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4-Terminal Tandem Photovoltaic Cell Using Two Layers of PTB7:PC₇₁BM for an Optimal Light Absorption

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Abstract:

A 4-terminal architecture is proposed in which two thin active layers (< 100 nm) of PTB7:PC₇₁BM are deposited on a two-sided ITO covered glass substrate. By modelling the electric field distribution inside the multilayer structure and applying an inverse solving problem procedure we designed an optimal device architecture tailored to extract the highest photocurrent possible. By adopting such 4-terminal configuration we numerically demonstrated that even when the two sub-cells use identical absorber materials, the performance of the 4-terminal device may overcome the performance of the best equivalent single junction device. In an experimental implementation of such 4-terminal device we demonstrate the viability of the approach and find a very good match with the trend of the numerical predictions.

1. Introduction

Recent progress in the performance of solution-processed organic solar cells has consolidated them as one of the alternatives to the standard photovoltaic (PV) technology.¹ In Organic PV materials, a large light absorption coefficient is combined with the mechanical flexibility of plastic materials.² This opens up the possibility to solar cell fabrication at room temperature with low-cost deposition techniques compatible with the use of flexible substrates. Another very interesting feature of the organic layer in a PV cell is its partial colorless transparency to visible light.³ Both, flexibility and a colorless transparency are key features for an optimal building integrated PV that only the organic technology may be able to offer.

In recent years, the power conversion efficiency (PCE) of single junction organic solar cells has been rising steadily by the implementation of several strategies that, among others, include an optical optimization,⁴ plasmonic enhancement,⁵⁻⁸ nanostructuring of active layers,⁹ new polymers design¹⁰⁻¹³ or interfacial engineering.¹⁴⁻¹⁵ With the PTB7:PC₇₁BM the average efficiency from many different research groups best cells is 7.98%¹⁶ while a certified

efficiency above 9 % has been reported once.¹⁴ However, further increasing the PCE is severely limited by the low charge carrier mobility.¹⁷ Many different factors including molecular packing, disorder or low crystallinity, presence of impurities, temperature, electric field, charge-carrier density, size/molecular weight and pressure can degrade such mobility.¹⁸ The detrimental effects become more apparent for thicker blends by causing a dramatic reduction in fill factor (FF) for the majority of polymers.¹⁹ Recent work explains that for sufficiently thick cells space charge becomes more important because it creates field free regions with low collection efficiency. Doping is suggested as the dominant factor on the space charge and the thickness dependence of the performance.²⁰ Thus increasing light absorption by means of thicker blends is not a viable alternative to obtain higher efficiencies. An interesting approach to increase solar cells efficiency is the tandem configuration obtained by stacking different materials with complementary absorption to harvest energy from a larger portion of the solar spectra.^{21,22} In a few occasions it has been shown that with the use of tandem or triple junction devices one may overcome the efficiency of the optimal single junction device,^{23,24} setting the PCE for organic tandem cells at above 10 %.²⁴

Tandem solar cells design and fabrication is, however, a demanding task due to the requirement of a suitable interconnection layer (ICL) for charge recombination. The ICL must guarantee a low resistance connection that introduces no electrical potential loss, but it also has to be robust to protect the underlying layers from damage when subsequent solution processing steps to fabricate the second cell are applied.^{25,26} Furthermore, the interlayer must be transparent to avoid optical losses. Additionally, the difficulty in testing the two or more cells independently makes the optimization of tandem cells a challenging task.

Herein, we report the design and fabrication of an optically optimized 4-terminal device in which two single junction sub-cells are fabricated using the same blend and are separated by a SiO₂ dielectric spacer. With this architecture we eliminate the need of an ICL and replace it

by an external connection that guarantees a proper recombination. Applying an inverse solving problem procedure we numerically designed a device architecture to obtain an optimal PV performance. In such 4-terminal configuration even when the two sub-cells use identical absorber materials one may improve the light harvesting capacity of the best single device. In an experimental implementation of the 4-terminal device using the same polymer blend for both sub-cells we find a very good match with the trend of the numerical predictions.

2. Materials and methods

We fabricated a 4-terminal cell by depositing each inverted sub-cell on either side of a bi-coated ITO glass substrate. In this configuration the dielectric spacer is a 1.1 mm thick piece of glass where a patterned ITO was deposited on one side and a second non-patterned ITO was deposited by RF sputtering on the other side, to obtain a bi-coated ITO substrate. The bi-coated ITO substrates were solvent cleaned and treated with ultraviolet-ozone for 10 minutes, each side. Fabrication of the bi-coated cells was successfully carried out without damaging any of the two sides using a lightweight aluminum holder, specially designed for the bi-facial spin coating processes. Such lightweight holder prevented any scratches on the deposited films by holding the samples only from the edges during spin coating. Additionally, to further protect the top and bottom surfaces vertical sample holders instead of petri dishes were used during the transportation of the substrates through the different processing steps.

The precursor for the sol-gel ZnO was prepared by dissolving zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Aldrich, 99.9%, 1 g) and ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, Aldrich, 99.8%, 10 mL) under stirring for at least 12 h.²⁷ Afterwards, it was spin-coated on the ITO and annealed at 150°C

for 10 minutes. The process was repeated for the other side of the ITO substrate, obtaining 30 nm thickness films. The samples were then transferred into a glovebox for further fabrication steps. An active layer of PTB7:PC₇₁BM, at a concentration of 10 mg/ml (1:1.5) dissolved in chlorobenzene, was spin-coated on one side of the ITO bi-coated substrate. 3% v/v diiodooctane (DIO) was added to the blend solution at least 1 h before spin coating. The active layer of 90 nm was left to dry in vacuum for 1 hour, followed by the evaporation of MoO₃ and a thick Ag electrode. After removing the samples out of the evaporation chamber, a second active layer of 90 nm was spin-coated on the other side of the substrate and left to dry in vacuum for 1 hour. A 3 nm MoO₃ layer was deposited prior to the evaporation of a thin Ag layer at a 6 Å s⁻¹ rate using a home-made holder cooled down to -5 °C. To finish the structure, another layer of MoO₃ was deposited on top of the device at a rate of 1 Å s⁻¹. Such last three layers formed the MoO₃/Ag(10nm)/MoO₃ (MAM) electrode with a four point probe measured sheet resistance of 7 ohms/square. The sub-cells were then removed from the inert atmosphere to be externally connected in series and characterized in air.

PCE of the fabricated devices was determined from current density – voltage curve measurements obtained under 1 sun AM 1.5G spectrum from a solar simulator (Abet Technologies, model Sun 3000). A calibrated monocrystal silicon reference cell from Rera Systems was used to monitor the solar simulator intensity. EQEs were measured using a QEX10 Quantum Efficiency Measurement System from PV Measurements.

3. Optical optimization

We consider a cell structure as the one shown in **Figure 1** consisting of two single junction solar cells separated with an intermediate dielectric spacer. The structure, corresponding to a 4-terminal device in a tandem configuration, is formed by two almost identical sub-cells on either side of a SiO₂ dielectric spacer. As indicated in the previous section, up to the Ag

electrode, the two sub-cells can be fabricated using the same processing steps and the same blend of PTB7:PC₇₁BM is used as photoactive material. The two sub-cells constructed in an inverted configuration use the same buffer layers, being the architecture of the anode the main difference among them. For the front cell such outer electrode is formed by the three layer MAM structure, while for the back sub-cell such electrode is a thick layer of Ag (cf. Figure 1). Light is entering into the structure through the MAM electrode front sub-cell while the back sub-cell is illuminated with the light not absorbed by the front cell.

An optimal light absorption by both sub-cells may be reached when the architecture of the entire device is optimized to enhance absorption in both active layers. For the design of such optimal architecture we used an optical model based on the transfer matrix to numerically calculate the field distribution and absorption within each layer.^{28,29,30} Incident light undergoes reflection, absorption and transmission at any of the layers of the device determined by the complex index and thickness of the given layer and the adjacent ones. The wavelength dependent complex refractive index for the layers used in our numerical analysis is given in the Supporting information. To optimize both cell architectures simultaneously we followed an inverse integration procedure in which the EQEs from both cells, for 24000 different combinations of layer thicknesses, were computed. The total number of combinations considered was determined by the number of different layer thicknesses considered for the active, HBL, thin silver and dielectric spacer layers which were varied within the intervals given in **Table 1**. The ITO, MoO₃, thick silver electrode thicknesses, as well as, the total thickness of active material were kept fixed. From the 24000 solutions obtained, the optimal one corresponds to the one exhibiting the largest short circuit current when the currents from both cells are matched within a 0.5 mA/cm². To avoid any detrimental effect over the FF when real devices were to be fabricated, we restricted the thickness of either of the two blend layers to a maximum of 130 nm.

In our calculations we considered a total active layer thickness ranging from 130 nm to 210 nm. The largest J_{sc} was obtained when the total blend thickness was 190 nm, distributed in a front sub-cell blend of 88 nm, 90 nm and 91 nm, together with a back sub-cell blend of 102 nm, 100 nm and 99 nm, and an Ag thickness of 10 nm, 6 nm and 4 nm, respectively. The dielectric spacer and ZnO thicknesses are also different depending on the thickness of the front silver electrode. The layer thicknesses for the optimal 4-terminal device are listed in **Table 1**.

The optimal J_{sc} in terms of the total active layer thickness for three different configurations of the MAM electrodes and a configuration with ITO instead of MAM is shown in **Figure 2a**. As seen in Figure 2a, the J_{sc} for the 4-terminal devices is strongly dependent on the front electrode, exhibiting a very good performance when the silver layer in the MAM is thinned down to 4 nm. This performance could be further improved if an electrode with higher transparency such as ITO were to be used. A comparison of the transmissions for the different MAM electrodes and the ITO is shown in Figure 2b. Note that the 4, or 6 nm thick Ag and ITO front electrodes of the 4-terminal devices exhibit a significantly improved performance relative to the best equivalent single junction. For the optimal 4 nm Ag MAM device, the calculated improvement relative to the best single junction reaches 7.1% and for the ITO device the improvement is almost doubled to 13 %. Remarkably, such enhanced performance is obtained using the same blend in both sub-cells and, in a device configuration where the thickness for such layers is less than 100 nm.

The numerically calculated external quantum efficiencies (EQEs) for both sub-cells are shown in **Figure 3a** for the optimal configuration when the thickness of the Ag layer in the MAM electrode is 4 nm. At long wavelengths above 650 nm light absorption is larger in the back sub-cell while at the opposite edge, for short wavelengths below 500 nm, light absorption is dominated by the front sub-cell. In the entire wavelength range a local

maximum in the EQE for the front sub-cell corresponds to a local minimum for the EQE in the back sub-cell and viceversa. This kind of behavior is weakly dependent on the transparency of the light entrance electrode. In **Figure 3b** we show the EQEs for the optimal configuration when the thickness of the Ag electrode is 10 nm. Again, we observe that the EQE at long wavelengths is larger for the back sub-cell while at shorter wavelengths is larger for the front sub-cell. As can be seen in Figure S2 of the SI, the observed trend in the EQE wavelength distribution between the two sub-cells is maintained when the thickness of the spacer layer is increased.

4. Results and discussion

The optical optimization of the multilayer structure disguises the spectral dependence to the active blend extinction coefficient leading to an EQE which is strongly linked to the electric field distribution inside the solar cell. The normalized field intensity distribution map is shown in **Figure 4a** as a function of wavelength and position inside the solar cell for the optimal configuration. To enhance photon harvesting, the electric field intensity must be maximized within the active layers inside the structure. As seen in **Figure 4a**, such electrical field intensity is clearly enhanced within the back sub-cell active layer for most of the wavelength range. Because of material dispersion, this confinement of the largest field density within the active layer is not so apparent for the front sub-cell. However, when the cell architecture is optimal, as in **Figure 4a**, the minima in field intensity for the front cell are, to a certain degree, compensated with field intensity maxima in the back sub-cell. For comparison, in **Figure 4b** the field intensity distribution map is shown for a non-optimized configuration with the same total thickness of active material. Note that in this case the field intensity in the active layer of the front sub-cell is weaker for almost the entire wavelength range being very apparent that the thickness of the active layer is thinner than it should be.

This decrease in electric field intensity translates into a reduced photocurrent for such front sub-cell, thus limiting the total short-circuit current when a serial connected device is considered.

One of the advantages of the 4-terminal tandem configuration we study over the standard 2-terminal tandem is that the performance of the two sub-cells can be studied independently from each other when already integrated in the entire device. An average of the PV parameters from 7 devices of 0.06 cm^2 is given in **Table 2**. In terms of photocurrent generation both sub-cells in the implemented architecture exhibited a rather good match which is important when the cells are connected externally in a series configuration. The match of the voltages we obtained is also desirable when the cells are connected in parallel. On the other hand, we observe that the FF for the front cell is slightly worse than the one for the back cell which may be attributed to the lower conductivity of the electrodes for the front cell when compared to the back thick silver electrode.

The J-V characteristic curves for the front and back cells measured independently and externally connected in series are shown in **Figure 5**. We performed a statistical study to determine the average values for the J_{sc} , V_{oc} and FF of the series connected devices. As expected the J_{sc} is limited to the smallest one of the two sub-cells, the V_{oc} is very close to two times the average V_{oc} for the single junction sub-cells and the FF is slightly larger than the average FF for the single junction sub-cells. In other words, no degradation in the electrical performance is observed for the 4-terminal device when connected in series relative to the single junction devices.

The absorbing layers were fabricated following the same recipe to obtain thicknesses of around 90 nm for both sub-cells, which corresponds to the thicknesses predicted by the numerical modeling of the optimal configuration. The layer architecture of the entire

fabricated device is given in **Table 1**. At present, there are several experimental limitations that prevent the fabrication of the optimal device according to the results shown in **Figures 2a** and **3a**. Such limitations include: a lack of control at the nanoscale over the thickness of the dielectric spacer; ultrathin metallic layers typically favor the formation of non-continuous or granular films with low conductivity causing the electrical properties of the MAM electrodes to degrade rapidly when the thicknesses below 10 nm are considered;³¹ in some cases the optimal thickness for buffer layers extracted from the optical simulation can not be obtained as, for instance, when the ZnO layer is prepared by sol-gel. Among these, the limited transparency of the 10 nm Ag front electrode is the largest hurdle for 4-terminal devices to overcome the performance of the single junction cell.

The experimentally measured EQEs for the front and back sub-cells are shown in **Figure 6**. Note that the interference like pattern observed in **Figures 3a** & **3b** is washed out because of the large thickness of the dielectric spacer which is around 1 mm in the fabricated devices. However, the overall trend of the numerically optimized EQEs is maintained in the experimentally implemented devices. As seen in **Figure 6**, for wavelengths larger than 700 nm the EQE of the back sub-cell is large while for wavelengths below 500 nm the EQE of the front sub-cell dominates. In the region in between, the EQEs alternate.

5. Conclusion

By numerically determining the optimal layer configuration in a 4-terminal tandem cell of the same active blend we demonstrated that it is possible to obtain devices that perform better than single junction devices with an equivalent thickness of active material. In other words, the configuration we proposed is optimal to increase light absorption by using active layers with thicknesses below 100 nm which is the limit thickness to reach good electrical

performance for the majority of the low band gap polymer cells.³² We have used the optical simulations as a guideline to fabricate a proof of principle 4-terminal device using PTB7:PC₇₁BM blend as the blend material for the active layers of two inverted sub-cells. We fabricated the two sub-cells on each side of a 1.1 mm thick glass substrate coated on both sides with ITO. The overall trend of light harvesting capacity seen in the experimentally measured EQEs for the two sub-cells of the fabricated devices is in agreement with the EQEs predicted by the optical model. We have demonstrated that no degradation in the electrical performance of the 4-terminal cell relative to the single junction devices is seen when the two sub-cells are connected in a series configuration. At present, the strongest limitation to obtain 4-terminal devices with a performance overcoming the performance of an equivalent single junction device is in the limited transparency of the front semi-transparent electrode. Provided that semi-transparent electrodes that can be deposited on top of polymer cells, such as electrodes composed of Ag nanowires³³ or graphene,³⁴ were to be used, the 4-terminal device performance would be considerably improved and most certainly surpass the one from the single junction device. We demonstrated this numerically by considering an ITO front electrode. Finally, one should note that the 4-terminal device has some advantages over the traditional tandem series connected approach. Cells can be connected either in series or in parallel while current or voltage matching would not strictly necessary if the cells were made to operate independently.

Supporting Information

Refractive indexes for the different materials used in the numerical simulations. EQE for sub-cells when the thickness of the spacer layer is increased. This material is available free of charge via the Internet at <http://pubs.acs.org>

Acknowledgements

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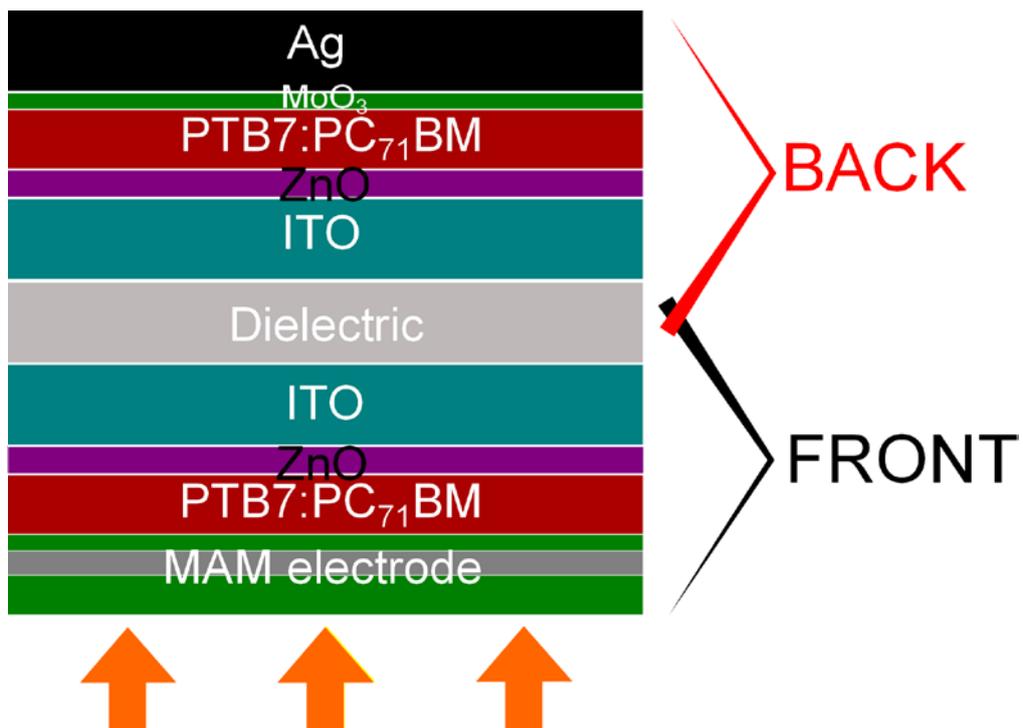
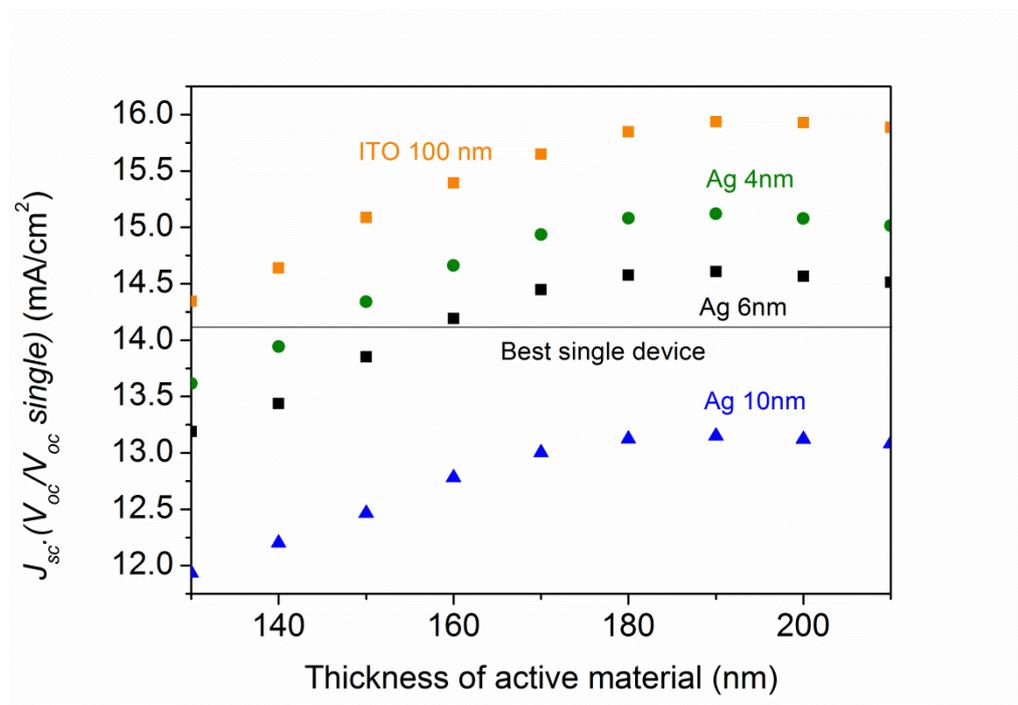
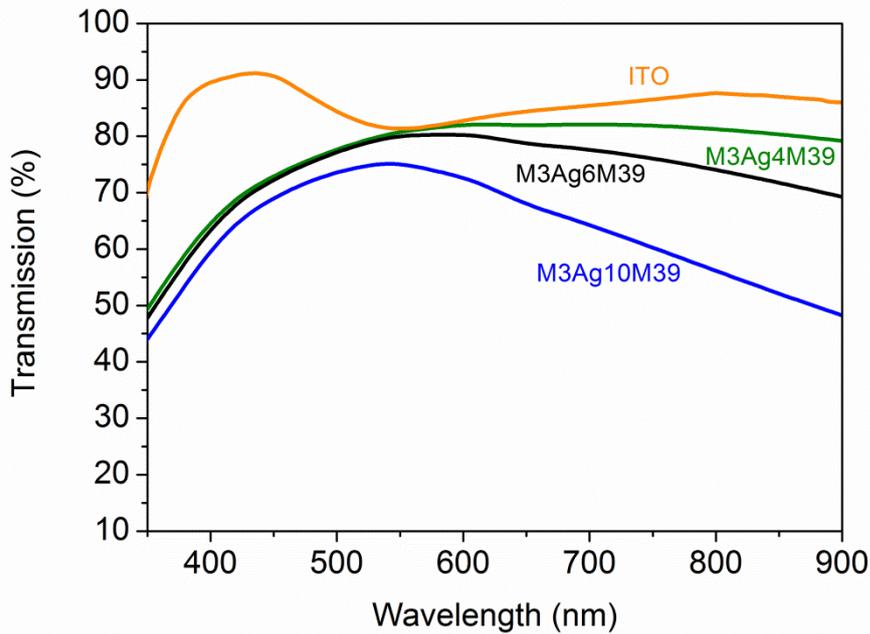


Figure 1. Device architecture.

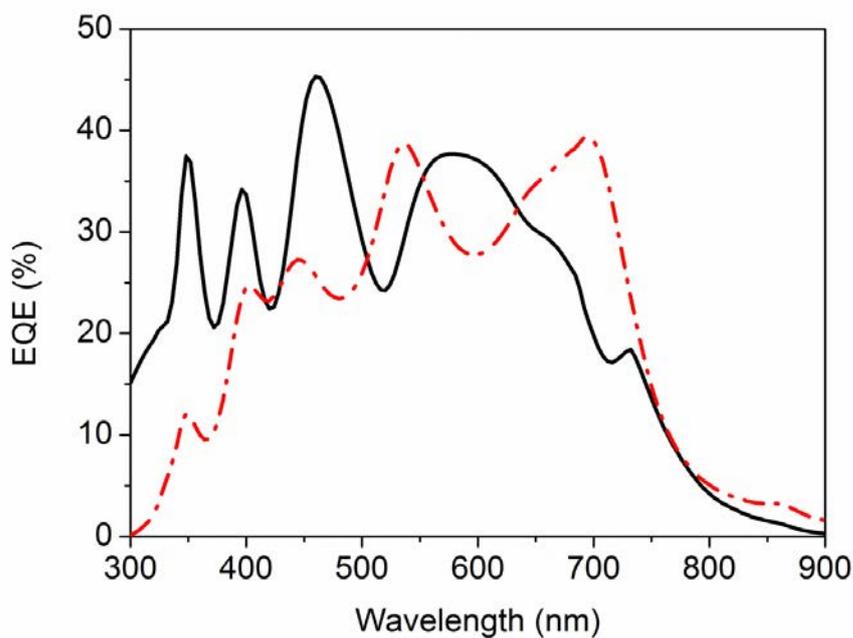


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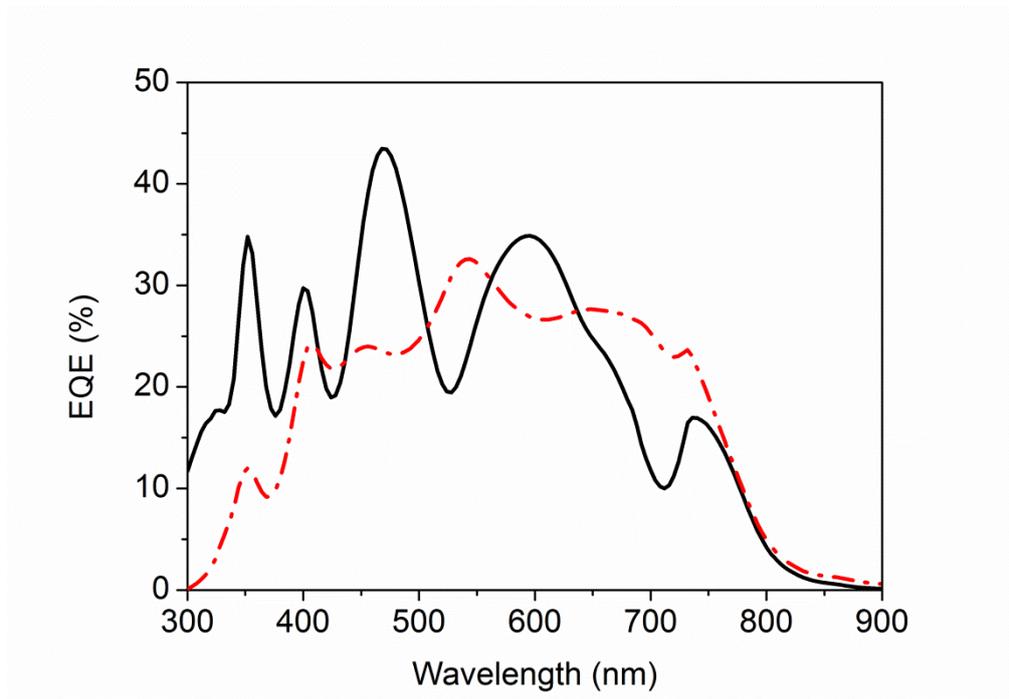


b)

Figure 2. a) Calculated Power density normalized against the V_{oc} of a single device in terms of the total thickness of active material for the 4-terminal devices when the Ag thickness in the MAM electrode is 10 nm (blue triangles), 6 nm (black squares), 4 nm (green circles) and ITO of 100 nm (orange squares). The case of the best single device is shown in a straight line. In the graph, the power density normalized to the single device V_{oc} is used to be able to compare it with the two series connected cells which would exhibit a V_{oc} equivalent to the sum of the V_{oc} from two single junction cells. b) Modeled spectral transmission of MAM electrodes depending on the silver thickness and ITO.

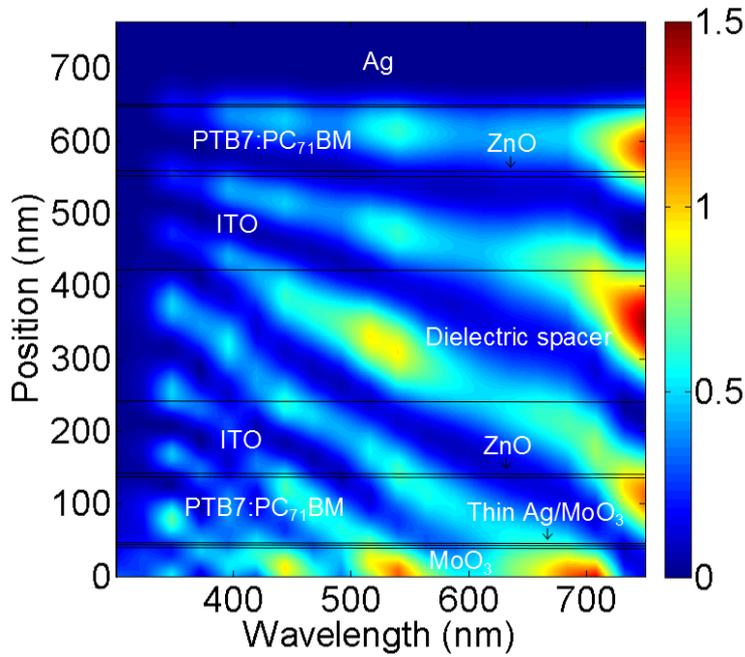


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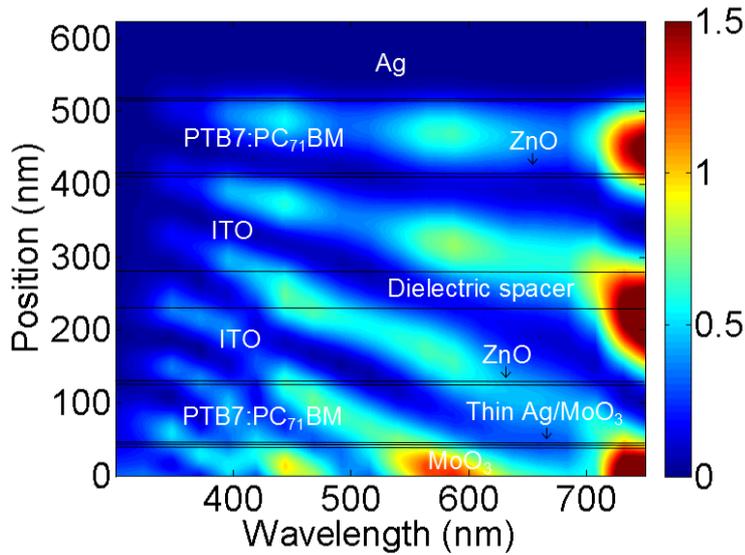


b)

Figure 3. Numerically calculated EQE for front sub-cell (black continuous line) and for the back sub-cell (dash-dotted line) for (a) a MoO₃(39)/ Ag (4)/ MoO₃(3)/PTB7:PC₇₁BM (91)/ZnO(5)/ITO(100)/Dielectric spacer (182)/ITO(130)/ZnO (8.75)/ PTB7:PC₇₁BM (99)/ MoO₃(3)/ Ag (100) nm architecture and (b) for a MoO₃(39)/ Ag (10)/ MoO₃(3)/PTB7:PC₇₁BM (91)/ZnO(5)/ITO(100)/Dielectric spacer (182)/ITO(130)/ZnO (8.75)/ PTB7:PC₇₁BM (99)/ MoO₃(3)/ Ag (100) nm architecture.



a)



b)

Figure 4. Calculated electric field intensity normalized with respect to the incident field intensity as a function of wavelength (a) for an optimized architecture with the following thicknesses in nm (a) a MoO₃(39)/ Ag (4)/ MoO₃(3)/PTB7:PC₇₁BM (91)/ZnO(5)/ITO(100)/Dielectric spacer (182)/ITO(130)/ZnO (8.75)/ PTB7:PC₇₁BM (99)/ MoO₃(3)/ Ag (100) and (b) non-optimized architecture with the following thicknesses in nm MoO₃(39)/ Ag (4)/ MoO₃(3)/PTB7:PC₇₁BM (80)/ZnO(5)/ITO(100)/Dielectric spacer (50)/ITO(130)/ZnO (5)/ PTB7:PC₇₁BM (110)/ MoO₃(3)/ Ag (100). The non-optimized architecture leads to a current mismatch, originated from the bottom sub-cell which generates a photocurrent above 1mA/cm² with respect to the front sub-cell. The limiting current for this architecture remains below that of the optimized device.

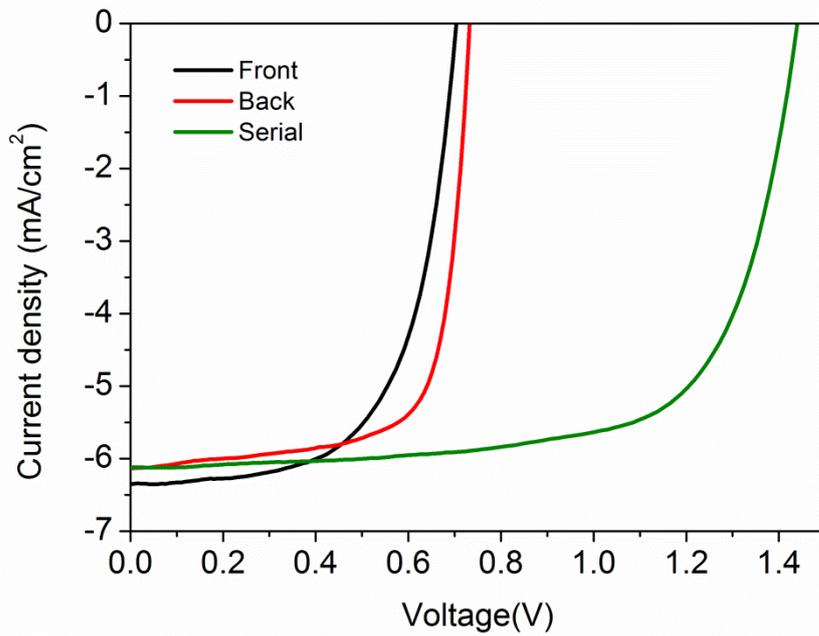


Figure 5. IV curves of front sub-cell (black), back sub-cell (red) and serial connected (green). The curves correspond to the best device.

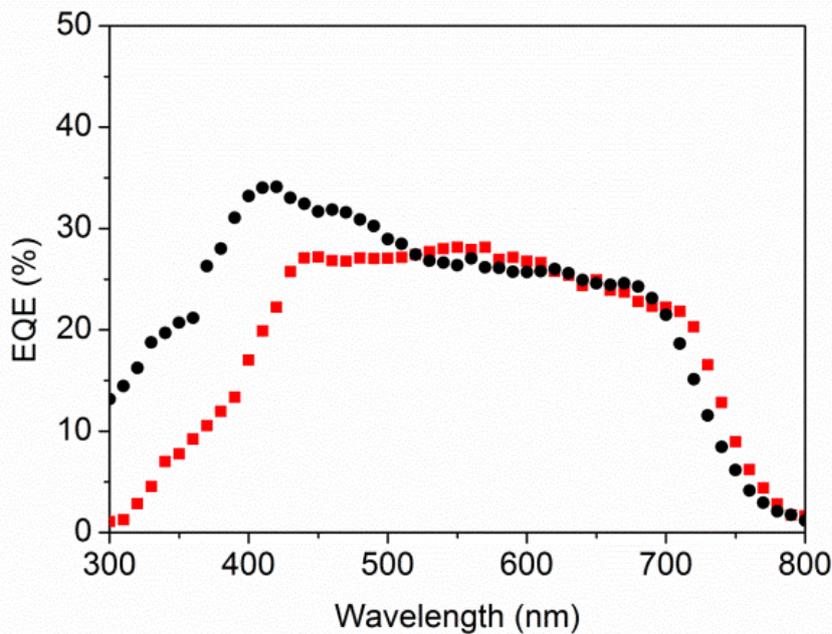


Figure 6. Measured EQE for front sub-cell (black dots) and for the back sub-cell (red dots). Note that the large thickness of the dielectric spacer in between the two sub-cells eliminates the oscillatory behavior seen in the numerical prediction shown in Figure 3b.

Table 1. Layer thicknesses ranges used in the numerical calculations and layer thicknesses for the optimal and fabricated 4-terminal device.

Layer	Range [nm]	Optimal device [nm]	Experimental values [nm]
Total Active Layer (TAL)	130 - 210	190	180
MoO ₃	Fixed at	39	39
Ag	4 – 6 - 10	4	10
MoO ₃	Fixed at	3	3
PTB7:PC ₇₁ BM top (AL1)	70 - 100	91	90
ZnO	Fixed at	5	30
ITO	Fixed at	100	135
D. spacer	50 - 290	182	1100 μ m
ITO	Fixed at	130	140
ZnO	5 - 30	8.75	30
PTB7:PC ₇₁ BM bottom (AL2)	TAL- AL1	99	90
MoO ₃	Fixed at	3	3
Ag	Fixed at	100	100
Total Active Layer (TAL)	130 - 210	190	180

Table 2. Solar cells parameters.

Cell	J _{sc} [mA/cm]	V _{oc} [V]	FF [%]	PCE [%]
Front	6.36±0.28	0.703±0.007	62.42±2.46	2.79±0.13
Back	6.13±0.57	0.732±0.010	72.44±3.07	3.25±0.43
4T Series	6.13±0.53	1.439±0.007	69.19±3.14	6.10±0.42
Ratio of the 4T in series relative to single sub-cells	-	0.9979 ^{a)}	1.0392 ^{b)}	-

^{a)} The average of the sum of the front and back sub-cells V_{oc} in the 4-terminal devices is compared to the average of the measured V_{oc} for the serial connected cells. ^{b)} The average FF of the independent sub-cells is compared to the FF of the serial connected 4-terminal devices.

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