Organic donor/acceptor photovoltaics: The role of C_{60}/metal interfaces

Christian Melzer and Victor V. Krasnikov a)
Department of Polymer Chemistry, Material Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Georges Hadzioannou b)
Ecole Européenne Chimie Polymères Matériaux (ECPM), University Louis Pasteur Strasbourg, 25 rue Becquerel, F-67087 Strasbourg Cedex 2, France

(Received 13 September 2002; accepted 4 March 2003)

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 C_{60} 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 C_{60}/metal interfaces. The correlation between the photovoltaic performances and film morphologies is discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1570936]

The introduction of organic semiconductors has triggered interest in the field of photodetectors 1–3 and solar cells 4–7 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, 8 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. 4,5,9 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 this letter, we reveal the impact of the interfaces in a donor/acceptor photovoltaic cell on the device performance by investigating single-layer, double-layer, and blended photovoltaic systems of the donor (E,E,E,E)-1,4-bis[(4-styryl)styryl]-2-methoxy-5-(2’-ethylhexoxy)benzene (MEH-OPV5) and the acceptor C_{60}, with indium-tin-oxide/ polyethylene dioxythiophene polystyrene sulfonate (ITO)/PEDOT:PSS (synthetic metal, $\phi = 5.2$ eV) as anode and Al ($\phi = 4.3$ eV) as cathode.

Organic donor/acceptor photovoltaic cells were prepared on ITO-coated glass substrates used as anode ($\phi = 4.7$ eV). ITO glass (Merck KGaA, <100 Ω/□) was cleaned by a wet cleaning procedure. PEDOT:PSS was spin-coated from a water dispersion (Baytron P TP Al 4083 without modification) on cleaned ITO plates and dried under $10^{-2}$ Pa at 130 °C for several minutes. MEH-OPV5 and C_{60} (BuckyUSA, 99% C_{60}) films were obtained via vacuum vapor deposition at dynamic vacuum better than $2 \times 10^{-4}$ Pa. Double-layer cells were obtained by successive deposition of the two compounds, whereas percolated structures were prepared by codeposition. The deposition rate for both materials where determined to be 0.88 V, resulting in a monochromatic power conversion efficiency of around 0.054 A/W and a high fill factor of 0.45. The open-circuit voltage ($U_{oc}$) was constant over a broad range in dark and under illumination. The cell showed a photovoltaic performance of around 10%.

In Fig. 1, we present $I$–$V$ curves of an ITO/PEDOT:PSS/MEH-OPV5/C_{60}/Al double-layer cell in dark and under illumination. The cell showed a photovoltaic sensitivity ($S$) of around 0.054 A/W and a high fill factor (FF) of 0.45. The open-circuit voltage ($U_{oc}$) was measured to be 0.88 V, resulting in a monochromatic power conversion efficiency of ~2%. $S$ was constant over a broad range in light intensity ($I_L$). $U_{oc}$ saturated to almost 1 V at $I_L$ of approximately 10 mW/cm$^2$. The saturated open-circuit voltage ($U_{oc}$) of 0.9 ± 0.1 V averaged over several samples matches the difference in $\phi$ of the metal electrodes which is $U_{oc}$ predicted by a metal/insulator/metal (MIM) model. $S$ of an ITO/PEDOT:PSS/MEH-OPV5+C_{60}/Al codeposited cell was measured to be 0.078 A/W (Fig. 1, $I_L = 1$ mW/cm$^2$). At low $I_L$ (<0.1 mW/cm$^2$), $S$ was about 0.1 A/W, twice higher than that of the double-layer cell. $S$ decreased with an increase in $I_L$, like it was observed elsewhere.

What is remarkable is that $U_{oc}$ of the codeposited cell...
was found to be only 0.65 V. \( U_{oc} \) saturated to 0.7 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.\(^{10} \) 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 codeposited cell is due to the change of het-
erojunction distribution or whether other phenomena are in-
volved. 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\(_{60}\)/Al single-layer cell was 0.3
± 0.2 V, suggesting that the C\(_{60}\) phase is responsible for the
low \( U_{soc} \) of the codeposited cell. It should be noted that,
unlike \( U_{soc} \) of the other cells, \( U_{soc} \) of the C\(_{60}\) 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\(^{11,12} \) at the PEDOT:PSS/C\(_{60}\) and/or
Al/C\(_{60}\) interfaces with the total strength of 0.6 ± 0.2 V.

\( C-V \) measurements on single-layer C\(_{60}\) cells showed the
bias independent geometrical capacitance at high frequencies
(> 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 sur-
face states, etc., predict such bias dependant capacitance with
slow dynamics. In the low-frequency regime, a linear depen-
dence 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 I.** Summary of the main cell characteristics.

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>( U_{soc} ) [V]</th>
<th>( U_{bi} ) [eV]</th>
<th>( N_i ) ( \times 10^{16} ) cm(^{-3} )</th>
<th>( W_{0V} ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer C(_{60})</td>
<td>0.3 ± 0.2</td>
<td>0.3 ± 0.2</td>
<td>1.1 ± 0.4</td>
<td>110 ± 20</td>
</tr>
<tr>
<td>Single-layer MEH-OPV5</td>
<td>1.1 ± 0.1</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Double layer</td>
<td>0.9 ± 0.1</td>
<td>...</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>
<td>240 ± 7</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 depletion 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$_{60}$ 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.

The authors thank P. F. van Hutten for many fruitful discussions. This research was financially supported by the Dutch Organization of Scientific Research (NWO-CW) and the Priority Program Materials (PPM).