All-oxide MoOx/SnOx charge recombination interconnects for inverted organic tandem solar cells

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All-Oxide MoO\textsubscript{x}/SnO\textsubscript{x} Charge Recombination Interconnects for Inverted Organic Tandem Solar Cells

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Multijunction solar cells are designed to improve the overlap with the solar spectrum and to minimize losses due to thermalization. Aside from the optimum choice of photoactive materials for the respective sub-cells, a proper interconnect is essential. This study demonstrates a novel all-oxide interconnect based on the interface of the high-work-function (WF) metal oxide MoO\textsubscript{x} and low-WF tin oxide (SnO\textsubscript{x}). In contrast to typical p/n-type tunnel junctions, both the oxides are n-type semiconductors with a WF of 5.2 and 4.2 eV, respectively. It is demonstrated that the electronic line-up at the interface of MoO\textsubscript{x} and SnO\textsubscript{x} comprises a large intrinsic interface dipole (≈0.8 eV), which is key to afford ideal alignment of the conduction band of MoO\textsubscript{x} and SnO\textsubscript{x} without the requirement of an additional metal or organic dipole layer. The presented MoO\textsubscript{x}/SnO\textsubscript{x} interconnect allows for the ideal (loss-free) addition of the open circuit voltages of the two sub-cells.

There is a variety of recent reports on single junction organic solar cells (OSCs) with a power conversion efficiency (PCE) exceeding 10%.\textsuperscript{[1–4]} The highest efficiencies in single junction cells have been achieved in the so-called inverted device layout, where electrons are collected via the bottom (substrate) electrode while holes are extracted via the top contact.\textsuperscript{[5–7]}

Multijunction OSCs, e.g., tandem or triple cells, where two or three sub-cells with different photoactive layers are stacked and connected in series bear the potential to unlock efficiency levels beyond 15%.\textsuperscript{[8,9]} As of today, multijunction OSCs have been shown to reach a PCE of 13.8%.\textsuperscript{[10]}

Aside from the optimum choice of photoactive materials for the respective sub-cells along with a sophisticated optical design of the stacked device structure, a proper interconnect between the sub-cells is essential. In an inverted tandem solar cell, the holes extracted from the bottom sub-cell must recombine with the electrons stemming from the upper sub-cell, ideally without any loss of voltage and fill factor (FF). Thus, tandem cells involve an electronic interface between a hole extraction layer (HEL) and an electron extraction layer (EEL). Typical HEL materials are poly(3,4-ethylenedioxythiophene) polystyrene (PEDOT:PSS) or high-work-function (WF) transition metal oxides (TMOs)\textsuperscript{[11]} like MoO\textsubscript{3} \textsuperscript{[12]} or VO\textsubscript{2} \textsuperscript{[13]} as EEL, materials like titanium oxide (TiO\textsubscript{2})\textsuperscript{[14]} and zinc oxide (ZnO)\textsuperscript{[15,16]} have been established. More recently, Trost et al. reported SnO\textsubscript{2} as an advantageous EEL for OSCs.\textsuperscript{[17,18]} As an alternative, conjugated polyelectrolytes (CEEs) have been considered as EELs.\textsuperscript{[19,20]}

Aside from its electronic functionality, the interconnect must be optically transparent, and in the case of solution processed photoactive materials, the interconnect must concomitantly provide chemical protection for the bottom cell against dissolution due to the solvents involved in the deposition of the upper sub-cell. This set of requirements severely limits the freedom in the design of the interconnect and the choice of materials. The state of the art of interconnects for multijunction OSCs has been reviewed by several authors.\textsuperscript{[21–23]} A plethora of interconnects is based on PEDOT:PSS as HEL and TiO\textsubscript{2} or ZnO as EEL.\textsuperscript{[24,25]} However, PEDOT:PSS has been evidenced to be an origin of reliability issues in organic electronic devices\textsuperscript{[12,26,27]} and it suffers from a limited optical transmittance, which becomes a significant issue if more than one interconnect is required, e.g., in a triple junction cell.\textsuperscript{[28]} Due to a lack of promising alternatives, most multijunction OSCs still rely on the use of PEDOT:PSS in their interconnects.\textsuperscript{[29,30]}

The pH-neutralized variant (n-PEDOT:PSS) is sometimes used to avoid etching of the adjacent ZnO layer.\textsuperscript{[31]} For n-PEDOT:PSS a substantially lowered work function, about...
0.5 eV lower than that of conventional PEDOT:PSS, has been reported, which disqualified the material to properly interface to photoactive materials with deep highest occupied molecular orbital (HOMO) levels.\cite{41}

Substantial work has been devoted to replace PEDOT:PSS by a high-work-function TMO, e.g., MoO\textsubscript{x}, in next generation interconnect architectures. Interestingly, the one-by-one exchange of PEDOT:PSS by MoO\textsubscript{x} to form a MoO\textsubscript{x}/EEL interconnect did not result in satisfactory cell characteristics, and thus a thin metal layer (thickness: \textasciitilde 0.5–10 nm) had to be thermally evaporated in-between, e.g., MoO\textsubscript{x}/(Al, Au)/ZnO\textsuperscript{[31,34]} MoO\textsubscript{x}/Al/TiO\textsubscript{x}\textsuperscript{[35]} or MoO\textsubscript{x}/Ag/CPE.\textsuperscript{[36,37]} The addition of the metal mitigates the formation of a detrimental counter diode, helps to form an ohmic contact\textsuperscript{[33]} and increases the number of “recombination centers” in the recombination contact.\textsuperscript{[18,39]}

In any case, the metal layer critically affects the optical properties of the interconnect and severely compromises its transmittance. Moreover, it is challenging to deposit thin metal films with sub-nm control and large-area homogeneity.

Shim et al. reported a metal-free, oxide-based interconnect MoO\textsubscript{x}/Al:ZnO/polyethylenimine ethoxylated (PEIE).\textsuperscript{[40]} The Al:ZnO has been prepared by atomic layer deposition (ALD) as a so-called nanolaminate of Al\textsubscript{2}O\textsubscript{3} and ZnO. The PEIE polyelectrolyte was important to properly interface to the fullerene acceptor of the upper sub-cell. The interconnect afforded tandem cells with a PCE of 6.5%, which however did not significantly exceed that of the single junction devices (PCE = 6.4%). Lu et al. have reported an interconnect consisting of MoO\textsubscript{x}/“dipole layer”/TiO\textsubscript{x}.\textsuperscript{[41]} Here, the “dipole layer” was formed by a conjugated polymer with highly polar amino-N-oxide functionalized side groups.\textsuperscript{[42]} Without the insertion of the polar moiety, only extremely poor characteristics of the tandem cells were achieved.

In this communication, we demonstrate a novel all-oxide recombination interconnect, which is based on the interface of the high-WF metal oxide MoO\textsubscript{x} and low-WF tin oxide (SnO\textsubscript{2}). Remarkably, both oxides are n-type semiconductors with a WF of 5.2 and 4.2 eV, respectively. The electronic line-up at the interface of MoO\textsubscript{x} and SnO\textsubscript{2} comprises a large intrinsic interface dipole (\textasciitilde 0.8 eV), which affords near to ideal alignment of the conduction band of MoO\textsubscript{x} and SnO\textsubscript{2}, without the requirement of an additional metal or organic dipole layer. As a result, electrons extracted via the SnO\textsubscript{2} from the upper sub-cell are efficiently handed over from the SnO\textsubscript{2} to the MoO\textsubscript{x}. The actual recombination of electrons with holes takes place at the interface of organic/MoO\textsubscript{x} at the lower sub-cell. The mechanism of charge recombination in our tandem cells is in inverse analogy to that evidenced previously in multijunction organic light emitting diodes (OLEDs), where the individual light emitting units are connected by so-called charge generation layers which comprised high-WF TMOs.\textsuperscript{[43]} Moreover, the working principle in our interconnects contrasts the established picture used in the case of highly doped organic p-/n-type tunnel junctions, which have been frequently used in tandem cells.\textsuperscript{[39]}

There, charge recombination occurs in the center of the interconnect as electrons tunnel from the lowest unoccupied molecular orbital (LUMO) of the n-doped electron transport layer to the HOMO of the p-doped hole transport layer.

The presented MoO\textsubscript{x}/SnO\textsubscript{2} interconnect allows for the ideal addition of the open circuit voltages (\textit{V}\textsubscript{oc}) of the two sub-cells. In stark contrast to the vast majority of TiO\textsubscript{x} of ZnO based tandem interconnects, which require activation by UV light (“UV light-soaking”),\textsuperscript{[44,45]} our interconnect functions even in the absence of UV spectral components. We reason that this novel all-oxide interconnect will be generally applicable for the design of monolithically integrated organic multijunction solar cells.

The layer sequence of the inverted tandem OSCs in this study is shown in Figure 1a. The bottom sub-cell is based on poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDPTBT);[6,6]-phenyl-C71-butyr acid methyl ester (PC\textsubscript{70}BM) as photoactive material, while the upper sub-cell comprises poly[(2,5-bis(2-hexyldecyl)-2,3,5,6-tetraydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]-alt-[(2,2′-5′,2′′-terthiophene)-5,5′-diyl]) (PDPPT3T);[6,6]-phenyl-C61-butyr acid methyl ester (PC\textsubscript{60}BM).\textsuperscript{[46]} The molecular structure of the donor polymers and the respective absorption spectra of the photoactive layers are shown in Figure 1b,c. We decided to use well-established photoactive materials\textsuperscript{[20]} to test and to demonstrate the functionality of our novel all-oxide interconnect. We are aware that these photoactive materials may impose limits for the achievable overall efficiency of the tandem device, but we
want to note that the presented interconnect will be applicable to future photoactive systems which may allow for elevated efficiencies. As EEL we use SnO$_2$, which is grown by atomic layer deposition at temperatures as low as 80 °C (see the Experimental Section for details of the preparation). In single junction OSCs, we have shown that SnO$_2$ forms a universal EEL with a low-work-function, which does not rely on activation with UV light.[17] Moreover, we have demonstrated that by the use of SnO$_2$ we can avoid the occurrence of photoinduced degradation of the FF and $V_{oc}$, which is commonly encountered in ZnO based devices upon prolonged exposure to solar radiation.[18] Recently, SnO$_2$ has also been considered as EEL for solar cells based on hybrid perovskites with improved efficiency and long-term stability.[47–50]

Initially, we have prepared single junction reference devices with a thickness of the photoactive layers identical to that of the sub-cells in the tandem devices. The optimum thickness of the active layers for current matching has been determined by an optical simulation taking into account the absorption characteristics of the photoactive layers in the tandem cell and the external quantum efficiency (EQE) of the single junction devices (Figure S1, Supporting Information). The optical simulation indicated an optimum thickness of the active PCDTBT:PC$_{70}$BM layer in the bottom sub-cell of about 130 nm and a concomitant thickness of >135 nm for the upper PDPP3T:PC$_{60}$BM active layer. Unfortunately, our batch of PCDTBT did not allow us to prepare devices with a layer thickness substantially in excess of 90 nm without severe losses in FF (Figure S2, Supporting Information). Moreover, the $J_{sc}$ did not increase significantly for a thickness higher than 90 nm. The reasons may be due to the molecular weight of the PCDTBT which did not allow for an optimum BHJ morphology. As such, we decided to use 90 nm for the PCDTBT:PC$_{70}$BM sub-cell. For current matching, the thickness of the active PDPP3T:PC$_{60}$BM layer in the upper cell was consequently chosen as 80 nm (Figure S1d, Supporting Information).

The respective characteristics of the single junctions are shown in Figure S3 (Supporting Information) and Table 1. The resulting tandem cells based on the monolithic series connection of these single junctions by a MoO$_3$/SnO$_2$ interconnect have been characterized according to a protocol detailed elsewhere.[51] Briefly, the EQE of the sub-cells in the tandem devices has been determined by using an appropriate choice of electrical and optical bias. For example, for the characterization of the PCDTBT:PC$_{70}$BM sub-cell, the PDPP3T:PC$_{60}$BM has been optically biased at 730 nm. Conversely, the PCDTBT:PC$_{70}$BM sub-cell has been biased at 530 nm. The resulting EQE spectra are shown in Figure 2a. The $J–V$ characteristics of the sub-cells have been obtained from the single junctions by tuning the illumination to afford the $J_{sc}$ calculated from the respective EQE spectrum (Figure 2b). From these data, the $J–V$ characteristics of the tandem cell have been constructed. In addition, the $J–V$ characteristics of the tandem cell measured with appropriate corrections for spectral mismatch are shown. Importantly, in the tandem cells an ideal addition of the $V_{oc}$ of the sub-cells is achieved, demonstrating the functionality of the MoO$_3$/SnO$_2$ interconnect. We find a device efficiency of up to 8.0% (7.6%, average over 11 devices) for the tandem cell, which is substantially higher than 5.4% and 4.2% for the PCDTBT:PC$_{70}$BM and the PDPP3T:PC$_{60}$BM sub-cells, respectively.

We note that the $J–V$ characteristics of the tandem cells are in excellent agreement with those constructed from $J–V$ data of the sub-cells, which evidences the loss-free connection of both sub-cells by the MoO$_3$/SnO$_2$ interconnect (Figure 2b).

To analyze the working mechanism of the MoO$_3$/SnO$_2$ interconnect in more detail, we have performed photoelectron spectroscopy (PES) as well as Kelvin probe (KP) analysis to assess the energy level line-up in the interconnect. To this end, we started with a 30 nm thick thermally evaporated MoO$_3$ layer. Thereafter, we step-wise deposited SnO$_2$ layers with a thickness of 0.5–50 nm on top. The X-ray photoelectron spectroscopy (XPS) spectra for Mo3d and Sn3d are shown in Figure S4 of the Supporting Information. No explicit band bending has been found in the MoO$_3$ upon deposition of SnO$_2$ on top. The resulting WF has been derived both from the secondary cut-off of the photoemission spectra (Figure S5a, Supporting Information) and the measured contact potential difference of our calibrated Kelvin probe, respectively. We repeated this experiment for several sets of samples (Figure 3a). In both PES and KP, a strong initial lowering of the WF is observed upon deposition of SnO$_2$ on top of the MoO$_3$. We start with a WF of 5.1–5.3 eV for MoO$_3$, which is in agreement with previous reports on thermally evaporated MoO$_3$ layers, which have seen a vacuum break.[52] Note that our MoO$_3$ has also been thermally evaporated, but we had to expose it to the glove-box atmosphere of our ALD system before deposition of the SnO$_2$.

According to KP data, we find an overall WF drop of $\Delta W_F = 1.07$ eV after deposition of 30 nm of SnO$_2$, lowering the WF from 5.25 eV for MoO$_3$ to a saturated value of 4.18 eV for SnO$_2$ (Figure 3a). Taking the XPS core level measurements into account, we can further derive a contribution of $\phi_{\infty} = 0.28$ eV in this WF drop (from the binding energy shift of the Sn3d peak) that can be attributed to band bending (Figure 3b). The large remaining part of the WF drop $\Delta = \Delta W_F - \phi_{\infty} = 0.79$ eV, which occurs for <5 nm of SnO$_2$, can be associated with an interface dipole.

### Table 1. Characteristics of the single junction and tandem devices.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single junction devices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCDTBT:PC$_{70}$BM (nom. 90 nm)</td>
<td>0.849</td>
<td>10.3</td>
<td>62</td>
<td>5.4</td>
</tr>
<tr>
<td>PDPP3T:PC$_{60}$BM (nom. 80 nm)</td>
<td>0.627</td>
<td>10.7</td>
<td>63</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Tandem device</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom sub-cell</td>
<td>0.847</td>
<td>9.1</td>
<td>62</td>
<td>4.8</td>
</tr>
<tr>
<td>Top sub-cell</td>
<td>0.627</td>
<td>8.6</td>
<td>63</td>
<td>3.4</td>
</tr>
<tr>
<td>Tandem constructed</td>
<td>1.473</td>
<td>8.9</td>
<td>62</td>
<td>8.1</td>
</tr>
<tr>
<td>Tandem measured</td>
<td>1.468</td>
<td>9.1</td>
<td>60</td>
<td>8.0</td>
</tr>
<tr>
<td>Average of 11 devices</td>
<td>1.475 ± 0.012</td>
<td>8.4 ± 0.3</td>
<td>61.2</td>
<td>7.6 ± 0.3</td>
</tr>
</tbody>
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To understand the possible origin of the large interface dipole, it is important to note that earlier work has shown a substantial lowering of the initially high-work-function of MoO$_x$ if the Mo$^{6+}$ species at the surface are reduced to Mo$^{5+}$ or Mo$^{4+}$.[53,54] Indeed, we also found an indication of reduced Mo$^{6+}$ in the Mo3d XPS spectra, as a shoulder at lower binding energies of the main Mo$^{6+}$ peak evolved upon deposition of SnO$_x$ (Figure S6a, Supporting Information). Therefore, we can

Figure 2. a) EQE spectra of the PCDTBT:PC$_{70}$BM (bottom) and PDPP3T:PC$_{60}$BM (top) sub-cells determined under appropriate biasing conditions (see the Experimental Section for details). b) $J$–$V$ characteristics of the sub-cells as obtained from the single junction devices upon tuned illumination to achieve the $J_{sc}$, determined from the respective EQE spectra, as well as constructed and measured $J$–$V$ characteristics of the tandem cell.

Figure 3. a) Variation of the work function upon deposition of SnO$_x$ on top of MoO$_x$ determined by photoelectron spectroscopy (PES, solid symbols) and KP (open symbols) for several sets of samples. b) Binding energy shift derived from XPS core level data of the Sn3d signal. The red dotted line is inserted as a guide to the eye. c) The energy level line-up at the MoO$_x$/SnO$_x$/interface, resulting from UPS/XPS and KP analysis (the line-up including core levels is shown in Figure S8, Supporting Information). The position of the conduction band minimum (CB) with respect to the valence band maximum has been determined from the respective optical band gap (see Figure S9, Supporting Information). Note that the gap states in MoO$_x$ have been omitted for simplicity. Possible band bending due to adsorbed water molecules at the surface of SnO$_x$ is also not shown.[18] A schematic of the working mechanism of the interconnect in a tandem cell is shown in (d). For simplicity, only the energy levels of the acceptor of the top PDPP3T:PC$_{60}$BM cell and the donor of the bottom PCDTBT:PC$_{70}$BM cell are shown. The recombination of electrons and holes occurs at the interface of MoO$_x$/PCDTBT (marked in green). Note that the energy levels are not to scale in this schematic.
attribute the interface dipole to the partial reduction of Mo$^{6+}$. We want to note that the sudden drop of the WF upon deposition of SnO$_x$ on top of the MoO$_x$ is not limited to the combination of MoO$_y$/SnO$_x$. In fact, we could show that the WF of MoO$_x$ likewise dropped by 0.7–1.1 eV upon deposition of a few nanometers of other metal oxides by ALD, e.g., ZnO, Al$_2$O$_3$, etc. (see Table S1, Supporting Information). As such, the nucleation of the ALD precursors on top of the MoO$_x$ layer gives rise to a reduction of the Mo$^{6+}$.

The WF of our SnO$_x$ layers is remarkably low compared to the WF of 5.7 eV reported for single crystalline SnO$_x$.\cite{55} We have previously shown that the lower WF of our ALD SnO$_x$ results from Sn$^{2+}$ surface species and adsorbed water molecules, which infer downward band-bending at the SnO$_x$ surface.\cite{17,56} The observed binding energy shift in the Sn3d peak corresponds to the variation of surface potential $\phi(d)$ with increasing the thickness $d$ of the SnO$_x$ (Figure 3b, red dotted line inserted as an eye guide). As can be seen in our discussion in Figure S7 of the Supporting Information, the progression of the surface potential $\phi(d)$ cannot be described by simple textbook semiconductor physics in the framework of the Schottky model over the total thickness range in this study. If we take defect induced gap states into account we can use a simplified distributed states model (DSM) that has been introduced by Mankel et al.,\cite{57} which provides a significantly better approximation of our experimental data. With the DSM, we cannot directly derive the carrier density in the SnO$_x$ layer. With a rough estimate, at least within the first 10 nm based on the Schottky model, we estimate a carrier density of $>10^{19}$ cm$^{-3}$, which is orders of magnitude higher than the carrier density we derive from the position of the Fermi level for thick SnO$_x$ layers (see below). This discrepancy can possibly be explained by taking into account the ALD specific nucleation phase in the first cycles of the ALD process, which may infer a higher number of defect states, that would give rise to a higher carrier density in the first few nanometers of layer growth. Unfortunately, the overall low electrical conductivity did not allow us to unambiguously determine the actual carrier density of the SnO$_x$ layers by Hall techniques.

The PES and KP data allow us to construct an energy level line up of the MoO$_y$/SnO$_x$ interface as shown in Figure 3c. Note that the WF and the band-bending is based on the results of the KP data. Using the WF from PES, instead, does not fundamentally change the line-up. It has to be noted that the WF and the band-bending is based on the results from Sn 2p and Mo 3d core levels. These values stand in contrast to the high carrier densities we derived from the band bending data for the first nanometers of SnO$_x$ that we attributed to nucleation effects in the ALD growth at the MoO$_y$/SnO$_x$ interface, as outlined above.

The WF on both sides of the interconnect appears excellently suited to interface with the donor (PCDDBT) of the lower sub-cell and the acceptor (PC$_{60}$BM) of the upper sub-cell. Consequently, a schematic can be constructed which visualizes the working mechanism of the interconnect in the tandem cells (Figure 3d). Electrons which are extracted from the upper sub-cell via the SnO$_x$/PC$_{60}$BM interface are efficiently transported in the CB of the SnO$_x$ to the CB of the MoO$_x$ where they further propagate to the PCDDBT/MoO$_x$ interface. There, they meet and recombine with the holes which are extracted from the PC$_{60}$BM. It has to be noted that even though MoO$_x$ is used for hole extraction in organic solar cells, it is a n-type material with a high-WF and an extremely deep lying CB (high electron affinity). The electronic line up at the interface organic/MoO$_x$ has been determined for a range of organic compounds (e.g., 4,4'-bis(N-carbazolyl)-1,1'-biphenyl(CBP), triis(4-carbazolyl-9-ylphenyl)amine, and N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine).\cite{11} Typically, the energetic position of the CB minimum of the MoO$_x$ is located close to the HOMO level of the adjacent organic material due to the formation of a large interface dipole. In addition, electron transfer from the organic material to the MoO$_x$ has been evidenced, which resulted in an upward bending of the HOMO in the organic layer—in other words, interfacial p-type doping of the organic layer.\cite{11} A similar finding has been reported for the interface of other high-WF TMOs adjacent to organic semiconductors, e.g., WO$_3$/CuPc,\cite{59} WO$_3$/spiro-MeOTAD,\cite{60} or V$_2$O$_5$/CBP.\cite{61} We want to note that an interconnect based on a single layer of MoO$_x$ (i.e., without the SnO$_x$) would not afford the same functionality. It has been shown that the electronic line-up at the interface of MoO$_y$/fullerene comprises a large energy offset between the LUMO of the fullerene and the CB of the MoO$_x$ even in cases where the MoO$_x$ surface had been exposed to air prior to the deposition of the fullerene.\cite{62} As such, in the absence of SnO$_x$, the energetic mismatch of MoO$_x$ and fullerene would lead to substantial losses of $V_{oc}$ for the tandem cell.

As stated initially, SnO$_x$ has shown notable advantages compared to ZnO or TiO$_2$ based EELs in single junction organic solar cells. Among them the absence of light-soaking problems, in contrast to ZnO or TiO$_2$ EELs, which need to be "activated" by UV light with photon energies larger than the band-gap of the metal oxide ($h\nu > E_g$).\cite{31,63-67} In this regard, the use of SnO$_x$ is favorable in cases where UV light activation is undesired or grown by ALD at low temperature, ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) data provided a band gap of 3.72 eV.\cite{48} Taking the latter value as the band-gap in our line-up (Figure 3c) would even result in a CB offset between MoO$_x$ and SnO$_x$ close to zero. From the distance of the Fermi level and the CB edge ($E_F - E_{CB}$), we can derive a complementary estimate of the carrier density in our SnO$_x$. The effective electron mass of SnO$_2$ is $m^* = 0.4 \times m_e$.\cite{58} With ($E_{CB} - E_F$) = 0.12–0.3 eV (depending on the technique to determine $E_{CB}$), the estimated carrier density varies between $4 \times 10^{13}$ cm$^{-3}$ and $5 \times 10^{16}$ cm$^{-3}$, which indicates a relatively low doping level of our SnO$_x$ bulk layer. These values stand in contrast to the high carrier densities we derived from the band bending data for the first nanometers of SnO$_x$ that we attributed to nucleation effects in the ALD growth at the MoO$_y$/SnO$_x$ interface, as outlined above.  

not even possible. In multijunction cells, the availability of UV photons to activate metal oxides in the recombination layers will be limited even without the dedicated use of UV-filters. There, the UV spectral range may be partially absorbed in the bottom sub-cell. To study this effect in our tandem cells, we fabricated tandem devices based on MoO$_3$/SnO$_x$ or MoO$_3$/ZnO interconnects (Figure 4a). As shown in Figure 4b,c, tandem cells with either MoO$_3$/SnO$_x$ or MoO$_3$/ZnO interconnects show similar characteristics when illuminated under full AM1.5 illumination, but both behave differently in the absence of UV-light. Impressively, the use of SnO$_x$ in the interconnect allows for well-behaved solar cell characteristics with high FF and PCE even under illumination with AM1.5, where the UV components have been blocked by a filter ($\lambda > 435$ nm), whereas the device comprising ZnO shows a strongly s-shaped $J$–$V$ curve under the same conditions. Note that the drop of the WF of MoO$_3$ inferred by the deposition of SnO$_x$ or ZnO is comparable for both oxides (Table S1, Supporting Information). In earlier studies, the necessity of UV activation in case of ZnO EELs has been associated with the electronic alignment at the EEL/fullerene interface. Similar issues have been encountered for ZnO-based interconnects before.

In summary, all-oxide MoO$_3$/SnO$_x$ recombination interconnects for organic multijunction solar cells have been demonstrated. The electronic line-up at the interface of MoO$_3$ x ($\approx 0.8$ eV) has been found to infer near to ideal alignment of the conduction band of MoO$_3$ and SnO$_x$. This favorable line-up is essential for the working principle of the interconnect: Electrons extracted via the SnO$_x$ from the upper sub-cell are efficiently handed over to the CB of MoO$_3$, while the actual recombination of electrons with holes takes place at the interface of organic/MoO$_3$ of the lower sub-cell. The presented MoO$_3$/SnO$_x$ interconnect allows for the ideal addition of the open circuit voltages ($V_{oc}$) of the two sub-cells. The resulting tandem devices significantly surpass the efficiency of the individual sub-cells. In stark contrast to similar devices based on MoO$_3$/ZnO which need to be activated by UV exposure, the MoO$_3$/SnO$_x$ based tandem cells function without any limitation even in the absence of UV light. We assume that our concept of all-oxide MoO$_3$/SnO$_x$ interconnects is generally applicable to other organic/hybrid photoactive material systems.

**Experimental Section**

**Materials Synthesis and Device Preparation:** Tin oxide was prepared by atomic layer deposition in a Beneq TFS 200 system (base pressure 1.5 mbar). As precursors, tetrakis(dimethylamino)tin(IV) (TDMASn), kept at 45 °C and water, kept at room temperature, were used. At a substrate temperature of 80 °C the growth rate was 1.056 Å per cycle. The zinc oxide layers were deposited at the same conditions (substrate temperature: 80 °C, base pressure: 1.5 mbar) using diethylzinc and water as precursors (both kept at room temperature).

The inverted single junction OSCs are based on the following layer sequence: glass/indium-tin-oxide (ITO)/SnO$_x$/photoactive layer/MoO$_3$/Ag with an active area of 0.03 cm$^2$. As photoactive material for the wide band gap cell, PPDPT and fullerene (PC$_{60}$BM (SES Research)) with a weight ratio of 1:4 were used. The polymer was dissolved in chlorobenzene and stirred in N$_2$ atmosphere at 80 °C for 2.5 h followed by adding the fullerene (stirring for 1.5 h). The solution was filtered (5 μm PTFE Filter) and spin coated in N$_2$ atmosphere. On the anode side, MoO$_3$ (10 nm) and Ag (100 nm) layers were thermally evaporated in high-vacuum (10$^{-6}$ mbar).

For the low-bandgap cell, PDDP3T and fullerene (PC$_{60}$BM from American Dye Source) (weight ratio of 1:2) were dissolved in a mixture of chloroform and o-dichlorobenzene (6 vol% o-DCB) with an overall concentration of 15 mg mL$^{-1}$. After stirring at 90 °C for 1 h the still warm solution was spin coated in N$_2$ atmosphere.

**Materials Characterization:** Optical parameters of the tin oxide and molybdenum oxide layers were obtained by spectral ellipsometry (M-2000V from J.A. Wollam) for thin film samples deposited on top of a Si wafer with native oxide (Figure S10, Supporting Information). For determining transmission and reflection spectra a Deuterium Halogen lamp (DH-2000-BAL, OceanOptics) and a spectrometer with a range from 186 to 1041 nm (USB 2000+XRII-ES) were used. For transmission measurements, 200 nm thick SnO$_x$ and 100 nm thick MoO$_3$ layers were deposited on quartz substrates.

The measurements of the surface potential were done with a McAllister KP6500 Kelvin-Probe (KP) system in vacuum (10$^{-6}$ mbar). Highly ordered pyrolytic graphite with a WF of 4.5 eV was used as reference.

The photocurrent spectra were measured without exposing the prepared samples to ambient environment. After preparation the
samples were stored in a glove-box and were transferred to the vacuum chamber in a dedicated vacuum shuttle. The XPS measurements were carried out using an ESCALAB 250 system from ThermoFisher. Monochromatic X-rays (1486.6 eV photoenergy) from an Al-Kr source were used. A magnetic lens was used to have a maximum collection of photoelectrons from the sample. Data were collected with pass energy of 10 eV in normal emission. The binding energy was calibrated with the Cu3d, Ag3d, and Au Fermi edge.

The UPS measurements were performed using He-I$_\alpha$ (h$\nu = 21.22$ eV) radiation. The experiments were carried out with a bias potential of 4 eV. The valence band maxima and the work function were determined from the linear extrapolation of valence band edge and secondary electron edge.

Device Characterization: The solar cells were characterized in ambient air without encapsulation using a Keithley 2400-C source meter and a solar simulator (300 W Newport, AM1.5G, 100 mW cm$^{-2}$).

The external quantum efficiency was determined using a calibrated tunable light source consisting of a 50 W tungsten halogen lamp (Osram 64610) and a monochromator (Oriel, Cornerstone 130) in combination with a lock-in amplifier (Stanford Research Systems SR 830). For the determination of the EQE of the tandem-cells a protocol was followed as recently reported.[13] The sub-cells were therefore characterized under accurate bias light and voltage conditions. These measurements were performed using an in-house built system, where the bias light was provided by monochromatic power LEDs (Thorlabs M530L3, M730L4).

The J–V characteristics of the tandem cell were thereafter recorded upon illumination with a light source which was adjusted to compensate spectral mismatch for both active layers. Therefore, the power of the light source was changed such that the deviations between $J_{sc}$ determined by EQE were equal for each reference single junction device.

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

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Conflict of Interest
The authors declare no conflict of interest.

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