Chapter 3
Tandem Polymer Solar Cell Using a Composite Metal Interlayer

Abstract

This Chapter deals with a solution-processed polymer tandem cell by stacking two single cells in series. The two bulk heterojunction sub cells have complementary absorption maximal at $\lambda_{\text{max}} \sim 850$ nm and $\lambda_{\text{max}} \sim 550$ nm, respectively. A composite middle electrode is applied that serves both as charge recombination center and as a protecting layer for the first cell during spin coating of the second cell. The sub cells are electronically coupled in series, which leads to a high open-circuit voltage of 1.4 V, equal to the sum of each sub cell. The layer thickness of the first (bottom) cell is tuned to maximize the optical absorption of the second (top) cell (optical matching). In the end a tandem cell with an unbalanced performance of the sub cells is compared with an optimized tandem cell. It becomes clear that the low light intensity due to high optical absorption of the middle contact leads to a low photo-generated current by the top cell. In series configuration, this low current of the top cell of the device limits the current extracted from the tandem device.

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3.1 Introduction

Most solution processable semiconducting polymers exhibit band gaps larger than 1.2 eV and narrow absorption bands, which results in a limited overlap of their absorption spectrum with the solar spectrum. Since a very broad absorption spectrum is not feasible in one single polymeric material, a tandem cell, consisting of multiple layers each with their specific absorption maximum and width, can overcome this limitation. In addition to covering a larger part of the spectrum, tandem solar cells offer the distinct advantage that the photon energy is used more efficiently, because the voltage at which charges are collected in each sub cell is closer to the energy of the photons absorbed in that cell. This was demonstrated for organic tandem photovoltaic cells processed by co-evaporation of small organic molecules. In this method, layers of organic molecules are thermally deposited on top of each other. If the tandem cell is stacked from two photovoltaic sub cells that were fabricated from the same conjugated polymer, the absorption spectra of both cells are identical and, consequently, can only be used for very thin organic films that do not absorb the intense solar flux (even with an aluminum mirror as top electrode). In such a tandem cell the coverage of the solar spectrum is not improved but more light of the same wavelength is absorbed. In this Chapter a solution-processed tandem solar cell is discussed consisting of two bulk heterojunction sub cells with complementary absorption spectra. In order to harvest as many photons of the solar spectrum as possible, the tandem cell (Figure 3.1C) consists of two cells with complementary absorption spectra (Figure 3.2). A composite middle electrode separates the two sub cells. The middle electrode serves two different purposes; as a charge recombination center, and as a protecting layer for the first cell during spin coating of the second cell. In general, because the sub cells have completely different absorption spectra, high energy photons are absorbed in the bottom cell and low energy photons are absorbed in the top cell. Consequently, the whole visible part of the solar spectrum can be covered. The sub cells are electronically coupled together in series, which results in an open-circuit voltage ($V_{oc}$) of the tandem cell that equals the sum of the $V_{oc}$ of each sub cell. Attenuation of incident light on the top cell, caused by absorption
and the optical cavity of the bottom cell, leads to the lower photocurrent of the top cell, which limits the current of the tandem cell. The structures of reference bottom (Figure 3.1A), reference top cell (Figure 3.1B) and the tandem cell (Figure 3.1C) is shown in figure 3.1.

**Figure 3.1.** A) Schematic structure of the reference bottom cell to determine the optical out coupling. B) The schematic structure of the reference top cell, which is the same as the top cell in tandem configuration but processed directly on glass. C) The schematic structure of the tandem cell. Two bulk heterojunction cells (bottom and top cell) are stack ed in series. The absorption spectra of the two semiconducting polymers PFDTBT and PTBEHT are complementary.
3.2 The middle electrode

The two organic solar cells are electronically linked together by a composite electrode. Since the two sub cells are connected in series, this composite middle electrode provides a site for recombination of electrons and holes approaching from bottom and top cell, respectively. Therefore, the middle electrode does not have to be highly conductive, since, in the tandem cell, no current is extracted from this electrode. Furthermore, to efficiently extract the electrons from the bottom cell and the holes from the top cell (in order to recombine at the middle electrode), the middle electrode has to provide an Ohmic contact for both sub cells, since an insufficient recombination results in limited currents in both devices. The middle electrode has to act as the cathode (with a low work function to align with the LUMO of the acceptor) for the bottom cell and, at the same time, as the anode (with a high work function to align with the HOMO of the donor) for the top cell. With a gold middle electrode, an Ohmic contact for both holes and electrons can not be obtained and, therefore, we added a very thin layer of 0.5 nm LiF and 0.5 nm Al on top of the bottom cell. The Ohmic contact provided by LiF/Al with the LUMO level of PCBM will extract the electrons generated in the bottom cell. Next, we evaporated 15 nm Au and topped it off by spin coating 60 nm PEDOT:PSS. The latter provides a stable and Ohmic contact for hole extraction from the top cell. The extracted electrons and holes then recombine in the middle electrode. A very thin layer of gold (as thin as 0.5 nm) provides already enough recombination sites for the holes and electrons that arrive at the middle electrode. However, in our case the gold layer has to protect the LiF/Al cathode of the bottom cell from being dissolved and oxidized during the spin coating of the water-based PEDOT:PSS. This means that the gold layer has to be a continuous, closed layer. On the other hand, the middle contact has to be as thin as possible to maximize the light transmission that is required as the input of the top cell (Section 3.3). We found that the thinnest possible layer that is required to protect the bottom layer during solution processing of PEDOT:PSS cell is 10–15 nm. At that thickness the gold layer forms a closed and continuous electrode, which can protect the cathode of
the bottom cell from being destroyed (the thickness that is required to form a closed layer depends on the roughness of the blend used for the bottom cell). The total composite middle electrode (LiF/Al/Au/PEDOT:PSS) protects the bottom cell from being dissolved during the spin coating of the active layer of the top cell.

3.3 Optical matching

Due to the relatively narrow absorption bands of the semiconducting polymers presently used in solar cells, the small band gap polymers will not significantly contribute to a better performance of a single cell (assuming similar transport properties), because the absorption spectrum is only shifted under the solar emission spectrum. Small band gap polymers can improve the overall efficiencies more significantly if used in a tandem cell. In such a tandem cell the utilization of two absorbing polymers with (partially) complementary absorption spectrum results in an enhanced photon harvesting of the solar spectrum. Figure 3.2 depicts the normalized absorption spectra of the large band gap polymers MDMO-PPV, P3HT, and PFDTBT and the small band gap polymer PTBEHT (chemical structures are shown in Figure 2.1) that are used in this study. Obviously, two large band-gap polymers are complementary with PTBEHT and could, in principle, be used in a tandem cell.
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Figure 3.2. Absorption spectra of the large band gap polymers PFDTBT, P3HT, and MDMO-PPV and of the small band gap polymer PTBEHT with its maximum at 850 nm.

It should be noted that the blend of the large band gap polymer and PCBM acts as a dielectric sandwiched between two thin semi-transparent layers of gold (bottom and middle electrode). Light transmitted through the active layer of the bottom cell interferes with the reflected light at the middle electrode, leading to optical cavities.\[39\] As discussed in Section 3.2, a middle electrode with a layer thickness of about 15 nm of gold is required to prevent the cathode from being destroyed by spin coating of the water-based PEDOT:PSS. This inevitably reduces the illumination intensity of the top cell. \[38,37\] Since such a semi-transparent middle electrode creates, together with the bottom electrode, optical cavities, the optical transmission through the first (bottom) cell needs to be optimized for the optical absorption of the second (top) cell. The optical cavity, and therefore the transmission, is affected by the thickness of the active layer, as demonstrated in Figure 3.3. Given the fact that the small band gap polymer (PTBEHT) absorbs between 700 and 950 nm, the optical cavities (or layer thickness) of the bottom cell have to be optimized in order to transmit at this wavelength range. Therefore, we
processed blends of large band gap polymers (MDMO-PPV, P3HT and PFDTBT with PCBM) in a similar sandwich as is used in the tandem cell (Figure 3.1C). The experimentally determined optimal layer thickness of the bottom cell (reference bottom cell in Figure 3.1A) can be derived from Figure 3.3 and amounts to 330 nm for a 1:4 MDMO-PPV:PCBM blend (Figure 3.3A), 120 nm for a 1:1 P3HT:PCBM blend (Figure 3.3B), and 110 nm for a 1:4 PFDTBT:PCBM blend (Figure 3.3C). Based on this transmission a bottom cell processed from PFDTBT would result in the most intense irradiation of the top cell (48 % transmission), since both MDMO-PPV and P3HT have transmission intensities of 34 and 37 %, respectively, in the wavelength range that is absorbed by the small band gap polymer PTBEHT. Furthermore, the width of transmitted intensity for MDMO-PPV is narrow, which also reduces the amount of photons that can be absorbed by the top cell. The third reason to process a bottom cell from PFDTBT is the current matching, which will be discussed in the following Section. Figure 3.4 demonstrates that a thickness of 110 nm for the bottom cell based on PFDTBT:PCBM (1:4) results in a perfect optical coupling between the light output of the bottom cell and the absorption spectrum of the top cell, since both have their maximum intensity at 850 nm.
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A.

Layer thickness blend
- 600 nm
- 330 nm
- 180 nm
- 160 nm
- 110 nm

B.

Layer thickness blend
- 180 nm
- 160 nm
- 120 nm
- 90 nm
- 40 nm

C.

Layer thickness blend
- 270 nm
- 190 nm
- 160 nm
- 110 nm
- 90 nm

Transmission [%] vs. Wavelength [nm]
Figure 3.3. Transmission of incident light through the bottom cell (or light input of the top cell). Due to optical cavities, the spectrum of the transmitted light shifts for different thicknesses of the active layer of the bottom cell a) for the blend of MDMO-PPV and PCBM (1:4), b) for the blend of P3HT and PCBM (1:1) and c) for the blend of PFDTBT and PCBM (1:4). The effect of the optical cavities allows for tuning the transmission optically.

Figure 3.4. The light output of the bottom cell consisting of glass/1 nm Cr/15 nm Au/60 nm PEDOT:PSS/110 nm PFDTBT:PCBM (1:4)/0.5 nm LiF/0.5 nm Al/15 nm Au (circles) and the absorption of the small band gap polymer (PTBEHT) of the top cell.

3.4 Current matching

Because the two BHJ sub cells are stacked in series, the current that can be extracted out of the tandem cell follows the lowest of the currents generated in the bottom and top cell. As demonstrated in Section 3.3, the top cell receives the light that is not absorbed by the bottom cell and is illuminated under lower light intensities. Consequently, the top cell produces lower photocurrents. This means that in a tandem structure the extracted current is almost the same as the photocurrent of the cell that generates the lowest current. When the bottom cell generates much more current (e.g., at short-circuit conditions), the excess electrons cannot recombine with the holes from the top cell and will charge the middle electrode. This charging will partially compensate the build-in voltage across the bottom cell until the current of the bottom cell matches the current of the top cell. At the same time, the charged middle contact leads to reverse-biasing of the top cell, which leads to a small improvement in performance of the top cell in a
tandem structure. The device operation of unbalanced tandem cells will be explained in more detail in Chapter 5. In the structure mentioned here, the matching of the photocurrent of the sub cells is presented as follows: There are many large band gap polymers (MDMO-PPV, P3HT, PFDTBT) suitable for the bottom cell. While their absorption spectra are almost the same, the charge carrier mobilities are different. Also treatments such as annealing at different temperatures in case of P3HT leads to different mobilities.\cite{81} Using materials with higher mobilities causes a higher generated photocurrent in the device. In this way, using proper material and processing methods, the photocurrent of the bottom cell can be tuned. To determine the photo current that can be generated in the top cell, a reference top cell (Figure 3.1B) was fabricated that mimics the top cell in the tandem geometry. This reference top cell was illuminated under various light intensities (100–1000 W/m², AM1.5), using neutral density filters, and the $J–V$ characteristics are measured and from this the $J_{SC}$ was extracted \cite{38,37} (Figure 3.5). The maximum light intensity that reaches the top cell is estimated from Figure 3.3 and amounts to 34, 37 and 48 % for blends based on MDMO-PPV, P3HT and PFDTBT, respectively. Consequently, a top cell that is processed on a bottom cell based on MDMO-PPV:PCBM (1:4) or on P3HT:PCBM (1:1) will generate a short-circuit current of ~ 6 A/m², whereas a top cell fabricated on a blend of PFDTBT:PCBM (1:4) will generate a $J_{SC}$ ~ 10 A/m² at 48 % light intensity (or 480 W/m²). Since the top cell is already deprived of photons due to the absorption and optical cavity of the bottom cell, processing with PFDTBT:PCBM as the bottom cell is advantageous for the performance of the tandem cell due to the higher transmission intensity at the relevant wavelengths (Section 3.3) as well as the higher $V_{OC}$ of the bottom cell.
Figure 3.5. The short-circuit current density of the reference top cell under illumination with different light intensities (AM1.5 solar spectrum).

As described above, the current densities of the two cells, bottom and top, have to match quantitatively. Therefore, the $J-V$ characteristics of all the reference bottom cells from Figure 3.3 were measured and compared to the characteristics of the top cell under various illumination intensities. The important parameters of the bottom cell are the transmitted light intensity, $J_{SC}$, $FF$, and $V_{OC}$. In Figure 3.6 the current density versus voltage is plotted for the bottom cells with the correct optical cavities (layer thickness), as determined from Figure 3.3, which are: 110 nm PFDTBT:PCBM (1:4), 120 nm P3HT:PCBM (1:1), and 330 nm MDMO-PPV:PCBM (1:4). Figure 3.6 clearly demonstrates that the bottom cell based on PFDTBT:PCBM (1:4) generates a $J_{SC}$ of $\sim 10$ A/m$^2$, which is required to match the top cell. Bottom cells based on P3HT:PCBM (1:1) and MDMO-PPV:PCBM (1:4) with an active layer optimized for the optical matching (Section 3.3) generate $J_{SC}$ that is higher and does not match the photo current generated in the top cell (Figure 3.5). Therefore, the combination of PFDTBT/PCBM (1:4) for the bottom cell (large band gap) and PTBEHT/PCBM (1:4) for the top cell (small band gap), as shown in Figure 3.4, results in an optimized optical (Section 3.3) and electronic coupling (this Section) for the tandem cell in series.
3.5 Optimum tandem photovoltaic device

In the tandem geometry, the bottom and top BHJ solar cells are stacked in series, which implies that, for a well performing tandem cell, the open-circuit voltage \( (V_{OC}) \) of the tandem cell is equal to the sum of the \( V_{OC} \) of both individual cells. The short-circuit current \( (J_{SC}) \) of the tandem cell is limited by the lowest short-circuit current \( (J_{SC}) \) of the two individual cells. For the maximum performance of the tandem cell with series configuration, the \( J_{SC} \) of each sub cell has to be matched (Section 3.4). In the tandem cell geometry, the bottom and top cell can be measured individually by contacting the bottom (anode) and middle (cathode) electrode for the bottom cell, and the middle (anode) and top (cathode) electrode for the top cell. As explained above, the combination of 110 nm PFDTBT/PCBM (1:4) for the bottom cell (large band gap) and PTBEHT/PCBM (1:4) for the top cell (small band gap), results in an optimized optical (Section 3.3) and electronic coupling (Section 3.4) for the tandem cell in series. The thickness of the active layer (PTBEHT:PCBM, 1:4) of the top cell is optimized for its performance and amounts to 90 nm. The
The current density–voltage (J–V) measurements of the individual top and bottom cell, and of the tandem cell are depicted in Figure 3.7. The values of the $V_{OC}$, $J_{SC}$, and the fill factor (FF) extracted from the measurements are summarized in Table 3.1.

![Figure 3.7. The current density–voltage characteristics measured separately of the bottom, top and tandem cell in dark and under illumination (AM1.5, 1000 W/m$^2$).](image)

<table>
<thead>
<tr>
<th>Cells</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [A/m$^2$]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>0.9</td>
<td>~10</td>
<td>50</td>
<td>0.35</td>
</tr>
<tr>
<td>Top</td>
<td>0.5</td>
<td>~9</td>
<td>64</td>
<td>0.23</td>
</tr>
<tr>
<td>Tandem</td>
<td>1.4</td>
<td>~9</td>
<td>55</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Table 3.1. The quantitative values extracted from the J–V measurements of the individual cells. Illumination conditions: 1000 W/m$^2$, AM1.5 simulated solar spectrum.
A high open-circuit voltage ($V_{OC}$) of 1.4 Volt is achieved which amounts to the sum of the open-circuit voltages of the bottom cell (0.9 Volt) and the top cell (0.5 Volt). Figure 3.7 and Table 3.1 demonstrate that the tandem structure improves the performance of the individual sub cells (bottom and top cell), since the efficiency of the tandem cell is 1.6 times higher than the bottom cell and 2.5 times higher than the top cell.

The top cell generates a lower current than the bottom cell and limits the performance of the tandem cell in series configuration. To demonstrate that the bottom and top cell are optically coupled in a proper manner, the reference top cell, that is processed directly on glass, was illuminated under 400 and 600 W/m$^2$ by using neutral density filters. Those two intensities were close to the 500 W/m$^2$ already predicted by measuring the transmission through the bottom cell (Figure 3.3). The $J$–$V$ characteristics of the reference top cell illuminated under 400 and 600 W/m$^2$ were compared with the illuminated top cell (top cell in Figure 3.7) in a tandem geometry, and plotted in Figure 3.8. From the short-circuit currents in Figure 3.8, the light intensity that is transmitted through the bottom cell and that illuminates the top cell is estimated to be about 500 W/m$^2$, which is in perfect agreement with the measurements in Figure 3.3 and 3.5.
Figure 3.8. The $J$–$V$ characteristics of the PTBEHT/PCBM (1:4) cell in dark and under illumination with intensities of 400 (squares) and 600 (circles) W/m$^2$ (AM1.5 solar spectrum), and the $J$–$V$ characteristics of only the top cell (top cell in Figure 7) as measured in the tandem configuration (triangles) in the dark and under 1000 W/m$^2$, AM1.5 solar spectrum.

3.7 Fabrication aspects of the device

The bottom cells were fabricated by using blends in a 1:4 ratio of poly((2,7-(9,9-dioctyl)-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) PFDTBT (see inset Figure 3.3C) and the fullerene derivative [6,6]-Phenyl-C$_{61}$-butyric acid methyl ester (PCBM) or poly(2-methoxy-5-(3',7'-dimethoxyloxy)-1,4-phenylene vinylene) (MDMO-PPV, see inset Fig 3.3A) and PCBM. Also bottom cells based on blends in a 1:1 ratio of regioregular poly(3-hexylthiophene) (P3HT, see Figure 3.3C)) and PCBM were fabricated. The top cell was processed from a CHCl$_3$ solution of the poly(di-2-thienylthienopyrazine) derivative PTBEHT (see inset Figure 3.2) and PCBM in a 1:4 ratio. Poly[5,7-di-2-thienyl-2,3-bis(3,5-di(2-ethylhexyloxy)phenyl)-thieno[3,4-b]pyrazine] (PTBEHT) was synthesized from the corresponding dibrominated monomer via a condensation polymerization using bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$]. The PTBEHT was extensively purified by removing Ni with EDTA disodium salt, Soxhlet extraction using different solvents, and finally a BioBeads GPC column to remove the low molecular weight fraction. The molecular weights as determined with size exclusion chromatography
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are $M_n = 52,000$ g/mol and $M_w = 160,000$ g/mol (PDI = 3.1). PTBEHT is soluble in most common organic solvents. The devices were fabricated on cleaned glass substrates. For the bottom contact, by using a shadow mask, 1 nm Cr (as adhesion layer) and 15 nm Au were vapor deposited (at $10^{-7}$ mbar) on the substrate. Both Cr and Au layers were deposited with very low evaporation-rate ($\sim 0.02$ nm/s) in order to increase the flatness of the electrode (Anode). A 60 nm thick poly(3,4-ethylene dioxythiophene) : polystyrenesulfonic acid (PEDOT:PSS, Bayer AG) was spin coated and dried in the oven at 140 °C for 15 minutes. All conjugated polymers and PCBM were dissolved in chloroform and mixed in the designated weight ratio. A proper spin program was chosen to tune the thickness of the layers. For the middle electrode, using a shadow mask, 0.5 nm LiF + 0.5 nm Al and 15 nm Au were vapor deposited (at $10^{-7}$ mbar) without breaking the vacuum. The combination of LiF and Al used in the middle contact were deposited with very low rate ($\sim 0.01$ nm/s) to reach a very smooth interlayer. The gold (Au) used in the middle contact was deposited with a very high evaporation rate ($\sim 2.2$ nm/s) in order to prevent penetration of the gold atoms into the polymer surface. This is important since experience shows that the integrity of the layers is necessary to achieve a well-performing tandem device. The high evaporation rate (or cooling the substrate during the evaporation processes) leads to creation of bigger gold islands at the middle contact and a sharper interface with the active layer of the bottom cell. Therefore, such a layer better protects the bottom cell against dissolving, during the processing of the top cell. A 60 nm thick PEDOT:PSS was spin coated onto the middle electrode. This PEDOT layer was dried in a vacuum chamber at $10^{-2}$ mbar (1 Pa) for 30 minutes. For the active layer of the top cell, the polymer PTBEHT (as electron donor) and PCBM (as electron acceptor) were used in a 1:4 ratio. Both were dissolved in chloroform. A proper spin program was chosen to tune the thickness of the layers. The reference top cell was fabricated on a glass substrate that consisted of the same electrodes and active layer as the top cell in the tandem configuration. For the top contact, using a shadow mask, 1 nm LiF and 100 nm aluminum (Al) were thermally evaporated. The thicknesses of the different layers were measured by a Dektak 6M profilometer. All optical measurements were performed on a Perkin–Elmer Lamda 900 Spectrometer. For
optical measurements under different light intensities, neutral density filters were used. The $J-V$ measurements (in dark and illuminated) were done by using a Keithley 2400 source meter. The illumination was done using a AM1.5 simulated solar spectrum from a Steuernagel SolarConstant 1200 light source with an intensity of 1000 W/m$^2$ (unless noted otherwise). The processing was done in a glove box under nitrogen and at room temperature.

3.5 Summary

A solution-processed organic tandem cell has been fabricated, using the same solvent (chloroform) for both active layers. Dissolving of the first layer was prevented by using a composite middle electrode that is semitransparent. The layer thickness of the bottom cell was optimized in order to create an optical cavity that efficiently transmits the required wavelength for the top cell. The top cell is processed from a small band gap polymer that allows the collection of a broader range of the solar spectrum. The bottom and top cell are complementary with respect to their absorption spectra. Since the bottom and top cell are electronically stacked in series, the open-circuit voltages of the tandem cell equals the sum of the open-circuits voltages of both sub cells, and the short-circuit current is limited by the lowest value. In this way an open-circuit voltage of 1.4 V is achieved. For highly efficient tandem cells, new materials with higher mobilities and proper optical absorption spectra are needed. The high optical absorption at longer wavelengths of the metallic electrodes (Au) limited the light intensity at the top cell.