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Relation between fluorescence quantum yield and open-circuit voltage in complete perovskite solar cells

Mariia Kramarenko, Catarina G. Ferreira, Guillermo Martínez-Denegri, Constanza Sansierra, Johann Toudert,* and Jordi Martorell*

M. Kramarenko, C. G. Ferreira, G. Martínez-Denegri, C. Sansierra, Dr. J. Toudert, Prof. J. Martorell

ICFO – Institut de Ciències Fotòniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels (Barcelona), Spain

E-mail: mariia.kramarenko@icfo.eu, johann.toudert@icfo.eu

Prof. J. Martorell

Departament de Física,

Universitat Politècnica de Catalunya,

Terrassa 08222, Spain

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Abstract. Bringing the V_{oc} of a perovskite solar cell toward its radiative value, corresponding to a 100% external fluorescence quantum yield (QY) of the cell, has been pursued to reach the highest performance photovoltaic devices. At such aim, many works have focused on maximizing the QY of the active layer isolated from the rest of the cell layers. However, such quantity does often not correlate with V_{oc} following the ideal diode relation. Herein, the QYs of complete $FA_{0.8}MA_{0.2}PbI_{3-y}Br_y$ solar cells are reported, ranging from 0.1 to 3%, and compare them with their V_{oc} s, ranging from 1 to 1.13 V. By combining these measurements with electromagnetic simulations based on a full-wavevector detailed balance and a fluorescence power loss model, it is demonstrated that a non-optimal V_{oc} in mixed-cation lead halide perovskite cells is not only due to non-radiative photocarrier recombination at traps. Besides the expected parasitic absorption of the emitted photons in the electrode layers, discrepancies appear between V_{oc} and QY. These discrepancies are attributed to the rise of energy barriers, a side-effect of trap removal. Indeed, although surface passivation may enhance the QY, its beneficial effect may be counterbalanced by the emergence of such barriers between active and charge transporting layers.

1. Introduction

Perovskite solar cells (PSCs) are under the spotlight of photovoltaics, material science and photonics research since a few years ago, thanks to their outstanding optoelectronic properties and relatively affordable fabrication by solution processing. These advantages have fostered the increase of their power conversion efficiency to reach values above 25% faster than many photovoltaic technologies before. However, the current efficiencies still lag several percentage points below the theoretical optimum predicted by Shockley-Queisser's detailed balance model. Achieving the maximum power conversion efficiency for a single junction PSC requires, among several aspects, its open-circuit voltage V_{oc} to be maximized.

It has been proposed by several authors ^[1-8] that to present a maximized V_{oc} , a cell with a given design should re-emit all the incident photons absorbed by its active layer. This was initially proposed by Shockley and Queisser on the basis of detailed balance calculations (that are now widely used for the estimation of the maximum achievable solar cell efficiency and other photovoltaic parameters such as V_{oc}), ^[8] and by Ross on the basis of simple thermodynamic considerations. ^[5] Their approaches led to the relation described by Equation (1), ^[1-8] which predicts that V_{oc} increases with the cell's *external fluorescence quantum yield*, abbreviated hereafter as QY. QY is the ratio of the number of photons re-emitted by the active layer *and escaping the cell* to the number of incident photons absorbed by the active layer.

$$V_{oc} = V_{oc,rad} + \frac{kT}{q} \ln(QY) \quad (1)$$

In Equation (1), $V_{oc,rad}$ is the so-called radiative V_{oc} reached when $QY = 100\%$. $V_{oc,rad}$ is mainly driven by the absorbance of the active layer, which is set by the whole cell design. In actual

solar cells, QY is smaller than 100%. Such non-optimum value may result from the non-radiative recombination of photogenerated carriers within the cell.^[6, 7] It may also result from parasitic absorption of the photons re-emitted by the active layer in non-active layers of the cell.^[6, 7] Note that, as almost any analytical relation, Equation (1) is based on a number of assumptions that are further detailed in refs 6, 7 and 8. An important assumption is that the solar cell presents an ideal diode behaviour, which means that its V_{oc} is equal to the quasi-Fermi level splitting (QFLS).^[9] However, the V_{oc} of actual solar cells may not follow such ideal diode behaviour and present V_{oc} s lower than predicted from Equation (1), which presents an upper limit for the achievable V_{oc} . Known reasons for such deviation from Equation (1) are: shunt resistance, carrier recombination not following the diode equation (Supporting Information S1), losses at contacts, or strong energy level offsets at interfaces.^[9] In sum, there are several non-idealities that may contribute to making the V_{oc} of actual solar cells depart from $V_{oc,rad}$.

The high QY values reported for hybrid perovskite active layers (above 40%) when isolated from the rest of the cell layers,^[10, 11, 12] make these materials appealing to produce solar cells with V_{oc} s approaching $V_{oc,rad}$. However, the V_{oc} of current PSCs lags on average significantly below the expected $V_{oc,rad}$.^[13, 14] Finding the origin of this behaviour is needed to produce optimal devices. This requires measuring both the QY and V_{oc} of complete solar cells and analysing the obtained data with suitable theoretical models to determine the nature of the non-idealities lowering V_{oc} . However, because of the relatively few available experimental data on this matter in the case of PSCs,^[9, 15-19] the literature on this topic is still somewhat scarce. In fact, it is only very recently that works discussing the correlation between QY and V_{oc} of PSCs on the basis of experimental results emerged.^[15,16,18,19] In the most recent works,^[9, 18] the QY and V_{oc} of PSCs with different transport layers were compared. Differences between V_{oc} and QFLS were observed, and their origin was discussed in relation with energy level offsets at interfaces. A very recent review of advances on this matter is provided by ref. 19.

Herein, measurements of the QY and photovoltaic properties of a series of complete solar cells based on a $\text{FA}_{0.8}\text{MA}_{0.2}\text{PbI}_{3-y}\text{Br}_y$ perovskite produced by the two-step method are demonstrated (section 2.1). By combining these measurements with electromagnetic calculations, the dominant non-idealities in the studied devices are discussed. The cells present QYs and V_{oc} s ranging from 0.1 to 3% and from 1 to 1.13 V, respectively (section 2.2). Full-wavevector generalized detailed balance simulations taking into account the real cell structure yield a $V_{\text{oc,rad}}$ of 1.28 V. The V_{oc} values lower than $V_{\text{oc,rad}}$ obtained are attributed to: (a) the low QY and (b) a deviation from the ideal diode behaviour (V_{oc} not following Equation (1)).

To address the origin of the low QY, first the QY saturation curves were measured (section 3.1). This shows the primordial role of non-radiative recombination at long-lived traps in limiting the QY. Second, a model to calculate the fluorescence power loss in each non-active layer of the cell was developed (section 3.2). From the calculations, it is observed that QY is not only limited by non-radiative recombination, but also by parasitic absorption in the electrode layers. Such parasitic absorption, which is found to occur mostly in the ITO front electrode of the cell, would limit QY drastically if non-radiative recombination was rubbed out.

To address the origin of the deviation from the ideal diode behaviour (V_{oc} not following Equation (1)) this deviation was correlated with the photovoltaic parameters of the cells: power conversion efficiency (PCE), short-circuit current (J_{sc}), fill-factor (FF), series resistance (R_{s}), shunt resistance (R_{sh}) (section 4). From these results it is proposed that the deviation appears due to the rise of energy barriers occurring as a side-effect of trap removal, which degrade the efficiency of the cell.

At the light of our results, the dominant non-idealities in cells reported in the literature are discussed (section 5) and provide guidelines for future works to fabricate optimal devices (section 6). Concluding, the fabrication of efficient PSCs with an ideal diode behaviour (i.e. V_{oc}

following Equation (1)) and with V_{oc} approaching $V_{oc,rad}$ will require future works to follow a holistic optimization method taking both electronic and optical features into account.

2. V_{oc} and QY of complete perovskite solar cells

2.1. Solar cell structure and optical properties

A series of solar cells based on a $FA_{0.8}MA_{0.2}PbI_{3-y}Br_y$ perovskite were produced with the two-step method.^[13, 20, 21, 22] The fabrication recipe is described in Supporting Information S2. The cells present a n-i-p configuration with the structure depicted in **Figure 1a**: Glass/ITO/SnO₂/Perovskite/Spiro-OMeTAD/Au. In this structure, a 100 nm ITO layer grown on a glass substrate acts as front electrode, a 20 nm SnO₂ layer as electron transport layer, a 550 nm - thick perovskite acts as active layer, a 140 nm Spiro-OMeTAD layer acts as hole transport layer and a 80 nm Au layer acts as reflecting back electrode. As exemplified in **Figure 1b**, the fabricated perovskite presents a bandgap absorption edge near 1.54 eV (805 nm), and the cells show a clear fluorescence signal peaking at this edge. Note that all the cells were fabricated to present similar optical and photovoltaic properties. In particular, the layer thicknesses in all the fabricated cells are similar to those in the cell shown in **Figure 1a**. However, due the limited reproducibility that impacts in particular the electronic properties of the perovskite layer, as discussed later, the different cells present different QYs and V_{oc} s.

2.2. Measured QY and V_{oc} and full-wavevector generalized detailed balance simulations

The QY of the solar cells was measured with a home-built integrating sphere - based setup with the configuration shown on **Figure 2a**. A 532 nm laser beam with a 1 sun-equivalent intensity was used to excite the perovskite fluorescence. The reflected/scattered laser intensity and fluorescence intensity were collected separately to determine QY. The V_{oc} of the cells was measured with a solar simulator. For comparison, V_{oc} was also measured under laser illumination (532 nm, 1 sun-equivalent) on selected cells. Similar V_{oc} values were obtained

with both approaches. Further details about the measurement methods are given in Supporting Information S3.

Full - wavevector generalized detailed balance simulations were run to calculate the $V_{oc,rad}$ of the series of cells according to:

$$V_{oc,rad} = \frac{kT}{q} \ln \left(\frac{\int_0^{\theta_{sun}} \int_0^\infty A(E,\theta) S(E) \sin\theta \cos\theta d\theta dE}{\int_0^{\frac{\pi}{2}} \int_0^\infty A(E,\theta) B(E) \sin\theta \cos\theta d\theta dE} \right) \quad (2)$$

The numerator stands for the sunlight absorbed by the perovskite layer, and the denominator stands for the fluorescence of this layer escaping from the cell, as shown in **Figure 2b**. $S(E)$ is the solar spectrum, $B(E)$ is the blackbody radiation spectrum of the cell, and $A(E,\theta)$ is the energy and angle-dependent absorbance of the perovskite layer. $A(E,\theta)$ is calculated in the coherent transfer matrix formalism.^[23] To compute $A(E,\theta)$ for our cells, a realistic layered structure was used, as the one shown in **Figure 1a**, with the energy-dependent dielectric functions of the layers constituting the cell being determined experimentally. Our simulation method is further described in Supporting Information S4. Note that it is based on the exact calculation of $A(E,\theta)$. This contrasts with most other methods reported in the PSC literature, which neglect coherent effects in the calculation of absorbance or assume that absorbance is angle-independent and/or presents a step-function energy profile. Such simplifications are not correct for PSCs due to their wavelength-scale thickness.^[24] In PSCs, optical interference and cavity modes make the absorbance depart from the incoherent optics (Beer-Lambert) prediction and show angular dependence and a non-step-function energy profile. For an accurate determination of $V_{oc,rad}$, these features must be taken into account by calculating exactly $A(E,\theta)$, as done in this work.

To illustrate this fact, Equation (2) was used to calculate the $V_{oc,rad}$ of a cell structure as the one shown in **Figure 1a**, yet with the perovskite thickness being varied. The other layer thicknesses were taken from **Figure 1a**. As shown in **Figure 2c**, the thereby calculated $V_{oc,rad}$ decreases by about 0.025 V upon increasing the perovskite layer thickness from 0.2 to 1 μm . In contrast, a calculation considering a step-function angle-independent absorbance would yield a thickness-independent V_{oc} . This can easily be seen from Equation (2), in which the $A(E,\theta)$ terms in the numerator and denominator would rub out, leaving a $V_{oc,rad}$ expression depending only on the thickness-independent $S(E)$ and $B(E)$. The decrease in $V_{oc,rad}$ with the perovskite thickness can be qualitatively attributed to an increased optical absorption mostly in the bandgap region, which implies a decrease in the perovskite effective optical bandgap.^[1, 4, 25] Besides this decreasing trend, one observes an oscillatory pattern that results from optical interference. This clearly demonstrates the importance of performing calculations taking into account coherent effects, angle-dependence and a realistic cell structure with realistic layer thicknesses and energy-dependent dielectric functions.

In **Figure 2d** are represented the QYs and V_{oc} s measured for our series of solar cells (black dots). They show different values ranging from 0.1 to 3% and from 1 to 1.13 V, respectively. As mentioned in section 2.1, such different values from cell to cell are not caused by deliberately different fabrication parameters but by a limited reproducibility impacting in particular the electronic properties of the perovskite layer. Despite reaching rather high values compared with the literature,^[13] the measured V_{oc} s lag significantly below the $V_{oc,rad}$ of 1.28 V calculated from Equation (2) using the structure and layer thicknesses taken from **Figure 1a**. This can be attributed in part to the low QY of the cells, which remains much below 100%. Another cause to the non-optimal V_{oc} of the cells is the deviation from the ideal diode behaviour: the measured V_{oc} s (black dots and black dashed trend line) depart from the ideal diode $V_{oc} = f(\text{QY})$ calculated from Equation (1) with $V_{oc,rad}$ of 1.28 V (black solid line) and the

measured QY. This deviation, materialized by a voltage loss $\delta V = V_{oc,ideal\ diode} - V_{oc,measured}$, increases with the QY. This suggests that, in the cells, the microscopic mechanism that leads to an improved QY also introduces non-idealities that limit the V_{oc} increase and thus do not allow it to approach $V_{oc,rad}$.

For the sake of completeness, are also presented in **Figure 2d** the data from two recent references that reported V_{oc} and QY measurements on complete PSCs ^[15, 16] and the calculated ideal diode $V_{oc} = f(QY)$ relations for these cells, which have been obtained from Equation (2) with the cell structures and layer thicknesses taken from the corresponding references. ^[15, 16] The thereby calculated relations yield higher V_{ocs} than those calculated for our cells. This is mainly because the perovskites considered in these references ($MAPbI_3$ and $Cs_xFA_{1-x-y}PbI_3$) present a larger bandgap, thus implying a higher $V_{oc,rad}$. Note, that in the cells from Ref. 16 the $MAPbI_3$ layer was very thin (280 nm), which contributes to further enhancing $V_{oc,rad}$ (according to **Figure 2c**). Comparing experimental and calculated data, it is seen that the $MAPbI_3$ and $Cs_xFA_{1-x-y}MA_{1y}PbI_3$ cells from Ref. 15 present QYs as high as those of our most fluorescent cells, and a similar or higher δV . In contrast, the $MAPbI_3$ cell from Ref. 16 shows a QY of 5% and a negligible δV . Consequently, it presents the highest V_{oc} reported in the literature for a $MAPbI_3$ cell ($V_{oc} = 1.26\ V$). ^[16]

3. Origin of the low QY

3.1. Non-radiative recombination

To determine the cause of the low QY of the solar cells, the contribution of non-radiative recombination was first studied. At such aim, their QYs were measured as a function of the incident light intensity I_{exc} , from 1 to 120 suns. An example of such measurement is given in Supporting Information S3. **Figure 3** shows the QY of the solar cells measured for different I_{exc} , plotted as a function of the corresponding QY measured under $I_{exc} = 1\ sun$. Upon increasing

I_{exc} , the QY of a given cell increases strongly and with a saturation behaviour. This shows that the low QY of the cells at 1 sun is in an important part due to non-radiative recombination at long-lived traps. ^[24, 26, 27] Upon increasing I_{exc} , the traps are filled thus removing non-radiative recombination paths and improving QY. Note that the QY increase with I_{exc} is more pronounced for the cells with the lowest QY at 1 sun, indicating that they present the highest density of long-lived traps. Note also that, at the maximum I_{exc} used in our measurements, the QY of the different cells does not reach the same value. The cells with the smallest QY at 1 sun still present a smaller QY than those with the highest QY at 1 sun. The first possible cause to this different QY's at high I_{exc} is that the long-lived traps in the cells with the lowest QY are not fully saturated even at the highest I_{exc} considered here. Another possible origin to the observed trend could be the existence of short-lived traps, which cannot be saturated upon increasing I_{exc} , ^[17, 28, 29, 30] and whose density would scale with that of the long-lived traps.

These effects may also partly explain why the maximum QY reached in **Figure 3** for the $I_{\text{exc}} = 120$ suns is only 20%. Another possible cause of the much below 100% is parasitic absorption. Even if non-radiative recombination in the perovskite layer was suppressed, absorption of the re-emitted photons in the non-active layers yields a non-optimal QY. The next section is focused on quantifying the effect of parasitic absorption as a limiting factor of the QY.

3.2. Parasitic absorption

Quantifying the contribution of parasitic absorption to the QY of a solar cell requires determining the fluorescence power losses in the layers constituting the cell. However, this task is usually left behind for PSCs, parasitic absorption being considered as a phenomenological parameter. ^[6,7] To estimate how drastically parasitic absorption limits the QY of the considered cell structure, a model that calculates the fluorescence power dissipated in each layer (ITO, SnO_2 , perovskite, Spiro-OMeTAD, Au) and escaping the cell was developed. Its only assumption is that the fluorescence power is homogeneously distributed within the cell. ^[31] This

holds if optical randomization of the fluorescence occurs within the cell. Achieving such randomization requires fluorescence to be weakly reabsorbed and efficiently re-emitted (weak non-radiative recombination, i.e. high η_{int}) by the perovskite. In a previous work,^[20] a proof of concept of optical randomization in PSCs was reported. However, this randomization did not concern the fluorescence but the sunlight impinging onto the cell. Since sunlight photons were impinging at normal incidence, roughness was needed to achieve their randomization. In contrast, in the present work, no roughness is needed for the randomization of fluorescence. This is because fluorescence is based on the emission by randomly oriented dipoles, thus resulting in an isotropic internal emission process. Moreover, an important fraction of the internally emitted photons falls outside the escape cone and is trapped in the cell by total internal reflection. These trapped photons are re-absorbed and eventually re-emitted, with a loss of memory of their initial wavevector. This provides an extra randomization mechanism of the fluorescence, which can develop in planar structures. Based on this assumption, it is found that QY is described by a simple expression:

$$QY = \eta_{\text{int}} \langle E \rangle \frac{\int_0^\infty \frac{X_{\text{esc}}(E)}{X(E)} \alpha(E) B(E) dE}{\int_0^\infty \left(E - \frac{\eta_{\text{int}} < E > X_{\text{reabs}}(E)}{X(E)} \right) \alpha(E) B(E) dE} \quad (3)$$

In this equation, η_{int} is the quantum efficiency of the fluorescence process, which is also often called *internal fluorescence quantum yield*. $\langle E \rangle$ is the average energy of the emitted photons. $X(E) = X_{\text{esc}}(E) + X_{\text{par}}(E) + X_{\text{reabs}}(E)$ is the fraction of the internal fluorescence power lost by the following ways: escape to the ambient medium (X_{esc}), by reabsorption in the perovskite layer (X_{reabs}), by parasitic absorption (X_{par}) in the other (non-active) layers of the cell and in the back mirror. To calculate $X_{\text{esc}}(E)$, $X_{\text{par}}(E)$ and $X_{\text{reabs}}(E)$, realistic thicknesses and the

experimentally-determined dielectric functions are considered for the different layers. Further details about our model and its implementation are given in Supporting Information S5.

Figure 4 shows the $QY = f(\eta_{\text{int}})$ curves calculated from Equation (3) for the cell structure and layer thicknesses taken from **Figure 1a**. In a first calculation, experimentally-measured dielectric functions were used for all the layers. Among these layers, only the Au and ITO ones cause parasitic absorption due to their non-zero optical absorption in the spectral region of the perovskite fluorescence. SnO_2 , Spiro-OMeTAD and glass do not contribute to parasitic absorption because they are transparent to the emitted photons. In a second calculation, the optical absorption by ITO was cancelled in the spectral region of the perovskite fluorescence. In a third calculation, the optical absorption by both ITO and Au was cancelled. This enables estimating the contribution of parasitic absorption in these two materials. For small η_{int} values, taking parasitic absorption into account makes a negligible difference on the QY value. In contrast, parasitic absorption would have a drastic effect on QY if radiative recombination was rubbed out, i.e. for $\eta_{\text{int}} = 100\%$. In this case, parasitic absorption in both ITO and Au limits QY to 60%. By cancelling the absorption by ITO, QY increases to 90%. By cancelling the absorption by ITO and Au, the 100% QY is recovered. Therefore, the main factor limiting QY in this case is parasitic absorption in the ITO front electrode.

For the sake of completeness, predictions of the current model are compared with those of one of the most advanced model recently used to compute the effect of parasitic absorption on the QY and V_{oc} of PSCs. This model stands on the use of Green functions and thus includes coherent effects to rigorously determine the spatial power distribution of dipole emission. Despite of the simplifying assumption of a homogeneous power distribution made to derive

Equation (3), both models lead to comparable QY values when $\eta_{\text{int}} \rightarrow 100\%$ and to the same conclusion that most parasitic absorption occurs in the ITO (Supporting Information S5.2).

4. Energy barriers causing a deviation from the ideal diode behaviour

To determine the origin of this deviation observed in section 2.1, a correlation was searched between the voltage loss δV and the photovoltaic parameters of the cells: PCE, J_{sc} , R_{s} , FF, R_{sh} . As already discussed in the caption of **Figure 2c**, the δV of each cell is the difference between its simulated ideal diode V_{oc} and the measured V_{oc} . The simulated ideal diode V_{oc} of a given cell from the $\text{FA}_{0.8}\text{MA}_{0.2}\text{PbI}_{3-y}\text{Br}_y$ series is calculated using Equation (1), with $V_{\text{oc,rad}} = 1.28$ V being obtained from Equation (2) and QY being set at the measured value for this cell. **Figure 5a** shows the current-voltage curves of selected cells representative of the whole series together with the corresponding V_{oc} , J_{sc} , FF and PCE. The different PCE of these cells mainly occurs due to their different FF and J_{sc} , while their V_{oc} is similar. The PCE, J_{sc} , FF, R_{s} and R_{sh} appear to be correlated, a high PCE occurring together with a high J_{sc} , high FF, low R_{s} and high R_{sh} (Supporting Information S6). δV seems to present a correlation with these photovoltaic parameters, as shown in **Figure 5b** where δV tends to decrease when PCE increases.

By combining the information from **Figure 5b** and **Figure 2**, it comes that the cells with a high PCE present a low QY and a low δV . On the opposite side, cells with a low PCE present a high QY and a high δV . This suggests that trap removal (high QY) occurs together with the formation of energy barriers that lower the PCE and induce an internal voltage drop (high δV). In particular, the lowered PCE is linked with a degraded charge extraction (low J_{sc}). It is proposed that these three phenomena occur simultaneously when the perovskite contains an excess PbI_2 . Excess PbI_2 passivates electron traps in the perovskite and thus tend to increase the QY.^[32-35] If accumulated at the electron transport layer/perovskite interface, it introduces simultaneously

a negative energy mismatch with SnO_2 , and a positive mismatch with the perovskite, as shown in **Figure 5c**.^[36] Such opposite mismatches are responsible for an internal voltage drop due to the offset of the electron quasi - Fermi level^[19, 37-39] and a degraded electron extraction,^[40-41] respectively. Similar effects can be caused due to an excess PbI_2 at the perovskite/Spiro-OMeTAD interface. In such case, as also shown in **Figure 5c** the PbI_2 introduces a negative energy mismatch with the perovskite that may induce an internal voltage drop due to the offset of the hole quasi – Fermi level, and a positive energy mismatch that degrades hole extraction.^[39] The presence of excess PbI_2 at both interfaces in the cells with a high QY, low PCE and high δV is confirmed by scanning electron microscopy (Supporting Information S7). In the corresponding microscope image, the bright regions stand for PbI_2 , as shown previously in other publications.^[13, 42, 43]

These findings go along the same line as previous reports,^[34] which showed that having the right amount of PbI_2 (not too much, not too few) in a PSC is necessary for an optimal cell performance. They also provide an example of how the variability of the two-step fabrication method can affect the perovskite composition and structure and thus the device performance. In other works, for example, the employed two-step approaches was shown to induce a PbI_2 deficiency^[34] or microscale inhomogeneities^[44] affecting the energy band alignment in the cell, hence lowering the V_{oc} .

5. Dominant non-idealities in cells from the literature

In the previous sections, the non-idealities that concur to limiting the V_{oc} of our cells were observed: non-radiative recombination (limits QY), parasitic absorption (limits QY), energy barriers (introduces a voltage loss δV with respect to the ideal diode behaviour), and analysed the contribution of these non-idealities. For the sake of completeness, a similar analysis is now

provided for the cells reported in Ref. 15 and 16, which present layered structures different from ours and were fabricated following different methods. This analysis gives insights into the impact of the cell structure and fabrication method on the different non-idealities and thus on V_{oc} . Remind that the measured V_{oc} and QY of these cells are shown in **Figure 2d** together with their calculated ideal diode $V_{oc} = f(QY)$ relations. Their corresponding energy diagrams and calculated $QY = f(\eta_{int})$ diagrams are given in Supporting Information S8.

For the cells of Ref. 15 (FTO/TiO₂/MAPbI₃ or Cs_xFA_yMA_{1-x-y}PbI₃/Spiro-OMeTAD/Au, Figures S8.1 and S8.2, respectively), the authors measured relatively high QYs (4-5%) resulting from an efficient reduction of non-radiative recombination. Nevertheless, their cell structure included a 500 nm thick FTO layer generating an important parasitic absorption. This parasitic absorption would limit the QY to 40% if non-radiative recombination was fully rubbed out. Moreover, they reported a significant δV that they tentatively attributed to losses at contacts, yet without further detail. Finding the origin of such δV is not straightforward. However, in the case of their Cs_xFA_yMA_{1-x-y}PbI₃ cell, a strong energy mismatch occurs at the perovskite/hole transport layer. In the case of their MAPbI₃ cell, the dominant energy mismatch occurs at the electron transport layer/FTO interface.

In Ref. 16 (ITO/PTAA/MAPbI₃/PCBM/Ag, **Figure S8.3**), the authors realized an efficient trap passivation by employing PTAA and PCBM charge transport layers, thus enabling a relatively high QY (5%) for their cells. This passivation, together with the material choice enabling a stair-like energy profile across the device with relatively small energy mismatches at the perovskite interfaces, led to a negligible δV . The ITO layer was thinner than usual, thus reducing the probability of parasitic absorption in this layer. In fact, parasitic absorption mainly occurs in the PCBM layer, which presents a significant optical absorption in the spectral region

of the MAPbI₃ perovskite fluorescence. Parasitic absorption in the PCBM would play a central role in limiting the QY of this type of cell to 25% if non-radiative recombination was fully rubbed out. Therefore, the PCBM layer has at the same time a positive effect (passivation) and a negative effect (parasitic absorption). This example, together with the trends observed in our cells, demonstrate that a device design approach thought to reduce one of the non-idealities may enhance the others.

6. Conclusions and outlook

Summarizing, the complete FA_{0.8}MA_{0.2}PbI_{3-y}Br_y solar cells considered in this work present *external quantum yields* QYs ranging from 0.1 to 3% and V_{ocs} from 1 to 1.13 V. These values, while being rather high compared with the literature, are far from optimal. In particular, the measured V_{ocs} are significantly lower than V_{oc,rad} (1.28 V). The first reason to that is the low QY of the cells. It was found that such low QY results in an important part from non-radiative photocarrier recombination at long-lived traps in the cell. It was also predicted that not only non-radiative recombination limits the QY of complete solar cells. If non-radiative recombination was suppressed, the QY would be far from reaching its maximal value because of parasitic absorption, first in the ITO front electrode and second in the Au mirror. The second and less expected reason to the non-optimal V_{oc} of the cells is a deviation from the ideal diode behaviour. This deviation is materialized by a voltage loss δV , which increases with QY. This shows that too efficient trap passivation in our cells (likely mediated by excess PbI₂), while being positive for QY, introduces energy barriers that are detrimental to the V_{oc} and cell efficiency. In fact, our champion cell, with a PCE of 19.6% (Supporting Information S9), presents a low level of trap passivation with a QY lower than 1% under 1 sun-equivalent illumination. After identifying the non-idealities that limit the V_{oc} of our cells and addressing their relative impact, their role in devices reported in the literature was discussed. It came from

this discussion that the cell structure and preparation method have important effects on these non-idealities, and that an approach thought to rub out one of them may enhance the others.

In conclusion, our study provides guidelines for future works to design efficient PSCs approaching $V_{oc,rad}$. The devices should be optimized in a holistic way taking into account both electronic and optical aspects. Hereafter a list of important requisites was made: (i) The layers constituting a cell must be chosen to enable a suitable band alignment, i.e. minimal energy barriers across the device. Note however that theoretical works suggested that energy barriers can be tolerated at interfaces showing very low density of traps. ^[39] (ii) The non-active layers must present an as low optical absorption as possible in the spectral region of the perovskite emission to minimize parasitic absorption. For instance, using ITO or PCBM should be avoided, and high - quality mirrors should be used. If no fully transparent material can be used, a mitigation solution may consist in thinning down the layers responsible for parasitic absorption. (iii) Efficient trap removal must be achieved to minimize non-radiative recombination, without introducing energy barriers.

Supporting Information

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

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Figures

Figure 1. Structure and optical properties of the perovskite solar cells. (a) Typical structure of the fabricated cells (scanning electron microscope image). (b) Spectrum of the absorption coefficient α of the FA_{0.8}MA_{0.2}PbI_{3-y}Br_y perovskite and typical fluorescence spectrum of the cells.

Figure 2. V_{oc} and QY of the perovskite solar cells: measurements and full-wavector generalized detailed balance simulations. (a) Scheme of the setup for QY measurements. (b) Solar cell structure considered to compute V_{oc} in the simulations. θ_{sun} is the aperture angle of the incident sunlight cone. (c) $V_{\text{oc,rad}}$ calculated from Equation (2) as a function of the perovskite layer thickness. (d) Measured V_{oc} and QY of our $\text{FA}_{0.8}\text{MA}_{0.2}\text{PbI}_{3-y}\text{Br}_y$ solar cells (black dots), of $\text{Cs}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ (green triangle) and MAPbI_3 (orange triangle) cells from Ref. 15, and of the MAPbI_3 cell from Ref. 16 (orange square). The black dashed line is a guide for the eye to show the experimental $V_{\text{oc}} = f(\text{QY})$ relation for our cells. The solid lines represent the simulated ideal diode $V_{\text{oc}} = f(\text{QY})$ according to Equation (1) with $V_{\text{oc,rad}}$ obtained from Equation (2) for each type of cell: our $\text{FA}_{0.8}\text{MA}_{0.2}\text{PbI}_{3-y}\text{Br}_y$ solar cells (black line), $\text{Cs}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ solar cell from Ref. 15 (green line), MAPbI_3 solar cells from Ref. 15 and Ref. 16 (orange line). As an example, the voltage loss δV is shown in (d) for one of our $\text{FA}_{0.8}\text{MA}_{0.2}\text{PbI}_{3-y}\text{Br}_y$ cells.

Figure 3. Excitation intensity-dependent QY of our perovskite solar cells. QY of our $\text{FA}_{0.8}\text{MA}_{0.2}\text{PbI}_{3-y}\text{Br}_y$ solar cells measured for different incident light intensities I_{exc} plotted as a function of the corresponding QY measured under $I_{\text{exc}} = 1$ sun. The full lines have been obtained by fitting the measured data (symbols).

Figure 4. Effect of parasitic absorption on the QY for our perovskite solar cells. QY calculated as a function of η_{int} according to Equation (3) with the cell structure and layer thicknesses of **Figure 1a** and experimentally-determined dielectric functions for the different layers (black solid line, real dielectric functions), with optical absorption cancelled in the ITO (blue solid line, no loss in ITO), with optical absorption cancelled in the ITO and Au (red solid line, no loss in ITO and Au). The losses in ITO and Au are shown as coloured areas (blue and pink, respectively).

Figure 5. Origin of δV in our perovskite solar cells. (a) Current-voltage curves of selected solar cells representative of the whole series. (b) Voltage loss δV plotted as a function of PCE. The solid line was obtained by fitting the experimental data points. (c) Energy diagrams for $FA_{0.8}MA_{0.2}PbI_{3-y}Br_y$ (FAMABr) solar cells without and with passivating PbI_2 layer.

To reach the theoretical photovoltaic performance limit, perovskite solar cells must re-emit all the photons absorbed by their active material. It was demonstrated that this does not only require an efficient perovskite passivation but also minimizing fluorescence re-absorption in the electrode materials. Also it is shown that excessive passivation, while enhancing the cell fluorescence, may introduce interfacial energy barriers lowering the cell performance.

Fluorescence management in perovskite solar cells

M. Kramarenko,* C. G. Ferreira, G. Martínez-Denegri, C. Sansierra, J. Toudert,* J. Martorell

Relation between fluorescence quantum yield and open-circuit voltage in complete perovskite solar cells