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Melzer, C.; Krasnikov, V. V.; Hadziioannou, G.

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Organic donor/acceptor photovoltaics: The role of C60/metal interfaces

Christian Melzer and Victor V. Krasnikov
Department of Polymer Chemistry, Material Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
Georges Hadziioannou
Ecole Européenne Chimie Polymères Matériaux (ECPM), University Louis Pasteur Strasbourg, 25 rue Becquerel, F-67087 Strasbourg Cedex 2, France

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The photovoltaic properties of thin films based on donor/acceptor heterojunctions, prepared by means of either consecutive evaporation or co-evaporation, and sandwiched between asymmetric contacts are investigated. (E,E,E,E)-1.4-bis[(4-styryl)styryl]-2-methoxy-5-(2’-ethylhexoxy)benzene (MEH-OPV5) and Buckminster fullerene C60 are employed as donor and acceptor materials, respectively. Current-voltage measurements and impedance spectroscopy on the donor and the acceptor single-layer cells suggest the presence of a strong dipole layer at the C60/metal interfaces. The correlation between the photovoltaic performances and film morphologies is discussed.

The introduction of organic semiconductors has triggered interest in the field of photodetectors and solar cells as devices of any shape can be produced at potentially low cost. However, efficiencies of such devices are currently much lower than those of their inorganic counterparts, demanding a further search for more efficient organic materials and better understanding of the device physics.

The photovoltaic effect involves the creation of electrons and holes under optical excitation and their successive collection at opposite electrodes. In organic semiconductors, illumination creates excitons that need to dissociate into free holes and electrons, suggesting donor/acceptor-type of photovoltaic systems. Currently, two basic donor/acceptor device structures are discussed. Double-layer device structures with a single planar heterojunction interface show good diode behavior, but the limited exciton dissociation interface causes a rather low sensitivity. In this respect, a percolated system of donor and acceptor phases, that is, a network of heterojunctions through the entire film, seems to be more promising. In such blended structures, however, disorder might limit the photovoltaic performance. Moreover, new interfaces appear that can strongly affect the device physics.

In Fig. 1, we present I–V curves of an ITO/PEDOT:PSS/MEH-OPV5/C60/Al double-layer cell in dark and under illumination. The cell showed a photovoltaic performance of around 1 mW/cm². The introduction of organic semiconductors has triggered interest in the field of photodetectors and solar cells as devices of any shape can be produced at potentially low cost. However, efficiencies of such devices are currently much lower than those of their inorganic counterparts, demanding a further search for more efficient organic materials and better understanding of the device physics.

What is remarkable is that Uoc of the codeposited cell was about 0.1 A/W, twice higher than that of the double-layer cell. S decreased with an increase in Iph, like it was observed elsewhere.

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was found to be only 0.65 V. $U_{oc}$ saturated to 0.7 V ± 0.1 V averaged over several samples at high $I_L$, inconsistent with $U_{soc}$ predicted by the MIM model. The same observations were reported on organic donor/acceptor photovoltaic cells of a similar system.\textsuperscript{10} It is not clear whether the decrease of the $U_{soc}$ from 0.9 ± 0.1 V for the double-layer cell to 0.7 ± 0.1 V for the co-deposited cell is due to the change of heterojunction distribution or whether other phenomena are involved. As a consequence however, the monochromatic power conversion efficiency was reduced to 1% because the increased $S$ was compensated by the low FF and the low $U_{oc}$. To reveal the origin of the low $U_{oc}$ observed in the blend we examined single-layer devices of the donor and the acceptor, respectively.

An ITO/PEDOT:PSS/MEH-OPV5/Al single-layer cell showed $U_{soc}$ around 1.1 ± 0.1 V (Fig. 2). In contrast, $U_{soc}$ of an ITO/PEDOT:PSS/C\textsubscript{60}/Al single-layer cell was 0.3 ± 0.2 V, suggesting that the C\textsubscript{60} phase is responsible for the low $U_{soc}$ of the co-deposited cell. It should be noted that, unlike $U_{soc}$ of the other cells, $U_{soc}$ of the C\textsubscript{60} single-layer cell deviated strongly from sample to sample. The most plausible causes of the low $U_{soc}$ are interfacial dipole layers or/and interfacial surface charges\textsuperscript{11,12} at the PEDOT:PSS/C\textsubscript{60} and/or Al/C\textsubscript{60} interfaces with the total strength of 0.6 ± 0.2 V.

$C$–$V$ measurements on single-layer C\textsubscript{60} cells showed the bias independent geometrical capacitance at high frequencies (\textgtrsim 1 kHz). At low frequencies (< 100 Hz), a steep increase of capacitance in forward bias was observed. Several models, including Schottky contact, $p$–$n$ junction, charging of surface states, etc., predict such bias dependant capacitance with slow dynamics. In the low-frequency regime, a linear dependence of $1/C^2$ on bias unveils a depletion capacitance and provides simultaneously its built-in potential ($U_{bi}$), ionized state density ($N_i$) and the depletion width ($W$) (e.g., at zero

<table>
<thead>
<tr>
<th>$U_{soc}$ [V]</th>
<th>$U_{bi}$ [eV]</th>
<th>$N_i$ [$10^{16}$ cm$^{-3}$]</th>
<th>$W_{0 \text{V}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer C\textsubscript{60}</td>
<td>0.3 ± 0.2</td>
<td>0.3 ± 0.2</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td>Single-layer MEH-OPV5</td>
<td>1.1 ± 0.1</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Double layer</td>
<td>0.9 ± 0.1</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Blend</td>
<td>0.7 ± 0.1</td>
<td>0.7 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
</tbody>
</table>
bias).\textsuperscript{11} Like the photovoltaic measurements, the $C-V$ measurements showed strong deviations of $U_{bi}$ from sample to sample and consequently of $W_{0V}$ and $N_i$. For each cell, however, the obtained $U_{bi}$ was close to the measured $U_{soc}$. $1/C^2$ versus $U$ for a 100-nm-thick single-layer $C_{60}$ cell was linear only in a narrow range in forward bias, whereas in reverse bias, the capacitance approached the geometrical capacitance. Film thickness increase of $C_{60}$ extended the deple-

tion capacitance region towards reverse bias, corroborating a one-side abrupt $p-n$ heterojunction type of contact between $C_{60}$ and one of the electrodes. Because a constant capacitance was observed over a wide range of bias and frequency for double-layer cells, the depletion layer is formed at the anode/$C_{60}$ contact. We infer that the $C_{60}$ layer is most likely $n$-doped with a rather low doping density of $10^{16}$ cm$^{-3}$. Although the origin of the doping is not known, diffusion of the top metal electrode into the bulk was reported to result in a doped organic semiconductor.\textsuperscript{13}

We now assume that the interfacial dipole strength and the ionized state density are proportional to the corresponding material densities. Under this assumption, $N_i$ is proportional to the density of $C_{60}$, and in turn the dipole strength is proportional to the surface density of the organic medium at the metal/organic interface. Since we deposited $C_{60}$ and MEH-OPV5 in a ration of 1:1, $N_i$ of a blended structure should be half of $N_i$ determined for the bare $C_{60}$ film and $W_{0V}$ twice longer, being confirmed by $C-V$ measurements (Table I). The dipole-layer strength in a single-layer MEH-OPV5 cell was found to be $-0.2$ eV. The interfacial MEH-OPV5 density in a blended cell is half of the interfacial MEH-OPV5 density of the bare MEH-OPV5 cell resulting in a dipole-layer strength of $-0.1$ eV at the MEH-OPV5/metal interfaces. Since the dipole-layer strength in a single-layer $C_{60}$ cell was measured to be $0.6$ eV, our assumption requires a dipole-layer contribution from the $C_{60}$/metal interfaces in the blend to be $0.3$ eV. The predicted total dipole-layer strength in a blended cell is then $0.2$ eV and the $U_{soc}$ should be $0.7$ V, in agreement with the measured value (Table I). Obviously, an additional verification of the model would require variations in the blend composition. This however, may create discontinuities of phases, resulting in a quasi double-layer structure, a situation not included in the model.

In this letter, the importance of the electrode/organic interfaces for the performance of organic donor/acceptor photovoltaic cells was demonstrated. $I-V$ and $C-V$ measurements revealed the existence of strong dipole layers at the metal/$C_{60}$ interfaces. We demonstrated that dipole layers have a deep impact on the built-in potential and consequently on the open-circuit voltage of organic composite photovoltaic cells. The photovoltaic performance of the blended structure could be explained by a simple dilution model.

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