



Cite this: *Energy Environ. Sci.*,  
2016, 9, 2286

Received 14th February 2016,  
Accepted 25th May 2016

DOI: 10.1039/c6ee00462h

www.rsc.org/ees

## Quantification of spatial inhomogeneity in perovskite solar cells by hyperspectral luminescence imaging†

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Vacuum evaporated perovskite solar cells with a power conversion efficiency of 15% have been characterized using hyperspectral luminescence imaging. Hyperspectral luminescence imaging is a novel technique that offers spectrally resolved photoluminescence and electroluminescence maps (spatial resolution is 2 micrometer) on an absolute scale. This allows, using the generalized Planck's law, the construction of absolute maps of the depth-averaged quasi-Fermi level splitting ( $\Delta\mu$ ), which determines the maximum achievable open circuit voltage ( $V_{oc}$ ) of the solar cells. In a similar way, using the generalized reciprocity relations the charge transfer efficiency of the cells can be obtained from the hyperspectral images. Very strong inhomogeneity, both in quasi-Fermi level splitting ( $\Delta\mu$ ) and in charge transfer efficiency, are found in these vacuum deposited perovskite solar cells. This implies that these efficient solar cells are still far from perfect as many areas in the device do not or only partially participate in the photon to electron conversion processes.

Photovoltaic devices based on hybrid organic–inorganic perovskites have attracted great attention due to the rapid evolution of their power conversion efficiencies.<sup>1–12</sup> By far the most efficient architectures have been prepared using a solution processed perovskite absorber, yet efficient solar cells using an evaporated perovskite layer have also been demonstrated.<sup>13–15</sup> It has become clear that not necessarily the preparation method but the perovskite grain size has a strong effect on the overall performance of the solar cells.<sup>16</sup> Indeed the carrier diffusion

### Broader context

High efficiency solar cells employing inexpensive hybrid perovskite absorbers have been widely studied as a potential future energy source. Investigation of the PL and EL properties of perovskites is a valuable tool to unveil their properties and limitations. Interestingly, many studies have highlighted a rather inhomogeneous spatial distribution of the luminescence, in contrast to the very high efficiencies reported. Most of those studies used local excitation at very high intensity and, importantly, the luminescence has been observed only qualitatively. In this study, we use hyperspectral luminescence imaging to study planar p–i–n solar cells employing vacuum deposited  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite absorbers. Through this technique, it is possible to quantify the number of photons emitted from every point of the device at every wavelength. We investigated spatial fluctuations from a few microns to the millimeter scale and show that both photo- and electroluminescence are spatially not uniform, leading to a distribution of the quasi-Fermi level splitting which strongly depends on the position in the device. We also map the carrier transport efficiency, finding areas where the photogenerated carrier collection efficiency is lower than 60%. We show that this inefficient charge collection is most likely due to interfacial resistance fluctuations. This work is relevant for perovskite and organic based opto-electronic devices.

length can be drastically enhanced to over 100  $\mu\text{m}$  when single crystals are obtained, thanks to a reduction in the density of trap states.<sup>17,18</sup> Even polycrystalline hybrid perovskite semiconductors are characterized by large and balanced charge diffusion lengths,<sup>19,20</sup> a consequence of the very low non-radiative recombination rates.<sup>21,22</sup> In an ideal case, charge recombination in a photovoltaic material should be purely radiative, since the same transitions involved in photoluminescence (PL) and electroluminescence (EL) are also responsible for light absorption. Recently, it was shown independently by two groups that perovskite solar cells obey the reciprocity relation as formulated by Rau,<sup>23</sup> which describes the equilibrium between absorption and emission of a single direct band gap semiconductor. Such a relationship implies that one can predict the photovoltage by measuring the external quantum efficiency (EQE) for EL and from the photocurrent generation efficiency.<sup>24,25</sup> The radiative efficiency for perovskite

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ee00462h

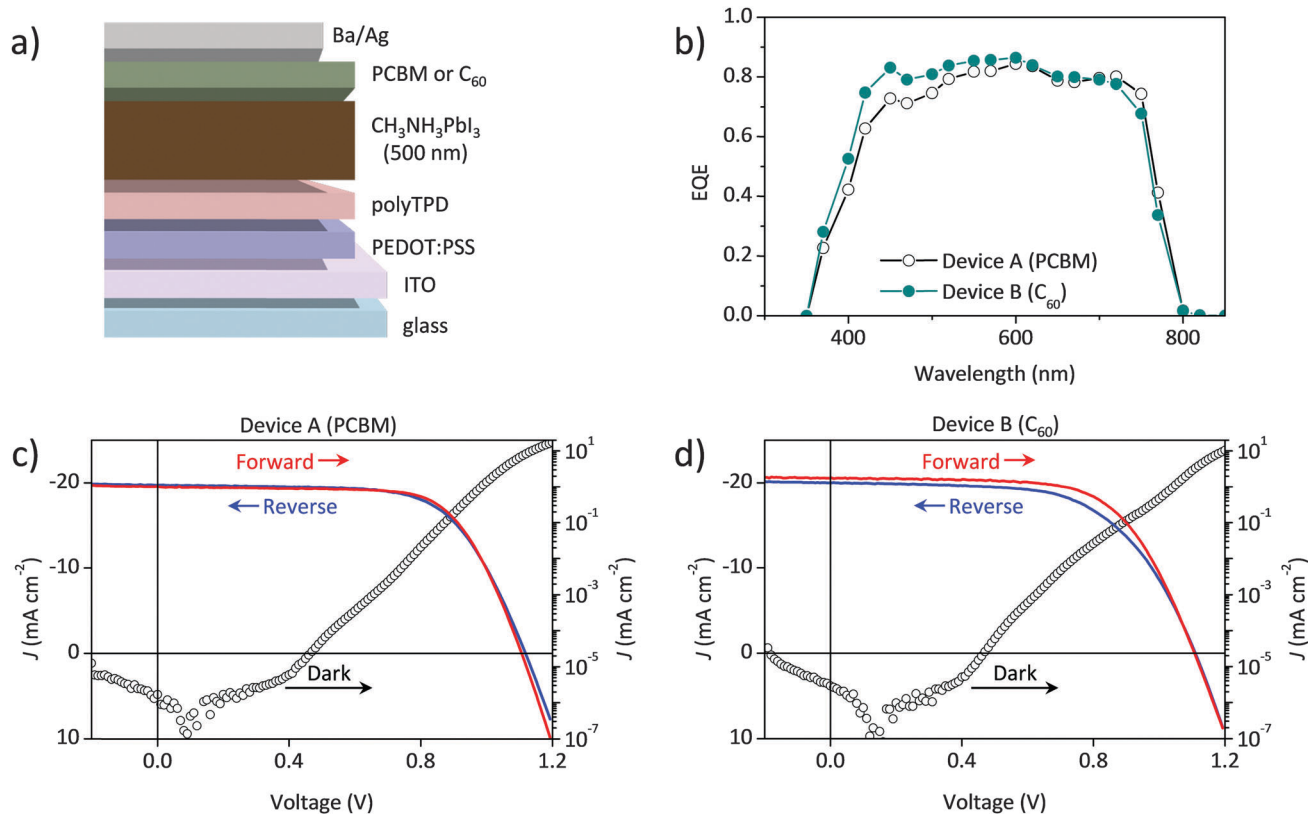
solar cells was found to be higher compared to inorganic materials such as amorphous silicon or cadmium telluride, and only slightly lower compared to Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells.<sup>24</sup> This is one of the reasons behind the generally high open circuit voltage ( $V_{oc}$ ) observed in methylammonium lead iodide (MAPbI<sub>3</sub>) based cells (1.0–1.1 V), in view of its bandgap of approximately 1.6 eV. Recently, by correlating confocal microscopy with scanning electron microscopy, the spatial variation of the photoluminescence (PL) intensity and lifetime, over different grain sizes and boundaries, has been reported.<sup>26</sup> Interestingly, substantial inhomogeneity in the PL mapping was observed, meaning that even efficient perovskite solar cells still contain regions with non-radiative recombination. In another study, the spatially resolved electronic excited-state dynamics have been observed by means of femto-second transient absorption spectroscopy coupled to an optical microscope.<sup>27</sup> The excited state relaxation was found to be very dependent on the location in the device, hence confirming the presence of substantial inhomogeneity over a large length scale. Very recently, EL and PL images were shown to have a good potential for studying spatial inhomogeneities at the millimeter scale, where the local series resistance can fluctuate.<sup>28</sup> These and other recent investigations<sup>29–34</sup> have highlighted the need for a spatially resolved analysis of the physical properties governing the photovoltaic behavior of perovskite solar cells. In particular, the correlation between the spatial variation of a certain physical quantity and the materials morphology will help in identifying strategies to improve the overall device performance.

Hyperspectral imaging of luminescence is a novel technique that offers spectrally resolved PL and EL maps of semiconductor devices, and has been recently applied in the characterization of GaAs,<sup>35,36</sup> silicon,<sup>37,38</sup> Cu(In,Ga)Se<sub>2</sub>,<sup>39</sup> multi-quantum wells and quantum dot solar cells.<sup>40</sup> A unique feature of this technique is the possibility of quantitatively measuring the luminescence flux.<sup>35,36</sup> Hyperspectral imaging, operating under uniform illumination of the device, allows the characterization of the cell in a state close to the operation conditions, and was found to be free from a variety of artefacts occurring from analysis in a confocal configuration.<sup>39</sup> Local excitation systems have several major limitations that are surpassed by hyperspectral imaging. First of all the luminescence intensity is only available in arbitrary units; additionally all the optoelectronic parameters that are deduced from local excitation maps are altered by lateral carrier diffusion in the proximity of the excitation spot. Finally, the PL mapping alone provides insights solely into the active material, while the EL analysis gives important and complementary information on the electrical characteristics of the device. Within this perspective, hyperspectral imaging combines both methods in a quantitative manner. From the hyperspectral PL imaging and by using the generalized Planck's law, one can obtain absolute maps of the depth-averaged quasi-Fermi level splitting ( $\Delta\mu$ ), which determines the maximum achievable open circuit voltage ( $V_{oc}$ ) of the solar cell.<sup>41–44</sup> Careful comparison with electrical measurements showed a consistent agreement between  $\Delta\mu$  and  $V_{oc}$  on a variety of devices, within 20 meV.<sup>41–44</sup> On the other hand, by applying Rau's reciprocity relations on the hyperspectral EL maps, the spatial distribution of the photovoltage can be obtained.<sup>45</sup>

Furthermore, the application of the generalized reciprocity relations allows us to obtain maps of the charge carrier transport efficiency.<sup>46</sup>

In this manuscript, state-of-the-art p–i–n perovskite solar cells are analyzed by hyperspectral luminescence imaging. We investigated spatial fluctuations from a few microns to the millimeter scale and compare samples having different hole blocking layers to understand the role of the front contact. To go further in the analysis we applied three different theories describing the luminescence emission, *i.e.* spatially resolved absolute quasi-Fermi level splitting from PL, from EL, as well as the carrier collection efficiency. We show that both photo- and electroluminescence are spatially not uniform, leading to a distribution of the quasi-Fermi level splitting which strongly depends on the position in the device. Interestingly, only small deviations from the measured global  $V_{oc}$  are observed, which we ascribe to the small hysteresis observed in these solar cells. On the other hand, we also quantify and map the device spatial inhomogeneity by calculating the carrier transport efficiency. Surprisingly, we found small, yet non-negligible areas where the photogenerated carrier collection efficiency is lower than 60%. We show that this inefficient charge collection is most likely due to interfacial resistance fluctuations. Therefore, the performance of perovskite solar cells can be significantly improved by engineering the charge extraction and energy bands of the charge selective layers rather than by improving the quality of the perovskite absorber.

The architecture for the perovskite solar cells used in this study (Fig. 1a) consists of an indium tin oxide (ITO) coated glass slide, covered with a 80 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) layer and a thin (20 nm) poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (polyTPD) film acting as the electron blocking layer. On top of this, the MAPbI<sub>3</sub> perovskite was thermally evaporated to a thickness of 500 nm using a previously described protocol.<sup>14</sup> Subsequently, a fullerene hole blocking layer was deposited on top of the perovskite absorber. In this study, we compared the behavior of a device with a solution processed [6,6]-phenyl C<sub>61</sub>-butyric acid methylester (PCBM, 40 nm) film (device A) with that of one employing an evaporated C<sub>60</sub> layer (also 40 nm, device B). The devices were completed with the evaporation of a Ba (10 nm) top electrode capped with Ag (100 nm). Details of the device preparation can be found in the Experimental section. Four cells were evaluated for each device configuration, showing virtually no difference in the observed performance. The EQE of both devices (Fig. 1b) is rather constant over the whole visible spectra, with a maximum of 85% at 600 nm, and shows the typical onset at 770 nm, corresponding to the perovskite band-to-band edge absorption. The current density ( $J$ ) vs. voltage ( $V$ ) characteristics under dark and 1 Sun illumination are shown in Fig. 1c and d, and the corresponding extracted key device parameters are reported in Table 1. As expected from the EQE, the short circuit current densities ( $J_{sc}$ ) are also high (19.90 mA cm<sup>−2</sup> for device A and 20.50 mA cm<sup>−2</sup> for device B), with the main difference between the two devices being the fill factor (FF, 0.687 for device A and 0.646 for device B), a consequence of the



**Fig. 1** (a) Structure schematics of the perovskite cells used. (b) EQE and  $J$ - $V$  characteristics under illumination (lines, left axis) and in the dark (symbols, right axis) for devices employing PCBM (c) and C<sub>60</sub> (d) as the electron transport layer.

**Table 1** Performance parameters for perovskite solar cells as a function of the electron transport layer (ETL) and voltage scan direction

Device, ETL	Scan direction	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	PCE (%)
A, PCBM	Forward	19.90	1109	0.687	15.16
	Reverse	19.72	1106	0.679	14.81
B, C <sub>60</sub>	Forward	20.50	1110	0.646	14.70
	Reverse	20.14	1107	0.615	13.71

Forward scan: from -0.2 V to 1.2 V. Reverse scan: from 1.2 V to -0.2 V. The scan speed was kept constant at 0.35 V s<sup>-1</sup>.

use of different electron transport materials. The measured  $V_{oc}$  was found to be 1109 mV for device A and 1110 mV for device B, resulting in high power conversion efficiencies close to 15% (15.1% for device A and 14.70% for device B). Device A did not exhibit any substantial  $J$ - $V$  hysteresis under the measurement conditions (scan speed of 0.35 V s<sup>-1</sup>), while a weak hysteresis effect was observed for device B. A comparison between the  $J$ - $V$  curves under illumination and in the dark (Fig. 1c and d) suggests that both perovskite solar cells do have carrier collection issues to some extent. This interpretation originates from the relatively low FF for both samples as compared to the good diode characteristics (no evident resistance issues) observed in the dark. These phenomena will be investigated by using hyperspectral luminescence imaging.

The experimental setup consists of a hyperspectral imager coupled to an optical microscope which allows recording spectrally

resolved images with a 2 nm spectral resolution and a 2  $\mu$ m spatial resolution. The perovskite solar cell is homogeneously illuminated with a 532 nm laser, and for the detection of the luminescence images, a visible Si CCD camera is used. The spatial, spectral and absolute calibration procedures of the whole setup are detailed elsewhere.<sup>36</sup>

As mentioned before, the hyperspectral imaging system quantitatively records luminescence maps, allowing the estimation of the quasi-Fermi level splitting ( $\Delta\mu$ ). This is achieved using the generalized Planck's law describing the luminescence spectrum of a material out of equilibrium.<sup>42</sup> By integration over the volume, the emission at a position  $r$  of the surface can be written as:

$$j_r^L(E, r) = A(E, r) \frac{\Omega \cos \theta}{4\pi^3 \hbar^3 c^2} \frac{E^2}{\exp\left(\frac{E - \Delta\mu(r)}{kT}\right) - 1}, \quad (1)$$

where  $A(E, r)$  is the absorption probability of an incident photon on the surface element, equal to its emissivity, by Kirchhoff's law,  $\Omega$  is the solid angle of the emission,  $\theta$  is the angle of the emission relative to the surface normal,  $\hbar$  is Planck's reduced constant,  $c$  is the speed of light,  $E$  is the photon energy and  $kT$  is the thermal energy. According to Rau's reciprocity relations and the generalized Planck's law, the spectral shapes of the EL and PL spectra differ mainly because of a mismatch between the material's absorption  $A(E)$  and its EQE( $E$ ). In our case the spectral shapes of PL and EL are identical (Fig. S6, ESI†), which can only be true if  $A(E)$  is equal to the EQE( $E$ ). Hence, the absorption  $A(E, r)$  can be

approximated by the solar cell EQE( $E$ ), within a factor close to unity. This assumption holds if the highest energy part of the calibrated PL spectra is used to estimate  $\Delta\mu$ . In any case, it only has a weak impact on the  $\Delta\mu$  values whose fluctuations are logarithmically related to luminescence flux and absorption. In fact, a 20% mismatch between  $A(E)$  and EQE( $E$ ) would only induce a variation of about 4 meV in the  $\Delta\mu$ , as calculated from PL measurements following eqn (1). This would still be within the global systematic error ( $\pm 20$  meV) associated with the calculation and mapping of  $\Delta\mu$ , as reported elsewhere.<sup>39</sup> Eqn (1) assumes that  $\Delta\mu$  is constant throughout the semiconductor's depth.<sup>41,42</sup> This assumption is valid in view of the reports on long carrier diffusion lengths for perovskite solar cells, which is found to be larger than the active layer film thickness.<sup>19,20</sup> It is hence likely that traps or interface defects impact the  $\Delta\mu$  throughout all of the depth. Hence, if the Fermi distribution is approximated by a Boltzmann distribution ( $E - \Delta\mu_{\text{eff}} \gg kT$ ), eqn (1) can be re-written as:

$$j_r^{\text{L}}(E, r) = A(E, r) \phi_{\text{bb}}(E, T) \exp\left(\frac{\Delta\mu(r)}{kT}\right), \quad (2)$$

where  $\phi_{\text{bb}}(E, T)$  is the black body radiation. For the calculation and mapping of  $\Delta\mu$  using eqn (2), EQE( $E, r$ ) and  $T$  need to be determined. The temperature  $T$  can be determined from the generalized Planck's law applied to a luminescence flux  $j_r^{\text{PL,EL}}$ , using the expression:

$$k \ln\left(\frac{j_r^{\text{PL,EL}}}{A(E, r) E^2}\right) = \frac{\Delta\mu(r)}{T} - \frac{E}{T} \quad (3)$$

By considering the high-energy part of the spectrum, where the absorption does not vary significantly, the temperature  $T$  is obtained from the slope of the latter equation plotted against the photon energy. The fit in Fig. 2 yielded  $T = 297$  K for device A and  $T = 303$  K for device B. Note that the uncertainty in the temperature calculation is  $\pm 20$  K, meaning that the observed variations are negligible. Once the temperature is determined, from the constant term in eqn (3), the quasi-Fermi level splitting can be calculated. On the other hand, when analyzing the EL spectra, the diode voltage  $V$  can be obtained. In that case transport properties have to be taken into account. Reciprocity relations have been demonstrated between PV and LED devices.<sup>23</sup> Therefore the EL spectrum can be expressed using the following relation:

$$j_r^{\text{EL}}(E, r) = \text{EQE}(E, r) \phi_{\text{bb}}(E, T) \exp\left(\frac{\Delta\mu(r)}{kT}\right) \quad (4)$$

wherein  $\Delta\mu(r) = qV(r)$ , with  $V(r)$  the local internal applied voltage and  $q$  the electronic charge. In order to measure the local voltage of the diode, an equivalent procedure as described above can be used.<sup>47</sup> The excitation power for all of the hyperspectral imaging experiments was kept below 1 Sun, allowing the characterization of the device under realistic operating conditions. This is an important criterion that is not often respected as usual PL characterizations, especially in confocal configuration, are obtained under several hundreds or even thousands of Suns. For the PL experiments, the laser was tuned to match the electrically measured

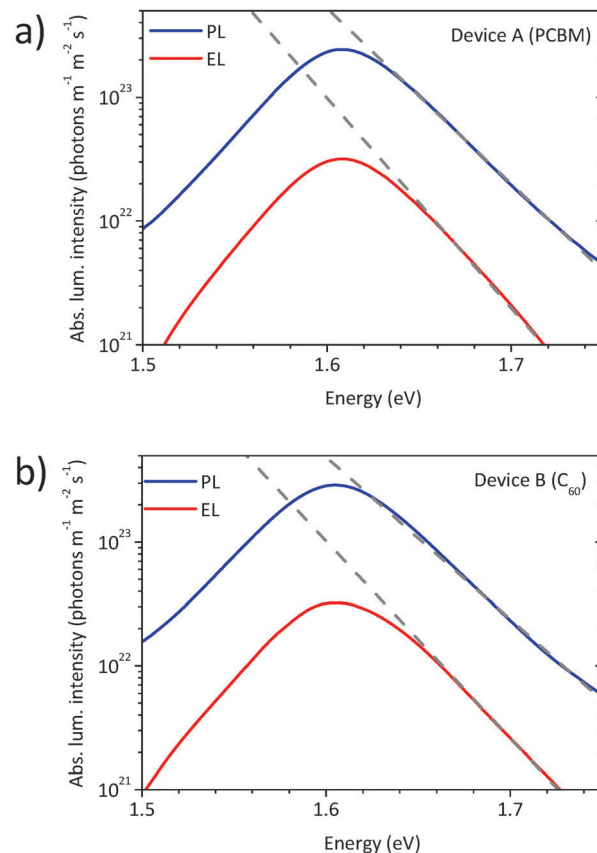


Fig. 2 (a) Photoluminescence (blue) and electroluminescence (red) spectra for device A, using PCBM, and for (b) device B, using C<sub>60</sub> as the electron transport layer. The linear fit of the high-energy tail of the spectra is used to calculate the temperature  $T$  following eqn (3).

short circuit current  $J_{\text{sc}} \sim 21 \text{ mA cm}^{-2}$ . As for the EL experiments, the same conditions were achieved with an applied bias of 1.15 V. We performed spectrally and spatially resolved luminescence imaging on both devices, obtaining absolutely calibrated PL and EL maps (photons per m per m<sup>2</sup> per s). From these images, one can extract the emission spectrum from each pixel (Fig. 2a and b). The EL and PL spectra exhibit similar shapes with equal emission maximum at 1.61 eV (770 nm), independently on the electron transport layer used.

By using the generalized Planck's law, maps of the quasi-Fermi level splitting  $\Delta\mu_{\text{eff}}$  can be extracted from the EL and PL hypercubes (Fig. 3). One can immediately notice the presence of circular spots with micrometric diameter that exhibit weak luminescence intensity and thus low quasi-Fermi level splitting. It is unlikely that these areas originate within the perovskite absorber. In fact, such spatial features are not directly related with the morphology/crystallinity of the perovskite layer, since the observed grain size is smaller than 200 nm (Fig. S1 in the ESI†). In this scenario, profound inhomogeneities in the perovskite would have a large impact on the electrical characteristics of the device (shunts and high current leakage, not seen here) that would strongly influence the efficiency and decrease the overall PL intensity. Hence the observed large inhomogeneities are most likely related to the deposition of the organic charge transport



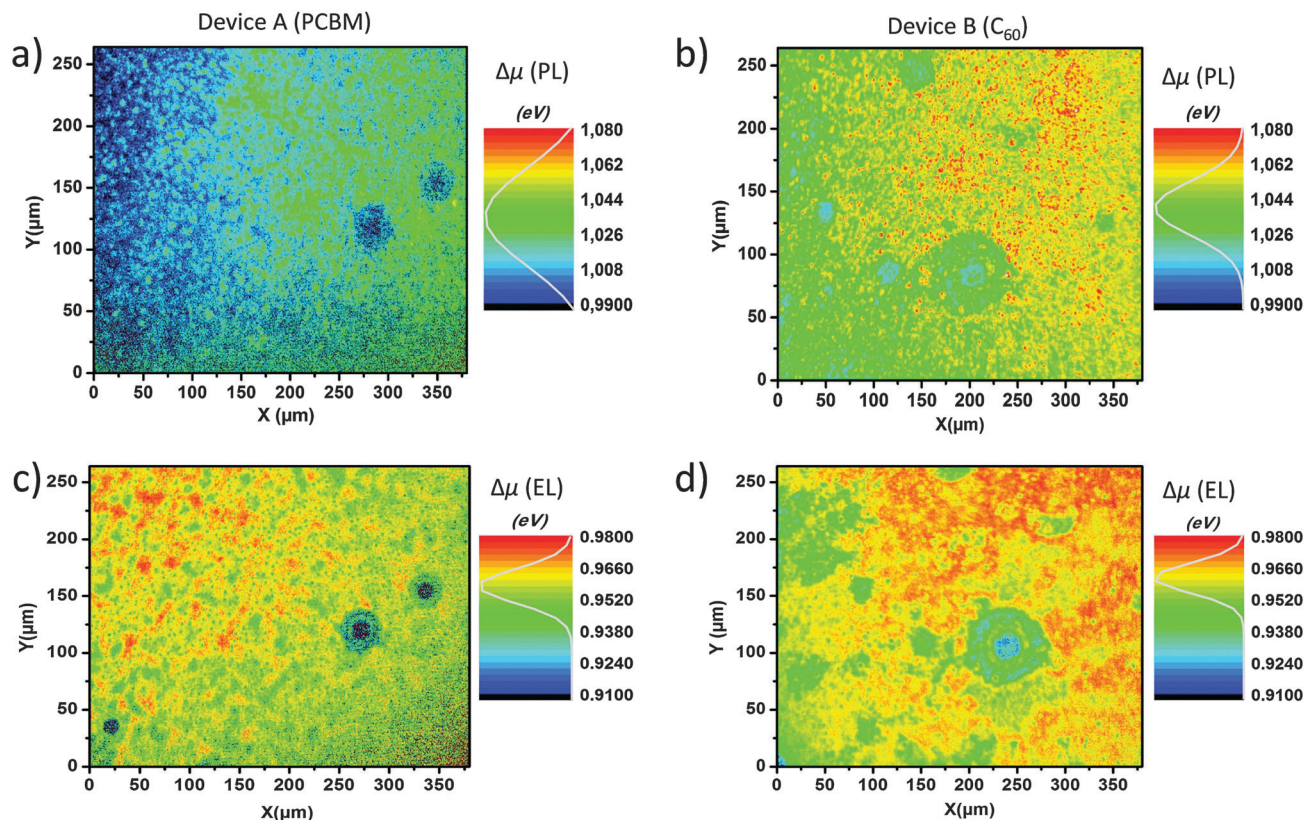


Fig. 3 (a) Absolute mapping of the quasi-Fermi level splitting derived from photoluminescence (a and b, top) and electroluminescence (c and d, bottom), for perovskite solar cells using PCBM (left, device A) or  $C_{60}$  (right, device B) as the ETL. The Gaussian distribution of the signal has been overlaid with the color scale as a guide to the eye.

layers (PEDOT:PSS and polyTPD). These areas are potentially a damaging factor and lead to a lowering of the maximum achievable  $V_{oc}$ . Additionally, these areas contribute to the reduction of the carrier transport efficiency as will be demonstrated in the next section. In order to analyze the maps of the quasi-Fermi level splitting, the corresponding histograms representing the statistical spatial distribution of  $\Delta\mu$  were obtained (Fig. S2 in the ESI†). Using a Gaussian distribution, the characteristic parameter from each hyperspectral analysis was extracted (the normalized Gaussian distributions are overlaid with the color bars in Fig. 3). For device A, and based on the map of  $\Delta\mu$  extracted from the PL emission, we found a mean value  $\Delta\mu_{PL}^{center} = 1.017$  eV with a full width at half maximum (FWHM) of 28.2 meV. This is in very good agreement with the reference, global  $V_{oc}$  electrically measured under illumination with the 532 nm laser (1.015 V) and highlights the very good quality of the perovskite absorber. For device B, however, the PL imaging yields a mean value  $\Delta\mu_{PL}^{center} = 1.049$  eV and a FWHM of 22.4 meV, which is slightly higher compared to the electrically measured  $V_{oc}$  of 1.002 V. This difference could originate from the particular area of the device under investigation, however full cell maps that will be described later appear to discard such effects. Most likely, the mismatch between  $\Delta\mu$  and the measured  $V_{oc}$  is related to the hysteresis observed in the  $J-V$  characterization (Fig. 1d) and to a hindered charge extraction by interface potential barriers.

In fact, discrepancies between the  $V_{oc}$  derived from PL experiments and that obtained from electrical measurements are indicators of the presence of interfacial charge trapping sites.<sup>24,25</sup> Hence, the  $C_{60}$  hole blocking layer employed in device B might not be able to passivate the perovskite surface as efficiently as PCBM.<sup>48,49</sup> For both devices the maximum spatial fluctuation of the quasi-Fermi level splitting is less than 50 meV (see Fig. S3 in the ESI†) and hence has a moderate impact on the global photovoltaic performance.<sup>50–53</sup> It is important to note that those fluctuations do not originate from spatial bandgap fluctuations, as demonstrated by the absence of spectral variations over the cell area.

The histograms of the spatially resolved  $\Delta\mu$  obtained from EL were also determined (Fig. S2 in the ESI†). In the case of device A, the corresponding histogram plot is characterized by a mean value of 0.960 eV and a FWHM of 15.2 meV. For device B, a very similar mean value of 0.963 eV with a FWHM of 13.1 meV is observed. In this case, both determined maximum  $\Delta\mu_{EL}^{max}$  values are significantly lower ( $\sim 190$  meV) compared to the applied voltage ( $V_{app} = 1.15$  V). This mismatch points towards charge injection issues implying, due to the reciprocity relation, that the carrier collection is also limited. This observation is in agreement with the relatively low FF observed for both types of perovskite solar cells.

The theoretical work developed by Wong and Green provides an extension of Rau's reciprocity relations between PV (EQE)

and LED operations (electroluminescence intensity).<sup>46</sup> This extension is based on the reformulation of Rau's work by including the terminal voltage and current, therefore extending its application to any device-operating point. The extended reciprocity relations take into account all the losses of elementary currents that occur while reaching the terminal, with an efficiency  $f_T$  given by:

$$f_T(x,y) = \frac{\partial I}{\partial I_L(x,y)_{\partial V_T=0}} = \frac{\partial V(x,y)}{\partial V_T}_{\partial I_L=0} \quad (5)$$

where  $I$  and  $V_T$  are the terminal current and voltage,  $I_L(x,y)$  the local light induced current collected at the junction, and  $V(x,y)$  the local diode voltage. This definition of a generalized relation connects the injection of carriers in the dark to the extraction of carriers under illumination. Hence collection efficiency maps can be experimentally accessible by using eqn (4), which relates the local EL intensity to the local voltage and EQE values. In fact, one can determine the current transport efficiency by differentiating the electroluminescence emission:<sup>45</sup>

$$f_T(x,y) = \frac{\partial \ln \phi_{em}(x,y)}{\partial \left( \frac{qV_T}{kT} \right)} \quad (6)$$

where  $\phi_{EL}(x,y)$  is the EL map. Therefore, depending on the bias we apply,  $f_T$  variations could arise from a bias dependence of the EQE (*i.e.* carrier collection function) or from local voltage

variations. This is further discussed below based on our experimental results. Two EL images were acquired by applying voltages of 1.15 V and 1.16 V and, by applying eqn (6), maps of the current transport efficiency were obtained for both types of devices (Fig. 4). The current transport efficiency exhibits spatial variations at the micron scale (Fig. 4a and b) which are similar in size and appearance to those previously observed for the quasi-Fermi level splitting obtained from both PL and EL (Fig. 3). The corresponding histograms are shown in Fig. S3 in the ESI,<sup>†</sup> and their deconvolutions are overlaid with the color bars in Fig. 4. In device A,  $f_T$  is broad and centered at 0.5, with low (0.27) and high (0.80) narrow components originating from the small regions visible in Fig. 4a. The current transport efficiency for device B (Fig. 4b) shows substantial inhomogeneities on a much larger scale, with  $f_T$  being dominated by a relatively low (0.42) and a high (0.78) broad components. For both devices, the spatial distribution of  $f_T$  shows areas approaching unity, indicating full collection of the photogenerated charge carriers, and small portions of the image where all charge carriers are essentially lost. It is important to point out, however, that in order to obtain a sufficient EL signal and respect the standard 1 Sun operation conditions, the applied voltage in our experiments should only be slightly above the  $V_{oc}$  obtained under 1 Sun illumination. This choice unavoidably underestimates the collection efficiency. In fact, at short circuit the carrier collection efficiency is much higher, as evidenced by the

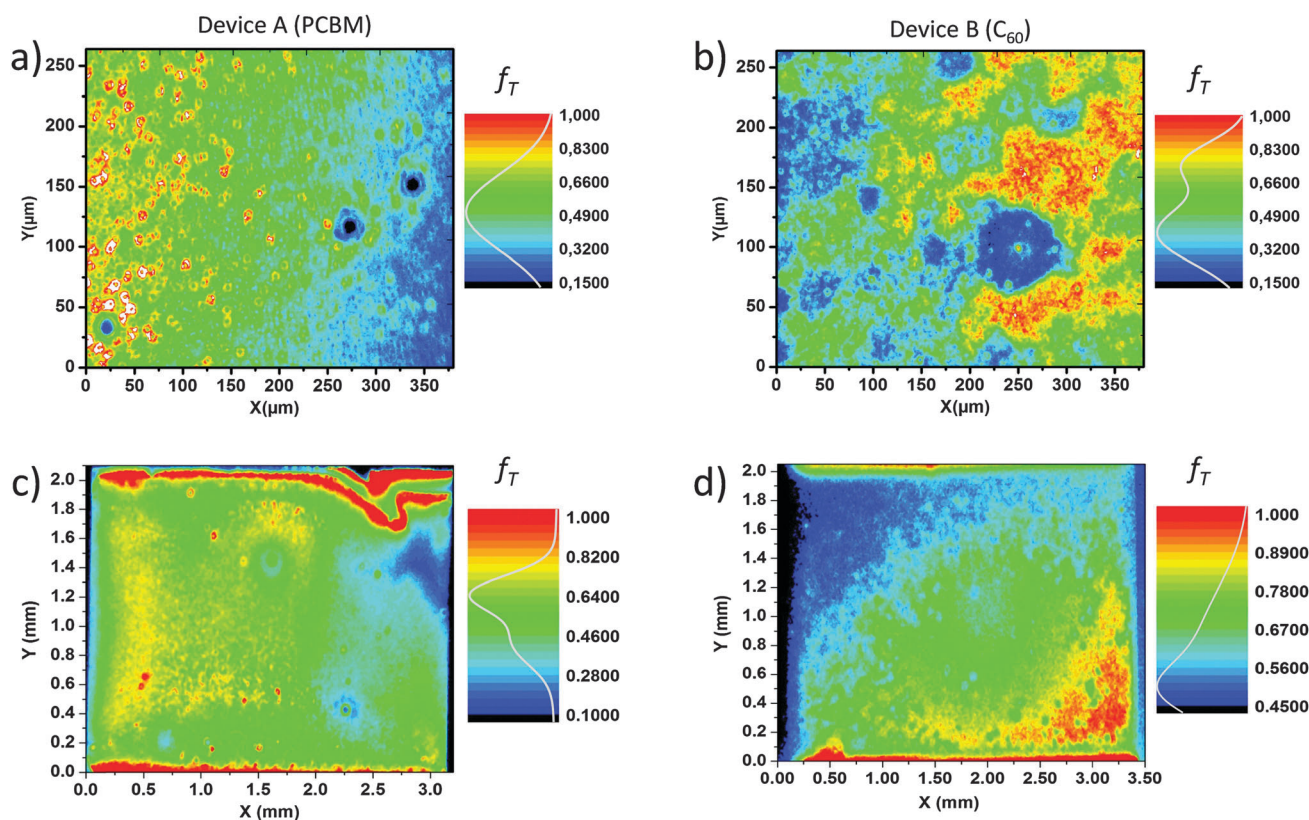


Fig. 4 Mapping of the current transport efficiency  $f_T$  obtained by applying eqn (5) to two EL hyperspectral images taken at 1.15 V and 1.16 V applied bias.  $f_T$  mapping was performed at the microscale (top) and at the whole device level (bottom) for perovskite solar cells using PCBM (a and c, device A) or  $C_{60}$  (b and d, device B) as the ETL. The interpolation of the signal distribution has been overlaid with the color scale as a guide to the eye.



measured  $J_{sc}$  of about  $20 \text{ mA cm}^{-2}$  (Fig. 1c and d). According to these maps, our perovskite solar cells, in spite of their high power efficiency, exhibit areas with substantially limited current transport efficiency. This observation is in good agreement with the low fill factor observed for the devices studied here. Our investigation has so far focused on the hyperspectral imaging of the luminescence emitted from an area that is small compared to the total device area ( $6 \text{ mm}^2$ ). In the following section the results from the analysis on the full device area are presented. As in the case of the micro-scale analysis, the EL images used to calculate  $f_T$  were taken at 1.15 V and 1.16 V applied bias. By examining the full scale  $f_T$  maps for both perovskite devices (Fig. 4c and d), strong spatial inhomogeneity with millimeter variations can be observed. These fluctuations are of the same order of magnitude compared to those observed at the micrometric scale. The spatial distributions of the carrier transport efficiency show the presence of multiple areas within the full device, each being dominated by different values of  $f_T$  (see histograms in Fig. S3 in the ESI† and their deconvolutions which are overlaid with the color bars in Fig. 4). For device A (Fig. 4c), only a few regions have a low transport efficiency ( $< 0.2$ ), while the distribution of  $f_T$  shows two main features at 0.43 and 0.64. The device using a  $C_{60}$  electron transport layer (device B) is characterized by a somewhat narrower distribution in the transport efficiency (Fig. 4d), with a main peak at 0.52 and a long shoulder at higher values of  $f_T$ , where the current transport is enhanced. Interestingly, areas exhibiting an almost complete collection of the photogenerated charges are present at the edges of the active area for both devices (red areas in Fig. 4c and d). Such edge effects are ascribed to small thickness variation due to the edge of the underlying patterned ITO electrode, which defines the active area of the solar cell. More importantly, these figures translate into a large loss of the photogenerated charge carriers even in high efficiency perovskite solar cells as those presented here. Moreover, carrier collection issues seem to be present at both local and global scales.

Poor carrier transport can originate either from the collection in the diode (classically called  $f_c$  collection function) or from a lateral transport within the electrodes.<sup>46</sup> In the case of the first hypothesis, one would expect a strong voltage dependence of the EQE values, a consequence of the presence of traps or of a limited mobility in the absorber. As this is not observed, (Fig. S5 in the ESI†), the collection function appears not to be the main reason for the observed inefficient charge transport. Additionally, in such a scenario, one would also expect a mismatch between EL and PL spectra, as the former reflects the  $\text{EQE}(E, r)$  and the latter reflects the absorption  $A(E, r)$ , which is also not observed here (Fig. 2 and Fig. S6 in the ESI†). Finally,  $\text{EQE}(E, r)$  variations indicate fluctuations of internal diode voltages<sup>45</sup> and thus spatial fluctuations of local series resistances (as opposed to the lateral spreading resistance). Since similar spatial variations are observed for samples A and B, the origin of such losses possibly originates from the front (ITO/PEDOT/polyTPD) rather than the back contact (fullerene). Although it deserves more investigation, this could also indicate the presence of an energy barrier (as mentioned before), as we see small

variations of the  $\text{EQE}(V)$  in the blue region of the spectrum. Regarding this phenomena and considering that the  $\text{EQE}(V)$  is a global measurement, one cannot *a priori* exclude a different behavior on a more local scale. Nevertheless, as the observed global tendency is not voltage dependent, a different local behavior would not influence the overall parameters. The second hypothesis implying lateral carrier transport issues as the cause for the low carrier collection efficiency would lead to a monotonous variation of the carrier collection function. This is not the case at the microscale but it might be responsible for larger fluctuations observed on the complete cell area. For device A, a  $f_T$  gradient is seen in the  $x$  direction only, while a gradient in both  $x$  and  $y$  directions is observed for device B. As the front contact is common to both devices (ITO/PEDOT:PSS/polyTPD), its lateral conductivity plays a role in the  $f_T$  spatial variations ( $x$  direction). On the other hand, the back side with the PCBM layer seems to have a higher lateral carrier extraction efficiency compared to the device using  $C_{60}$ . In fact for device B we observe  $f_T$  variations also in the  $y$ -direction. Although this effect has no impact under 1 Sun working conditions (both devices having similar properties), it will be more relevant for larger devices. These phenomena would also explain why only a few efficient large area perovskite cells have been reported so far, since the fill factor is normally lower than that in the equivalent smaller area cells.<sup>54</sup>

In summary, we have investigated efficient p-i-n hybrid perovskite solar cells through luminescence hyperspectral imaging. The small mismatch between the electrically measured  $V_{oc}$  and the optically (from both photoluminescence and electroluminescence) deduced quasi-Fermi level splitting is indicative of the high quality of the perovskite absorber. Yet the spatially resolved analysis identified profound inhomogeneities in this novel type of devices. These spatial inhomogeneities appear to be related to problems with carrier extraction, leading to the limited fill factor of the cells. This hypothesis is supported by the dispersion of the spatially resolved carrier transport efficiency function, which identifies areas of the cell with severely hindered charge transport. We ascribe these losses first to local fluctuations of interface series resistance and, with a lower impact, to inefficient lateral transport. The origin of the inhomogeneities observed here is not yet clear, but its understanding would allow us to significantly enhance the performance of these already efficient photovoltaic devices. This work also demonstrated that hyperspectral luminescence imaging is a powerful tool to investigate the lateral variations of novel devices such as hybrid perovskite solar cells.

## Experimental

### Perovskite solar cell fabrication

ITO-coated glass substrates were cleaned with soap, water and isopropanol in an ultrasonic bath, followed by  $O_2$  plasma treatment. PEDOT:PSS was spin-coated on top and annealed at  $150^\circ\text{C}$  for 15 minutes. PolyTPD was spin-coated from a chlorobenzene solution ( $7 \text{ mg mL}^{-1}$ ), obtaining a 20 nm thick layer. The substrates were transferred to a vacuum chamber

integrated into a nitrogen-filled glovebox and evacuated to a pressure of  $1 \times 10^{-6}$  mbar. Two ceramic crucibles containing MAI and  $\text{PbI}_2$  were heated at 70 °C and 250 °C, respectively. The film thickness was controlled by the  $\text{PbI}_2$  evaporation rate ( $0.5 \text{ A s}^{-1}$ ). After evaporation of a 500 nm thick  $\text{MAPbI}_3$  perovskite, a 40 nm film of  $\text{C}_{60}$  was evaporated on top without breaking the vacuum. Alternatively, a 40 nm thick PCBM layer was spin-coated from a chlorobenzene solution ( $20 \text{ mg ml}^{-1}$ ) under ambient conditions. The devices were completed by thermal evaporation of the top metal electrode under a base pressure of  $1 \times 10^{-6}$  mbar (10 nm Ba/100 nm Ag).

### Solar cell characterization and hyperspectral imaging

EQE measurements were performed using a white light halogen lamp (calibrated on a reference Si solar cell) in combination with interference filters (MiniSun simulator by ECN, the Netherlands). Current density–voltage ( $J$ – $V$ ) characteristics were measured using a Keithley 2400 source measure unit with and without illumination. The light source was a 10 500 solar simulator from Abet Technologies. Before each measurement, the exact light intensity was determined using a calibrated Si reference solar cell. The setup for the hyperspectral luminescence imaging consists of a hyperspectral imager from Photon *etc.* coupled to an optical microscope with a 50× objective and a numerical aperture of 0.8. An optical setup based on a Köhler system provided the homogeneous illumination of the perovskite devices. The global illumination inhomogeneity is found to be lower than 9%.

## Acknowledgements

This work has been supported by the Spanish Ministry of Economy and Competitiveness (MINECO) *via* the Unidad de Excelencia María de Maeztu MDM-2015-0538 and MAT2014-55200, PCIN-2015-255 and the Generalitat Valenciana (Prometeo/2012/053). C. M. and M. S. thank the MINECO for their pre- and post-doctoral (JdC) contracts. G. E. H. would like to thank the ANRT for financing the ongoing PhD thesis under the CIFRE convention No 923/2013. The authors acknowledge Photon *etc.* (M. Verhaegen and L.-I. Dion-Bertrand) for fruitful discussions and technical assistance.

## References

- 1 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050–6051.
- 2 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643–647.
- 3 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316–319.
- 4 N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seok, *Nat. Mater.*, 2014, **13**, 897–903.
- 5 H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, **345**, 542–546.
- 6 W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Science*, 2015, **348**, 1234–1237.
- 7 P. Gao, M. Grätzel and M. K. Nazeeruddin, *Energy Environ. Sci.*, 2014, **7**, 2448–2463.
- 8 M. Grätzel, *Nat. Mater.*, 2014, **13**, 838–842.
- 9 S. D. Stranks and H. J. Snaith, *Nat. Nanotechnol.*, 2015, **10**, 391–402.
- 10 J. Berry, T. Buonassisi, D. A. Egger, G. Hodes, L. Kronik, Y.-L. Loo, I. Lubomirsky, S. R. Marder, Y. Mastai, J. S. Miller, D. B. Mitzi, Y. Paz, A. M. Rappe, I. Riess, B. Rybtchinski, O. Stafsudd, V. Stevanovic, M. F. Toney, D. Zitoun, A. Kahn, D. Ginley and D. Cahen, *Adv. Mater.*, 2015, **27**, 5102–5112.
- 11 M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Prog. Photovoltaics*, 2015, **23**, 805–812.
- 12 D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Sci. Adv.*, 2016, **2**, e1501170.
- 13 M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395–398.
- 14 O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Graetzel, M. K. Nazeeruddin and H. J. Bolink, *Nat. Photonics*, 2014, **8**, 128–132.
- 15 Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn and P. Meredith, *Nat. Photonics*, 2015, **9**, 106–112.
- 16 W. Nie, H. Tsai, R. Asadpour, J.-C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H.-L. Wang and A. D. Mohite, *Science*, 2015, **347**, 522–525.
- 17 D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent and O. M. Bakr, *Science*, 2015, **347**, 519–522.
- 18 Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, 2015, **347**, 967–970.
- 19 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344–347.
- 20 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341–344.
- 21 C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith and L. M. Herz, *Adv. Mater.*, 2014, **26**, 1584–1589.
- 22 C. S. Ponce, T. J. Savenije, M. Abdellah, K. Zheng, A. Yartsev, T. Pascher, T. Harlang, P. Chabera, T. Pullerits, A. Stepanov, J.-P. Wolf and V. Sundström, *J. Am. Chem. Soc.*, 2014, **136**, 5189–5192.
- 23 U. Rau, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 085303.
- 24 K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov and H. J. Bolink, *Sci. Rep.*, 2014, **4**, 6071.
- 25 W. Tress, N. Marinova, O. Inganäs, M. K. Nazeeruddin, S. M. Zakeeruddin and M. Graetzel, *Adv. Energy Mater.*, 2015, **5**, 1400812.
- 26 D. W. deQuilettes, S. M. Vorpahl, S. D. Stranks, H. Nagaoka, G. E. Eperon, M. E. Ziffer, H. J. Snaith and D. S. Ginger, *Science*, 2015, **348**, 683–686.



- 27 M. J. Simpson, B. Doughty, B. Yang, K. Xiao and Y.-Z. Ma, *J. Phys. Chem. Lett.*, 2015, **6**, 3041–3047.
- 28 Z. Hameiri, A. Mahboubi Soufiani, M. K. Juhl, L. Jiang, F. Huang, Y.-B. Cheng, H. Kampwerth, J. W. Weber, M. A. Green and T. Trupke, *Prog. Photovoltaics*, 2015, **23**, 1697–1705.
- 29 X. Wen, R. Sheng, A. W. Y. Ho-Baillie, A. Benda, S. Woo, Q. Ma, S. Huang and M. A. Green, *J. Phys. Chem. Lett.*, 2014, **5**, 3849–3853.
- 30 C. G. Bischak, E. M. Sanehira, J. T. Precht, J. M. Luther and N. S. Ginsberg, *Nano Lett.*, 2015, **15**, 4799–4807.
- 31 Z. Guo, J. S. Manser, Y. Wan, P. V. Kamat and L. Huang, *Nat. Commun.*, 2015, **6**, 7471.
- 32 Y. Tian, M. Peter, E. Unger, M. Abdellah, K. Zheng, T. Pullerits, A. Yartsev, V. Sundstrom and I. G. Scheblykin, *Phys. Chem. Chem. Phys.*, 2015, **17**, 24978–24987.
- 33 M. Vrućinić, C. Matthiesen, A. Sadhanala, G. Divitini, S. Cacovich, S. E. Dutton, C. Ducati, M. Atatüre, H. Snaith, R. H. Friend, H. Sirringhaus and F. Deschler, *Adv. Sci.*, 2015, **2**, 1500136.
- 34 J. S. Yun, A. Ho-Baillie, S. Huang, S. H. Woo, Y. Heo, J. Seidel, F. Huang, Y.-B. Cheng and M. A. Green, *J. Phys. Chem. Lett.*, 2015, **6**, 875–880.
- 35 A. Delamarre, L. Lombez and J.-F. Guillemoles, *Appl. Phys. Lett.*, 2012, **100**, 131108.
- 36 A. Delamarre, L. Lombez and J. F. Guillemoles, *J. Photonics Energy*, 2012, **2**, 027004.
- 37 E. Olsen and A. S. Flø, *Appl. Phys. Lett.*, 2011, **99**, 011903.
- 38 M. P. Peloso, J. Sern Lew, T. Trupke, M. Peters, R. Utama and A. G. Aberle, *Appl. Phys. Lett.*, 2011, **99**, 221915.
- 39 A. Delamarre, M. Paire, J.-F. Guillemoles and L. Lombez, *Prog. Photovoltaics*, 2014, **23**, 1305–1312.
- 40 P. Rale, A. Delamarre, G. El-Hajje, R. Tamaki, K. Watanabe, Y. Shoji, Y. Okada, M. Sugiyama, L. Lombez and J.-F. Guillemoles, *J. Photonics Energy*, 2015, **5**, 053092.
- 41 G. Lasher and F. Stern, *Phys. Rev.*, 1964, **133**, A553–A563.
- 42 P. Wurfel, *J. Phys. C: Solid State Phys.*, 1982, **15**, 3967–3985.
- 43 B. Feuerbacher and P. Wurfel, *J. Phys.: Condens. Matter*, 1990, **2**, 3803–3810.
- 44 K. Schick, E. Daub, S. Finkbeiner and P. Würfel, *Appl. Phys. A: Solids Surf.*, 1992, **54**, 109–114.
- 45 U. Rau, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 085303.
- 46 J. Wong and M. A. Green, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 235205.
- 47 T. Kirchartz, U. Rau, M. Kurth, J. Mattheis and J. H. Werner, *Thin Solid Films*, 2007, **515**, 6238–6242.
- 48 Y. Shao, Z. Xiao, C. Bi, Y. Yuan and J. Huang, *Nat. Commun.*, 2014, **5**, 5784.
- 49 J. Xu, A. Buin, A. H. Ip, W. Li, O. Voznyy, R. Comin, M. Yuan, S. Jeon, Z. Ning, J. J. McDowell, P. Kanjanaboos, J.-P. Sun, X. Lan, L. N. Quan, D. H. Kim, I. G. Hill, P. Maksymovych and E. H. Sargent, *Nat. Commun.*, 2015, **6**, 7081.
- 50 U. Rau, P. O. Grabitz and J. H. Werner, *Appl. Phys. Lett.*, 2004, **85**, 6010–6012.
- 51 G. H. Bauer and L. Gütay, *Thin Solid Films*, 2007, **515**, 6127–6131.
- 52 E. Edri, S. Kirmayer, S. Mukhopadhyay, K. Gartsman, G. Hodes and D. Cahen, *Nat. Commun.*, 2014, **5**, 3461.
- 53 V. W. Bergmann, S. A. L. Weber, F. Javier Ramos, M. K. Nazeeruddin, M. Grätzel, D. Li, A. L. Domanski, I. Lieberwirth, S. Ahmad and R. Berger, *Nat. Commun.*, 2014, **5**, 5001.
- 54 O. Malinkiewicz, C. Roldán-Carmona, A. Soriano, E. Bandiello, L. Camacho, M. K. Nazeeruddin and H. J. Bolink, *Adv. Energy Mater.*, 2014, **4**, 1400345.