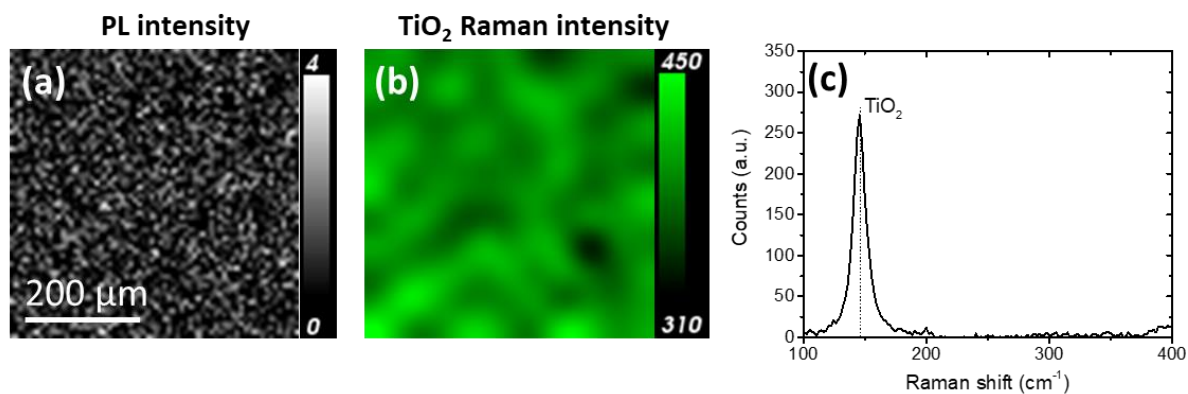
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11 **Figure. S1** Carrier generation profile at 532 nm in perovskite infiltrated in mp-TiO<sub>2</sub>/mp-ZrO<sub>2</sub> layers (assuming full infiltration  
12 and using a laser power of  $1.5 \times 10^5$  mW.cm<sup>-2</sup>).

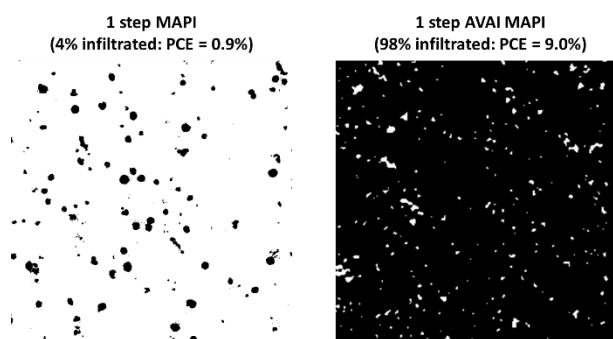
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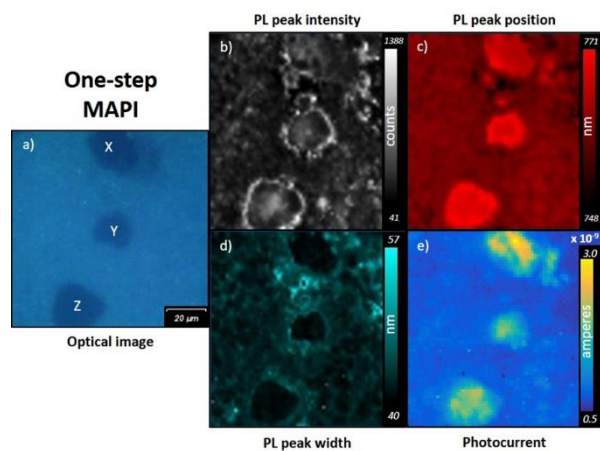
1  
2 **Figure. S2** Schematic carrier dynamic processes in (1) regions of bad electronic contact and (2) regions of good electronic contact  
3 with mp-TiO<sub>2</sub> ETL.



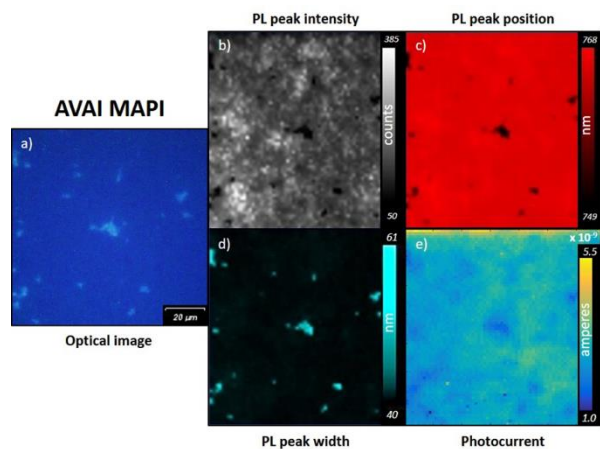
4  
5 **Figure. S3** 200 x 200 um maps of an empty mp-TiO<sub>2</sub>/mp-ZrO<sub>2</sub>/mp-carbon stack (before perovskite infiltration). (a) PL intensity  
6 at 775 nm, (b) TiO<sub>2</sub> Raman intensity at 144 cm<sup>-1</sup>, (c) typical Raman spectrum.



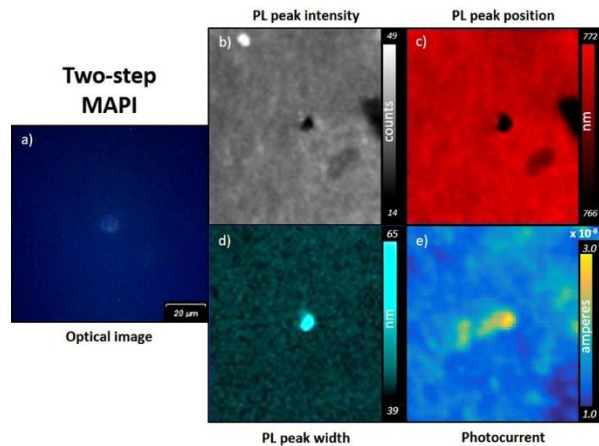
7  
8 **Figure. S4** Binary image of optical images shown in Figure 1a and 2a for the one-step MAPbI<sub>3</sub> and one-step AVAI-MAPbI<sub>3</sub> C-  
9 PSCs, respectively. The infiltrated areas shown in black represent 4% and 98% of the entire surface for the one-step MAPbI<sub>3</sub> and  
10 AVAI-MAPbI<sub>3</sub>, respectively.



1  
 2 **Figure. S5** a) 100 x 100 μm optical micrograph of a one-step MAPI device. b) PL peak intensity map (0.1 s acquisition time, 0.3  
 3 μW laser power, 1.5 μm step size). c) PL peak position. d) PL peak width. e) Photocurrent map displaying an increase in photo-  
 4 generated current over X, Y and Z regions.

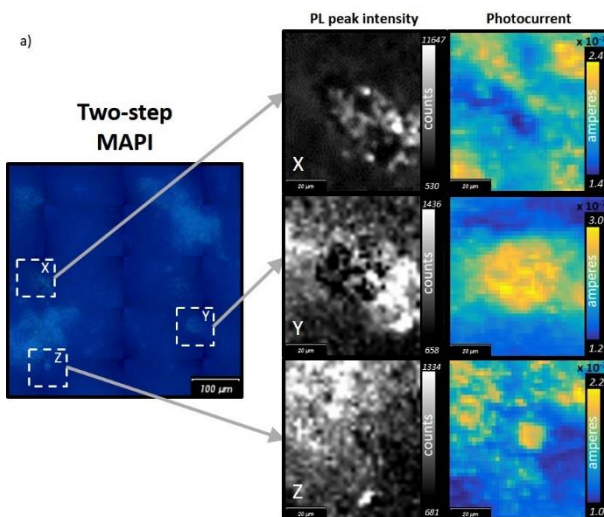


5  
 6 **Figure. S6** a) 100 x 100 μm optical micrograph of a cluster of defects on the one-step AVAI MAPI mesoporous carbon perovskite  
 7 device. b) PL peak intensity map (0.1 s acquisition time, 0.3 μW laser power, 1.5 μm step size). c) PL peak position. d) PL peak  
 8 width. e) Photocurrent.



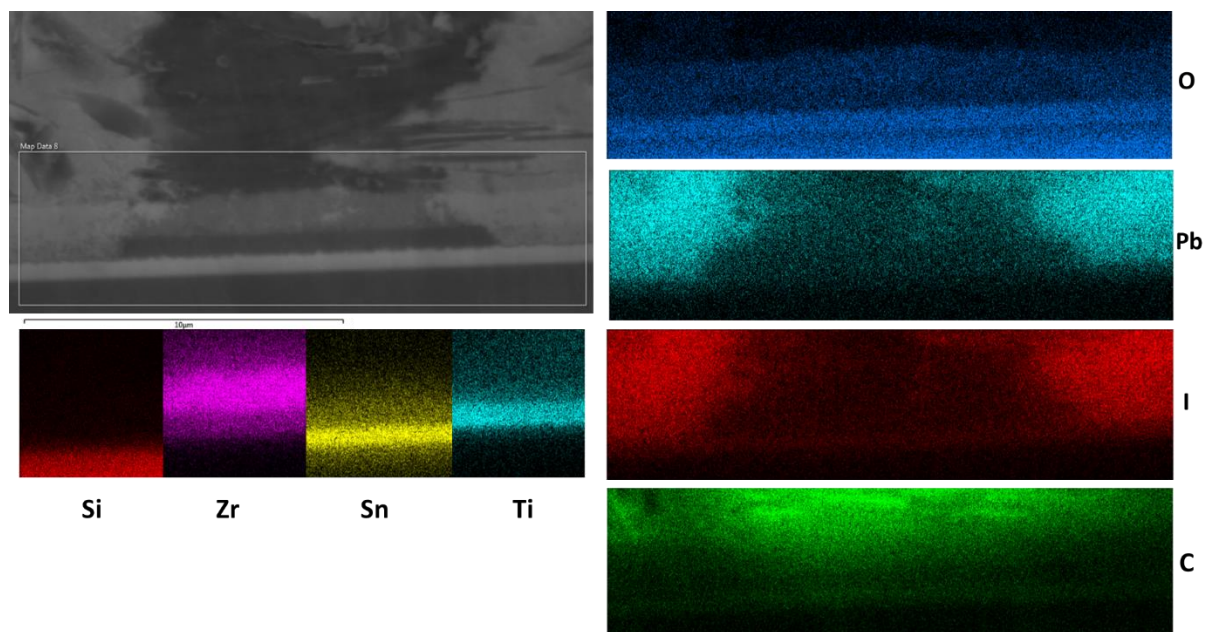
1  
 2 **Figure. S7** a) 100 x 100 μm optical micrograph of a defect found on the two-step mesoporous carbon perovskite device. b) PL  
 3 peak intensity map (0.1 s acquisition time, 0.3 μW laser power, 1.5 μm step size). c) PL peak position. d) PL peak width. e)  
 4 Photocurrent.

5



6  
 7 **Figure. S8** 500 x 500 μm optical microscopy image of the two-step MAPbI<sub>3</sub> cell and higher resolution 80x80 μm PL intensity and  
 8 photocurrent maps taken at 3 different regions showing various PL intensity/photocurrent correlations.

9



1  
 2 **Figure. S9** SEM-EDS cross-sectional maps of a one-step AVAI-MAPbI<sub>3</sub> mesoscopic perovskite solar cell. Each layer can be  
 3 identified by its primary element (C, Zr, Ti, Sn and Si) while the infiltrated MAPbI<sub>3</sub> is identified by Pb and I elements. It can be  
 4 seen that a large carbon flake induces a significant reduction in Pb and I below it, indicating poor perovskite infiltration.