Organic donor/acceptor photovoltaics: The role of C\textsubscript{60}/metal interfaces

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The introduction of organic semiconductors has triggered interest in the field of photodetectors\textsuperscript{1–3} and solar cells\textsuperscript{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,\textsuperscript{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 photovoltaic systems.\textsuperscript{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 characteristics. 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\textsubscript{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 \(\Omega/\square\)) 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\textsubscript{60} (BuckyUSA, 99% C\textsubscript{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 was about 0.1 A/W, twice higher than that of the double-layer cell. Aluminum was vacuum vapor deposited at 2\(\times 10^{-3}\) Pa.

All measurements were done under dynamic vacuum or nitrogen atmosphere using a Solatron Si 1260 impedance/gain–phase analyzer for impedance spectroscopy and a Keithley 236 source-measure unit for IV measurements. The cells were illuminated from the glass side with monochromatic light of 458 nm (argon-ion laser, Spectra-Physics, BeamLok 2060). \(I–V\) curves were taken at a light intensity \(I_L\) of around 1 mW/cm\(^2\).

In Fig. 1, we present \(I–V\) curves of an ITO/PEDOT:PSS/MEH-OPV5/C\textsubscript{60}/Al double-layer cell in dark and under illumination. The cell showed a photovoltaic performance 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 characteristics. 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\textsubscript{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.

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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 codeposited 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 codeposited 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 (> 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 $U_{bi}$).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
& $U_{soc}$ & $U_{bi}$ & $N_i$ & $W_{0V}$ \\
& [V] & [eV] & [$10^{16}$ cm$^{-3}$] & [nm] \\
\hline
Single-layer C\textsubscript{60} & 0.3 ± 0.2 & 0.3 ± 0.2 & 1.1 ± 0.4 & 110 ± 20 \\
Single-layer MEH-OPV5 & 1.1 ± 0.1 & ⋯ & ⋯ & ⋯ \\
Double layer & 0.9 ± 0.1 & ⋯ & ⋯ & ⋯ \\
Blend & 0.7 ± 0.1 & 0.7 ± 0.1 & 0.5 ± 0.1 & 240 ± 7 \\
\hline
\end{tabular}
\caption{Summary of the main cell characteristics.}
\end{table}
bias).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 transition from partly to fully depleted cell (Fig. 2) and suggesting 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.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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