Built-in voltage of organic bulk heterojunction p-i-n solar cells measured by electroabsorption spectroscopy

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Built-in voltage of organic bulk heterojunction p-i-n solar cells measured by electroabsorption spectroscopy

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We investigate the influence of the built-in voltage on the performance of organic bulk heterojunction solar cells that are based on a p-i-n structure. Electrical doping in the hole and the electron transport layer allows to tune their work function and hence to adjust the built-in voltage: Changing the doping concentration from 0.5 to 32 wt% induces a shift of the work function towards the transport levels and increases the built-in voltage. To determine the built-in voltage, we use electroabsorption spectroscopy which is based on an evaluation of the spectra caused by a change in absorption due to an electric field (Stark effect). For a model system with a bulk heterojunction of BF-DPB and C60, we show that higher doping concentrations in both the electron and the hole transport layer increase the built-in voltage, leading to an enhanced short circuit current and solar cell performance. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4873597]

I. INTRODUCTION

Organic electronics have several advantages compared to inorganic technologies, allowing flexible, transparent, and large-area products. In the last years, particularly the technology of organic solar cells (OSCs) has rapidly developed. Due to the synthesis of new materials and improved understanding of device principles, efficiencies of 12% were realized.1 Still, for wide-ranging applicability, further improvement is necessary.

For the charge carrier extraction, the built-in voltage (V_{BI}) is an important parameter. Its influence on the device performance is crucial; however, it highly differs between bulk heterojunction (BHJ) and planar heterojunction (PHJ) solar cells. For PHJ, a small influence of V_{BI} on the device performance is suggested due to the dominant diffusion current.2 Here, open-circuit voltages (V_{OC}) larger than V_{BI} were observed.3,4 Nevertheless, a strong influence on the shape of the j-V characteristic is observed, leading to significant s-kinks for small built-in voltages.4,5 An enhancement of both the short-circuit current and the fill factor of more than 10 % was previously observed in PHJ solar cells for an increased V_{BI}.6

In contrast, strong changes of the open-circuit voltage with the built-in field were observed for bulk heterojunction solar cells.4,5,7,8 In addition, a strong correlation of the photocurrent to the internal electric field was previously detected in BHJ solar cells,9 indicating V_{BI} plays a crucial role for the charge carrier extraction.

Many studies apply different materials in order to vary V_{BI}, which is defined as the difference of the electrode work functions.3,4,8,10,11 Still, interface effects and barriers often result in remarkable
variations of the energy level alignment of these materials. In order to study the nature of $V_{BI}$ in OSCs, a direct measurement is preferable.

The technique of electroabsorption spectroscopy (EA) is a non-invasive method which is able to determine $V_{BI}$ in complete solar cells. Here, the Stark effect is used which is a shift of transition energies of a molecule due to an electric field. It was recently applied to PHJ solar cells. In contrast to BHJ solar cells as investigated in this study, the electric field plays a different role. While the diffusion gradient caused by an accumulation of photogenerated charges is low for BHJ compared to PHJ solar cells, the effect of $V_{BI}$ is expected to be stronger for BHJ solar cells. For BHJ solar cells an influence of $V_{BI}$ on $V_{OC}$ is expected.

Systematic studies are possible by electroabsorption spectroscopy on organic solar cells based on the p-i-n concept. Here, the intrinsic heterojunction is embedded between a p-doped hole transport layer (HTL) and an n-doped electron transport layer (ETL). A variation of the doping concentration in the ETL as well as in the HTL allows to specifically tune their work function. Using this concept, a systematic analysis of the built-in voltage is possible without the requirement of changing the electrode material. In combination with electroabsorption, a precise and controlled analysis of the built-in voltage and its influence on the solar cell parameters is thus possible.

In this work, we investigate the built-in voltage of BHJ solar cells for varied doping concentrations in the ETL and HTL using electroabsorption spectroscopy. The evaluation includes both the spectra determined at the first ($\omega$) and at the second harmonic (2$\omega$) of the excitation frequency leading to reliable results despite contributions due to polar molecules that are present in the samples. A clear increase of $V_{BI}$ is observed for larger doping concentrations in the charge carrier transport layers, leading to an increased short circuit current and thus improved device performance.

II. ELECTROABSORPTION SPECTROSCOPY

Electroabsorption spectroscopy can be applied to determine the built-in voltage in semiconductor devices: the principle is the detection of a change in absorption due to an electric field (Stark effect). The electric field influences the electron density distribution of the molecular orbital (induced dipole moments), and thus affects the molecular transition energies. The field-induced change in absorption $\Delta \alpha$ can be analyzed for small energetic shifts $\Delta E$ evaluating the first two terms of a Taylor series:

$$\Delta \alpha = \frac{\partial \alpha}{\partial E} \Delta E + \frac{\partial^2 \alpha}{\partial E^2} \Delta E^2. \quad (1)$$

For an existing permanent dipole moment, the energetic change depends linearly on the electric field ($\Delta E \propto F$). However, this energetic change does not contribute to the first term of equation (1) for an isotropic distribution of permanent dipole moments. Furthermore, a polarization is induced to any molecule resulting in an energy shift proportional to the square of the electric field ($\Delta E \propto F^2$). This so-called quadratic Stark effect does contribute to both terms of equation (1), but is usually small and, therefore, negligible for the second term. As a result, the change in absorption depends on the square of the electric field ($\Delta \alpha \propto F^2$).

Experimentally, the change in absorption is determined indirectly via measurements in reflection geometry. Due to the strongly reflecting metal contact, the probe beam is transmitted through the sample twice resulting in $-\Delta R/R \propto \Delta \alpha$.

For an excitation field that is a superposition of a direct current (DC) and an alternating current (AC) field of frequency $\omega$ ($F_{DC} + F_{AC} \cdot \sin \omega t$), the signal at 1 $\omega$ is linearly dependent on the DC electric field:

$$\frac{\Delta R}{R}(E) \propto F_{DC}^2 + 2F_{DC}F_{AC} \sin \omega t + F_{AC}^2 \cdot \frac{1}{2}(1 - \cos 2\omega t). \quad (2)$$

The DC electric field inside the sample consists of the built-in field $F_{BI}$ and the externally applied field $F_{bias}$ ($F_{DC} = F_{bias} + F_{BI}$). For an externally applied bias voltage $V_{bias}$ compensating the built-in field inside the sample, the signal at frequency $\omega$ will vanish. Therefore, the voltage required to cause
The first harmonic frequency signal to vanish is interpreted as the opposite of the built-in voltage ($V_{\text{BI}} = -V_{\text{bias}}$).

The direct measurement of the built-in voltage is influenced by charge carrier injection at voltages close to the built-in voltage, because they contribute to the spectra. Therefore, the electroabsorption spectra at negative bias voltages are extrapolated to zero signal.

The above described method disregards the case of an electroabsorption signal linearly dependent on the electric field caused by permanent dipole moments. However, these spectral contributions may disturb the correct analysis. Significant contributions due to non-isotropic distributions of polar molecules or interface states were observed before.$^{20-23}$ Hence, the evaluation of the EA signal at only one wavelength results in compensation voltages highly dependent on the chosen wavelength. Previous investigations of the $V_{\text{BI}}$ of organic solar cells used an evaluation method which is able to minimize the influence of polar molecules.$^6$ A spectral range was evaluated which is spectrally separated from strong permanent dipole contributions. However, for a spectral overlap of the crucial EA signal and the contributions due to permanent dipole moments, as it is observed for these samples, an improvement of the suggested evaluation is required.

Therefore, the additional contributions caused by permanent dipole moments have to be considered in the analysis. The evaluation method applied here was previously described.$^{24}$ It exploits the difference of the lineshapes $x(E)$ and $y(E)$ of the signals linearly or quadratically dependent on the electric field:

$$\Delta \alpha(E) \propto x(E) \cdot F + y(E) \cdot F^2.$$  \hfill (3)

The absorption spectra of organic materials show strong inhomogeneous broadening resulting in a Voigt profile. Due to the dominant inhomogeneous broadening of the absorption spectra, a Gaussian-shaped absorption profile is a sufficient approximation decreasing the number of parameters. The change in absorption is assumed to be the difference of the absorption with or without the influence of the electric field:

$$\Delta \alpha = \alpha_2(F_{\text{DC}}, F_{\text{AC}}) - \alpha_1(F = 0).$$  \hfill (4)

The progression of several spectra obtained at different bias voltages $V_{\text{bias}}$, but with constant amplitude $V_{\text{AC}}$ is evaluated. Therefore, the different absorptions $\alpha_2$ differ in their bias voltages. The parameters amplitude $A$, mean energy $\mu$, and damping constant $\sigma$ are assumed to be linearly dependent on the electric field. Therefore, the change in absorption is zero for a vanishing DC electric field inside the sample:

$$\alpha_2 = \alpha_2(A_2, \mu_2, \sigma_2)$$ \hfill (5)

$$\alpha_1 = \alpha_1(A_1, \mu_1, \sigma_1)$$ \hfill (6)

with

$$A_2 = A_1 + \Delta A \cdot F_{\text{DC}}$$ \hfill (7)

$$\mu_2 = \mu_1 + \Delta \mu \cdot F_{\text{DC}}$$ \hfill (8)

$$\sigma_2 = \sigma_1 + \Delta \sigma \cdot F_{\text{DC}}.$$ \hfill (9)

Here, the parameters $\Delta A$, $\Delta \mu$, and $\Delta \sigma$ are proportionality factors accounting for the dependence of $A$, $\mu$, and $\sigma$ on the electric field. The spectral contributions with lineshape $x(E)$ that depend linearly on the electric field, only arise for the EA spectra at $1 \omega$, but are not dependent on the DC electric field (compare equation (10)). In contrast, they have no influence on the $2 \omega$ spectra. The EA spectra at $2 \omega$ entirely result from the quadratic Stark effect. Thus, different lineshapes of $1 \omega$ and $2 \omega$ spectra are a hint for dipole contributions:

$$1\omega : x(E) \cdot F_{\text{AC}} + y(E) \cdot 2F_{\text{DC}}F_{\text{AC}}$$  \hfill (10)
FIG. 1. Stack architecture of the investigated samples. They consist of a bulk heterojunction of C60 and BF-DPB embedded between a HTL made of BF-DPB doped by Fr-TCNQ (1 and 17.5 wt%) and an ETL made of C60 doped by W2(hpp)4 (0.5, 2.0, 8.0, and 32.2 wt%). The electrode materials are indium tin oxide and aluminum.

\[ 2\omega : y(E) \cdot F_{NC}^2. \]  \hspace{1cm} (11)

This is applied for the fitting routine, assuming the change in absorption caused by the quadratic Stark effect to be superimposed by an offset signal (not dependent on \( V_{DC} \)) for the 1 \( \omega \) spectra. In contrast, for the spectra at 2 \( \omega \), the signal is entirely caused by the quadratic Stark effect. Hence, the difference of the lineshapes is solely attributed to permanent dipoles:

\[ 1\omega : \Delta \alpha + \text{offset} \]  \hspace{1cm} (12)

\[ 2\omega : \Delta \alpha. \]  \hspace{1cm} (13)

Therefore, it is implemented that the signal at the isosbestic points results from the offset signal; i.e., isosbestic points significantly differing from zero signal are caused by permanent dipoles.

The fitting routine evaluates six spectra at 1 \( \omega \) (at six different bias voltages) and one obtained at 2 \( \omega \). The difference of the lineshapes is assumed to result from a Gaussian-shaped offset signal. The starting value for the offset mean value is guided by the isosbestic point differing from zero signal.

III. EXPERIMENTAL

For the electroabsorption spectroscopy, an external voltage is applied to the sample using a function generator (Agilent 33220A). A halogen lamp in combination with a monochromator (SPEX 500) is used as a probe beam. The probe beam is focussed on the sample and then reflected by the metal electrode at the back of the sample. Therefore, the probe beam passes the organic layers twice. The reflected beam is detected by a low-noise photodiode (Hamamatsu S2386 5K) and due to the modulation of the excitation voltage afterwards detected by a lock-in amplifier (Stanford Research 830). The lock-in technique significantly enhances the signal-to-noise ratio enabling the detection of changes in absorption up to accuracies of \( 10^{-6} \).

The investigated solar cells are produced by thermal evaporation in vacuum (pressure below \( 10^{-6} \) mbar) using shadow masks. The layer thicknesses are monitored by a quartz crystal.

The stack architecture is shown in Figure 1. According to the p-i-n concept,\(^{16,25}\) the BHJ is embedded between a p-doped HTL and an n-doped ETL which have enhanced conductivities due to the molecular doping.\(^{16,25}\) Therefore, they enable an efficient transport of charge carriers towards the contacts. The p-i-n concept is particularly suitable for systematic studies of \( V_{BH} \) on model systems, because an adjustment of the work function of the contact materials is possible without a variation of the stack architecture.\(^{12,13}\) The deposition of the BHJs and of the doped layers is carried out by co-evaporation of two materials.
FIG. 2. Electroabsorption spectra obtained at the first harmonic frequency (solid lines) and at the second harmonic frequency (dashed line) of a BHJ solar cell with 1 wt% doping concentration in the HTL and 32 wt% doping concentration in the ETL. The first harmonic frequency spectra show an isosbestic point with clearly non-zero signal. In addition a discrepancy of the lineshapes of the first and the second harmonic frequency spectra can be observed around 2.6 eV.

The solar cells are model systems containing heterojunctions of the light absorbing C₆₀ and the transparent BF-DPB which does not contribute to the EA signal. The number of materials that contribute to the EA spectra is reduced in order to allow an unambiguous evaluation of the EA spectra. The BHJs have a thickness of 60 nm and are made of C₆₀ and BF-DPB in the ratio 1:1. The HTL consists of BF-DPB p-doped by F₆-TCNNQ (30 nm) and the ETL of C₆₀ n-doped by W₂(hpp)₄ (10 nm). The doping concentrations in the ETL are 0.5, 2, 8, and 32 wt%. For the HTL, the doping concentration is either 1 or 17.5 wt%. Every HTL doping concentration is combined with every ETL doping concentration resulting in eight different BHJ samples. More information about the materials including the chemical name is provided in section VI.

The transparent bottom contact is indium tin oxide (ITO, Thin Film Devices, Anaheim, CA, USA; 90 nm, 30/cm²) that has been coated on the glass substrate. A metal layer (100 nm aluminum) is evaporated on top of the solar cells. The overlap of the ITO and the metal top contact is used as the active solar cell area (about 6.44 mm²). Finally, the solar cells are encapsulated with a glass cavity glued on top.

The UPS measurements are described elsewhere.¹³

IV. RESULTS

The EA spectra measured at the first and at the second harmonic frequency of a BHJ solar cell with 1 wt% doping concentration in the HTL and 32 wt% doping concentration in the ETL are shown in Figure 2 for several bias voltages. The bias voltage for the spectra observed at 1 ω is varied from -3.05 V to 0.95 V. The measurement was conducted in steps of 0.1 V, but only eight spectra are shown exemplarily. The voltage amplitude is 0.3 Vpp. The 2 ω spectra are measured with a voltage amplitude of 1.5 Vpp at a bias voltage of -2 V. By EA measurements on a contacted single layer of C₆₀, we identify the EA signal as resulting from C₆₀.

For bias voltages leading to a current in forward direction, injected charge carriers contribute to the signal of the change in absorption and lead to significant changes of the spectra’s lineshape. This is visible in Figure 2 for the 1 ω EA spectrum of 0.65 V bias voltage. Therefore, we only analyze the spectra measured at negative bias voltages and an extrapolation to the vanishing signal provides information about the built-in voltage.

At 2.6 eV, the isosbestic point of the 1 ω spectra is clearly shifted from zero signal indicating an offset. An additional contribution to the spectra obtained at 1 ω may occur which is non-sensitive
FIG. 3. Electroabsorption spectra of a BHJ solar cell with 1 wt% doping concentration in the HTL and 32 wt% doping concentration in the ETL. The spectra obtained at the first harmonic frequency (symbols) and the corresponding fit (solid lines) are shown. In addition, the fitted offset signal is shown (dashed line). The fit shows a good conformity with the measured spectra. The inset shows an electroabsorption spectrum obtained at the 2nd harmonic frequency together with the corresponding fit.

From Eq. (4) it is clear that the spectra observed at 1\(\omega\) and at 2\(\omega\) should have the same lineshapes. However, this is not the case for our measurements. A deviation of the first and second harmonic frequency spectra can be obtained between 2.6 and 2.7 eV. As the dipole effects do only contribute to the 1\(\omega\) spectra (Eq. (10)), the difference in lineshape must be caused by effects of permanent dipole moments in the sample.

Stampor\(^23\) attributed the significant changes of the first harmonic frequency spectrum to a non-isotropic contribution of polar molecules. He suggested to preferentially consider those energy ranges where the 1\(\omega\) lineshape resembles the 2\(\omega\) lineshape. However, for our measurements this approach is not suitable, because the Stark peak and the effect of permanent dipoles overlap spectrally. Thus, the application of the fitting routine evaluating both the 1\(\omega\) and the 2\(\omega\) spectra is required. Information about the offset signal can be determined from the spectra. Considering both the shift of the isosbestic point to a negative change in absorption ($\Delta\alpha \propto \Delta R/R$) and the deviation of the lineshapes (1\(\omega\) spectrum more negative than 2\(\omega\) spectrum around 2.6 eV), suggests an offset that is a negative signal around 2.6 eV as an appropriate starting value for the fitting routine.

The fitting routine provides good results. For every sample, we measured spectra at 20 to 30 different bias voltages. For an evaluation of any choice of six of these spectra, we obtained similar fitting parameters. The variation of the resulting fitting parameters is smaller than a factor of two for all evaluated samples.

In Figure 3, the EA spectra and the corresponding fitting results are shown for the BHJ solar cell with 1 wt% doping concentration in the HTL and 32 wt% doping concentration in the ETL. The bias voltage is varied from −2.05 to −0.55 V. The fitted offset is shown as a dashed line. The fitting parameters are as following. $A_1=7.1 \times 10^{-4}$, $\Delta A=2.6 \times 10^{-6}$, $\mu_1=2.5$, $\Delta \mu=-3.0 \times 10^{-3}$, $\sigma_1=0.30$, $\Delta \sigma=-2.7 \times 10^{-3}$, $V_{BI}=0.39$ V, $A_{offset}=-3.5 \times 10^{-6}$, $\mu_{offset}=2.6$, and $\sigma_{offset}=0.12$.

The fit is appropriate for the range between 2.3 and 2.7 eV, while deviations occur for higher and lower energies. The assumption of a Gaussian shaped absorption might give an explanation for the discrepancy, because it could lead to significant deviations far from the mean energy, i.e., in the marginal region of the absorption spectra.

For higher energies, an additional transition occurs. It is not considered in the fit, because no improvement for the built-in voltage determination is expected, but additional parameters would...
TABLE I. Work function of C₆₀ doped with W₂(hpp)₄ measured by UPS in dependence on the doping concentration.

<table>
<thead>
<tr>
<th>Doping concentration/wt%</th>
<th>0.5</th>
<th>2.0</th>
<th>8.0</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work function/eV</td>
<td>4.33</td>
<td>4.22</td>
<td>4.13</td>
<td>4.04</td>
</tr>
</tbody>
</table>

FIG. 4. The built-in voltage of organic BHJ p-i-n solar cells with 1 wt% (red triangles) and with 17.5 wt% (black squares) doping concentration in the HTL. A clear linear increase is shown for lower work functions of the electron transport layer.

complicate the fit. As a result, the consideration of the additional transition would not essentially lead to an enhancement and is, therefore, omitted.

In the inset of Figure 3, the 2 ω EA spectrum is shown with the corresponding fit. A sufficient fitting with stable results is achieved; however, deviations occur for energies of 2.6 eV and higher. As mentioned above for the 1 ω spectra, we suggest the omitted transition at 2.8 eV to be the reason for this discrepancy.

For the sample whose spectra are shown in the Figures 2 and 3, a $V_{BI}$ of $(0.39 \pm 0.05)$ V is determined.

The work function of the ETL material C₆₀ doped by W₂(hpp)₄ is shown for different doping concentrations in Table I. It decreases for higher doping concentration, i.e., as expected a higher doping concentration shifts the Fermi level towards the electron transport level (LUMO).

In addition to the changed Fermi energy, the conductivity of the n-doped C₆₀ is varied from 0.01 to 2 S/cm. Drift-diffusion simulations showed that no influence of the conductivity is expected as they are rather high even for the lowest doping concentration.

In the BHJ solar cells, the intrinsic layer consists of a mixture of C₆₀ and BF-DPB; as a result, the Stark signal generated by C₆₀ monitors the electric field of the entire intrinsic layer. In Figure 4, the determined built-in voltages are plotted versus the work function of the electron transport layer. The results are shown for BHJ solar cells with 1.0 wt% (red triangles) and 17.5 wt% (black squares) doping concentration in the HTL corresponding to work functions of 4.77 eV and 5.03 eV (measured by UPS). The shift of the work function towards the electron transport level induces a linear increase in $V_{BI}$. In addition, the increase of the HTL doping concentration further enhances $V_{BI}$. The slope of the increase of $V_{BI}$ over the ETL work function is about $-0.6$ V/eV for both the BHJ solar cells with a low and with a high doping concentration in the HTL. There is a strong dependence of $V_{BI}$ on the work function of the transport layers as observed before in PHJs. However, the slope significantly varies from unity. This might be caused by a level bending at the interfaces between the intrinsic and the doped layers. The EA signal vanishes for a compensated electric field. However, at the interfaces, level bending can occur. For our samples, we performed drift diffusion simulations which suggest a decreased electric field at the interfaces between intrinsic and doped layers. Therefore, the built-in voltage is overcompensated in order to reach a vanishing...
FIG. 5. The short circuit current density is shown for eight BHJ solar cells dependent on the built-in voltage. An increase is observed for higher built-in voltages.

TABLE II. A summary of the measured values of short-circuit current density, open-circuit voltage and fill factor for all samples.

<table>
<thead>
<tr>
<th>Doping concentration of ETL/wt%</th>
<th>0.5</th>
<th>2.0</th>
<th>8.0</th>
<th>32</th>
<th>0.5</th>
<th>2.0</th>
<th>8.0</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doping concentration of HTL/wt%</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>17.5</td>
<td>17.5</td>
<td>17.5</td>
<td>17.5</td>
</tr>
<tr>
<td>$V_{\text{OC}}$/V</td>
<td>0.70</td>
<td>0.75</td>
<td>0.75</td>
<td>0.76</td>
<td>0.64</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>$j_{\text{SC}}$/mA/cm$^2$</td>
<td>0.46</td>
<td>0.48</td>
<td>0.51</td>
<td>0.52</td>
<td>0.49</td>
<td>0.54</td>
<td>0.58</td>
<td>0.59</td>
</tr>
<tr>
<td>FF/$%$</td>
<td>34.3</td>
<td>26.9</td>
<td>27.0</td>
<td>27.0</td>
<td>34.6</td>
<td>27.1</td>
<td>27.2</td>
<td>27.3</td>
</tr>
<tr>
<td>Efficiency/$%$</td>
<td>0.11</td>
<td>0.10</td>
<td>0.10</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.12</td>
<td>0.12</td>
</tr>
</tbody>
</table>

electric field in the bulk of the sample. This effect is small for high doping concentrations, but it may lead to overestimated built-in voltages of the low doped samples. Hence, the $V_{\text{BI}}$ does not increase with a unity slope for a shift of the work function. We previously observed this effect in PHJ solar cells.\textsuperscript{6}

In Figure 5, the short-circuit current density ($j_{\text{SC}}$) is shown for different built-in voltages. This figure includes all data points of the eight BHJ solar cells of Figure 4. It can be seen that $j_{\text{SC}}$ increases linearly for higher $V_{\text{BI}}$. We interpret this enhancement as a more efficient charge carrier extraction reducing the recombination.

Menke \textit{et al.}\textsuperscript{16} observed a decrease in the conductivity for doping concentrations as high as 32.2 wt%. Despite the decrease of the conductivity, the charge carrier extraction is enhanced for our BHJ solar cells with the highest doping concentrations in the ETL. This is an indication that the improved charge carrier extraction is caused by an increased $V_{\text{BI}}$ and not by an increased conductivity.

The measured $V_{\text{OC}}$, $j_{\text{SC}}$, FF, and efficiencies of all samples are shown in Table II. These values are not mismatch corrected, but are measured at the same intensity (677 mW/cm$^2$) by a silicon reference diode. The open-circuit voltage is 0.75 V for all samples. However, for the samples with the lowest doping concentration in the ETL it is decreased to 0.64 V (HTL: 1 wt%) and 0.70 V (HTL: 17.5 wt%), respectively. A decrease of the open-circuit voltage due to very small built-in voltages was observed before in PHJ solar cells.\textsuperscript{6} In contrast to previous studies,\textsuperscript{2} a general limitation of $V_{\text{OC}}$ by $V_{\text{BI}}$ could not be observed in our studied BHJ solar cells.

The fill factor of all samples is rather limited. We attribute this to the amorphous and transparent donor material that is usually used as a hole transport material.
A small increase of the fill factor (from 26.9 to 27.3 %) was observed for larger built-in voltages. Again, the two samples of the smallest built-in voltage (ETL: 0.5 wt%) are an exception. Here, the fill factor was larger than 34% due to the decrease in the open-circuit voltage and the consequential change of the shape of the current-voltage characteristic.

The efficiency increases for larger built-in voltages. However, due to the missing second absorber material, the effect is very small and only slightly above the measurement error.

V. CONCLUSION

We show that the technique of electroabsorption spectroscopy is a reliable tool to determine the built-in voltage of complete solar cell devices even if non-isotropically distributed dipoles are present. Using electroabsorption spectroscopy, we found that the built-in voltage of our samples is strongly dependent on the work function of both the p-doped hole and the n-doped electron transport layer. A shift of the work function towards the transport levels increases the built-in voltage even for very high doping concentrations that induce a decrease of the conductivity. The short-circuit current density is increased from 0.46 to 0.59 mA/cm² corresponding to an improvement of 28% for a larger built-in voltage (from 0.19 to 0.46 V). A limitation of the open-circuit voltage by the built-in voltage was not observed.

VI. MATERIALS

The buckminster fullerene (C₆₀, supplier: IPMS, Dresden, Germany, used as obtained) is used as acceptor material. The donor material is, N’-((Diphenyl-N,N’-bis)9,9,-dimethyl-fluoren-2-yl)-benzidine (BF-DPB, supplier: IAPP, Dresden, Germany, used as obtained). The p-dopant is 2,2’-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F₆-TCNNQ, supplier: Novaled AG, Dresden, Germany, used as obtained) and the n-dopant is tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-alpyrimidinidino)ditungsten (II) (W₂(hpp)₄, supplier: Novaled AG, Dresden, Germany, used as obtained).

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