The influence of materials work function on the open circuit voltage of plastic solar cells

C.J. Brabec[a,*], A. Cravino[a], D. Meissner[a], N.S. Sariciftci[a], M.T. Rispens[b], L. Sanchez[b], J.C. Hummelen[b], T. Fromherz[c]

[a]*Christian Doppler Laboratory for Plastic Solar Cells, LIOS, Physical Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria*
[b]*Stratingh Institute and MSC, University of Groningen, 9747 AG Groningen, The Netherlands*
[c]*Institut für Halbleiter- und Festkörperphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria*

Abstract

Conjugated polymer/fullerene plastic solar cells of the first generation were consisting of two distinct layers, made of the donor polymer and of the acceptor fullerene, respectively, sandwiched between two metal contacts. By mixing the polymer and the fullerene components, thus replacing a single flat junction with an interpenetrating network bulk-heterojunction, the device efficiency was dramatically improved. As a further step to proceed with the development of plastic solar cells, we developed the bulk diffusion bilayer approach, allowing the creation of donor-acceptor diffused interfaces with less restrictions to the phase compatibility of the two components. For a novel series of fullerenes, the bulk diffusion bilayer approach is shown to yield devices with comparable efficiencies as the blend bulk heterojunction approach. Bulk-heterojunction devices show unusually high open circuit voltage (V_{OC}) values. These values cannot be explained by the metal-insulator-metal (MIM) model that has been often used for organic light emitting diodes. In order to investigate the origin of the V_{OC} in bulk-heterojunction plastic solar cells, we have prepared PPV based devices varying both the metal negative contact and the fullerene acceptor. Fullerene derivatives with varying acceptor strength, (i.e. the first reduction potential) were used as electron acceptors in bulk-heterojunction plastic solar cells produced with the blend as well as the diffusion bilayer approach. The open circuit voltage of the devices was found to correlate directly with the acceptor strength of the fullerenes, while it was rather insensitive to variations in the workfunction of the negative electrode metal. These results suggest that the quasi-Fermi level of the fullerene pins the Fermi level of the evaporated negative metal contact. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photovoltaic; Solar cells; Fullerenes; Conjugated polymers; Open circuit voltage

1. Introduction

The occurrence of a photo-induced electron transfer from non-degenerate ground-state conjugated polymers to fullerenes allows us to explore them as materials for photovoltaic applications [1,2]. The excellent photosensitivity and relatively high-energy conversion efficiencies obtained from interpenetrating network bulk-heterojunction devices are promising. We have recently demonstrated that the power conversion efficiency of bulk heterojunction plastic solar cells produced from a soluble poly(*para*-phenylene vinylene) (MDMO-PPV) and a soluble methanofullerene (PCBM) can be improved up to 2.5% under AM1.5 irradiation [3,4], thus already reaching a power performance close to industrial application. The built-in potential of solar cells, which can be estimated from the open circuit voltage V_{OC}, is an essential parameter of thin film photovoltaic devices, influencing charge dissociation and charge collection and thus mirroring the diode principle as well as the photophysical properties of the materials.

---

* Corresponding author. Current Address: Siemens AGCTMM1, Paul Gossenstr. 100, D-91052, Erlangen, Germany. Tel: +49-9131-7-42245; fax: +49-9131-7-32469.

E-mail address: christoph.brabec@erls.siemens.de (C.J. Brabec).

MDMO-PPV

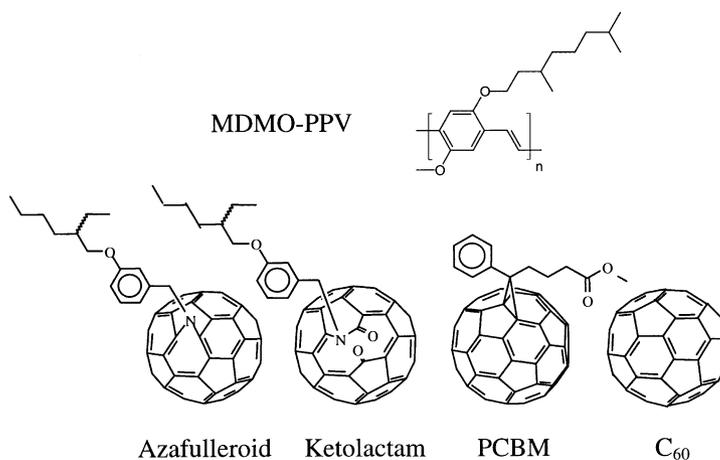Azafulleroid   Ketolactam   PCBM C_{60}

Fig. 1. Chemical structure of the investigated compounds.

Therefore, the question of the built-in potential is directly related to an extensively discussed phenomenon, the origin of the open circuit voltage V_{OC}.

In order to systematically prove the correlation between the open circuit voltage of plastic solar cells and the reduction potential of fullerenes, we investigated a series of highly soluble fullerene derivatives with varying acceptor strength, (i.e. first reduction potential). These fullerene derivatives, methanofullerene PCBM [5], a new azafulleroid and a ketolactam quasifullerene (Fig. 1), show a variation of almost 200 mV in their first reduction potential [6]. Additionally, cells made with [60] fullerene (C_{60}) were also compared. It is important to emphasize that, apart from C_{60}, these acceptors have a very comparable size of the solubilizing group. Effects due to a different donor–acceptor distance and/or different morphology should be minimized in this way, as required for a comparative study. Nevertheless, we realize that it is highly unlikely that the morphologies of the various active layers are identical.

In order to minimize further the influence of the morphology on the device performances, we developed an alternative device concept and production method, the bulk diffusion bilayer. This technique was developed as a first step on the way to develop molecular plastic solar cells using both organic synthesis and the supramolecular engineering approach. The initial emphasis was to investigate the behavior of soluble fullerenes derivatives when processed with soluble conjugated polymers on the device scale. This method is based on the diffusion profile of the low-molecular weight component (in our case, the fullerene) into a high molecular weight polymer film, resulting in a diffused phase interface between these two components, typically in the range of 20–30 nm. However, the dimension of this diffused interface can be tuned over the full thickness of the polymer layer. The bulk diffusion bilayers are

produced in a two step process. First, the pristine polymer film is deposited, typically by doctor blading. After drying, the fullerene layer is cast as a second layer, from a solvent or a combination of solvents that are allowed to swell or partially dissolve the underlying polymer film without removing it.

The difference in the fullerene distribution for the bulk heterojunction approach and the diffusion bilayer approach is schematically shown in Fig. 2. The diffusion bilayer is promising, especially for donor–acceptor compounds with low chemical similarity In such a case, the danger of phase separation and subsequent pinhole formation is significantly reduced in the bilayer diffusion geometry than in the bulk heterojunction geometry [7]. It is worth mentioning that the doctor blade technique turned out to be the preferred technique for the production of the diffusion bilayer devices over the spin casting technique.

In this paper we discuss the photovoltaic properties of devices from MDMO-PPV mixed with a series of fullerenes with varying acceptor strength. Moreover, devices produced in the conventional bulk heterojunction approach are compared to devices produced in the diffusion bilayer geometry.
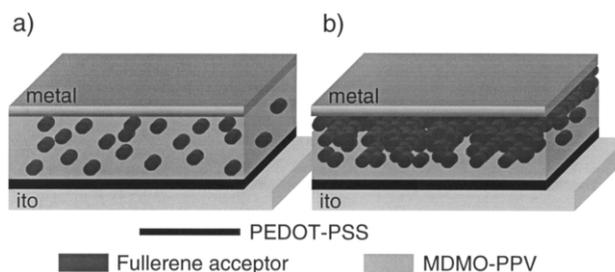
Fig. 2. The (a) blend bulk heterojunction vs. the (b) diffusion bilayer geometry.
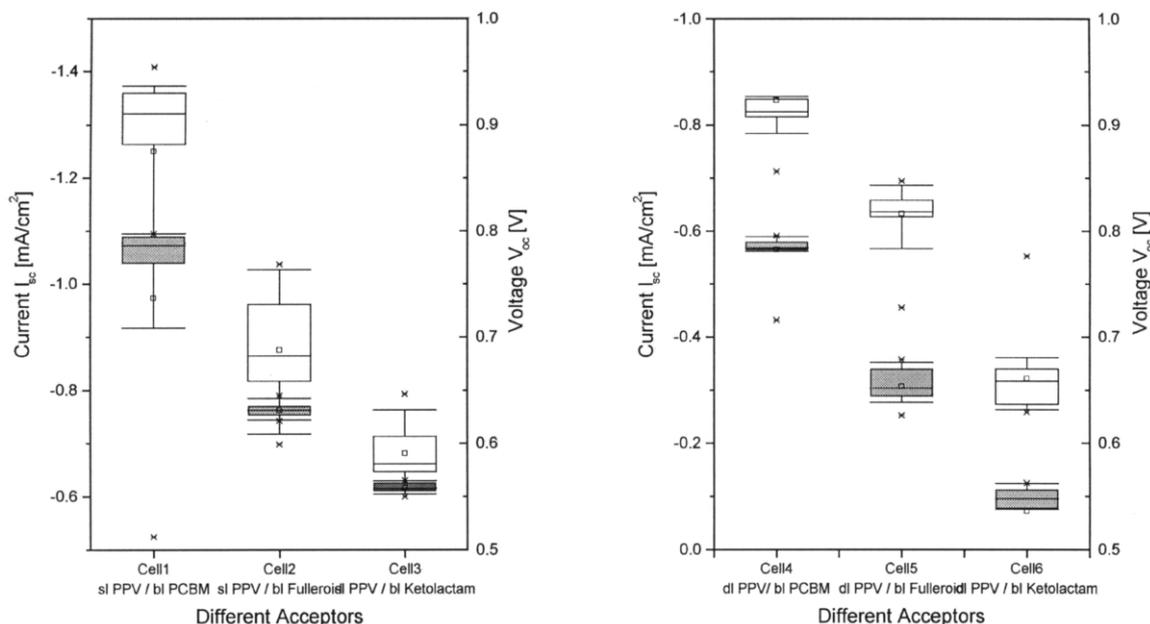
Fig. 3. I_{SC} and V_{OC} of diffusion bilayer devices with a single layer (a) and double layer (b) of MDMO-PPV. The transparent box plots represent the I_{SC} (left axis) while the shaded box plots represent the V_{OC} (right axis). The different acceptors are denoted at the x-axis. In the box plots, the horizontal lines denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The two symbols below and above the 5th/95th percentile error bar denote the highest and the lowest observed values, respectively.

2. Experimental

As polymeric donor MDMO-PPV (Fig. 2) was used in all experiments. This polymer has been used routinely in plastic PV research during the last few years [8].

The redox behavior of all the fullerene acceptors (Fig. 2) was determined by cyclic voltammetry (CV) and is described in detail elsewhere [6]. The results from the CVs are summarized in Table 1 for numeric comparison. All four CVs showed four reversible reduction waves corresponding to the reduction of the fullerene cage. However, the first reduction waves — indicative of the electron acceptor strength of the compounds — show distinctive differences. Ketolactam (–0.53 V vs. NHE) appeared to be a substantially better electron acceptor than C_{60} (–0.60 V) [9], whereas azafulleroid (–0.67 V) is close to C_{60}, and PCBM (–0.69 V) showed clearly diminished electron affinity.

Thin film diodes were prepared on cleaned polyester /ITO/PEDOT:PSS substrates by doctor blading the photoactive layers (either pristine MDMO-PPV or MDMO-PPV: acceptor (1:1 molar ratio) or pristine acceptor solutions from toluene). Then, the aluminum cathode was thermally deposited through a shadow mask to define a device area of 5 mm^2. Organics were cast in room conditions while the metallization and the device characterization were performed in a dry-box under argon atmosphere. Diffusion bilayer devices were produced in two different thickness, single layer and double layer devices.

Single Layer bilayer diffusion devices — in the first step, a layer of pristine MDMO-PPV was cast by doctor blading a 0.25%-wt. solution in toluene (giving approx. 100-nm-thick films); in the second step, the acceptor layer was cast on top of the dry MDMO-PPV layer by doctor blading a 1%-wt. solution of the acceptor in toluene. These devices are denoted as SL (single layer) PPV/Diffusion bilayer Fullerene.

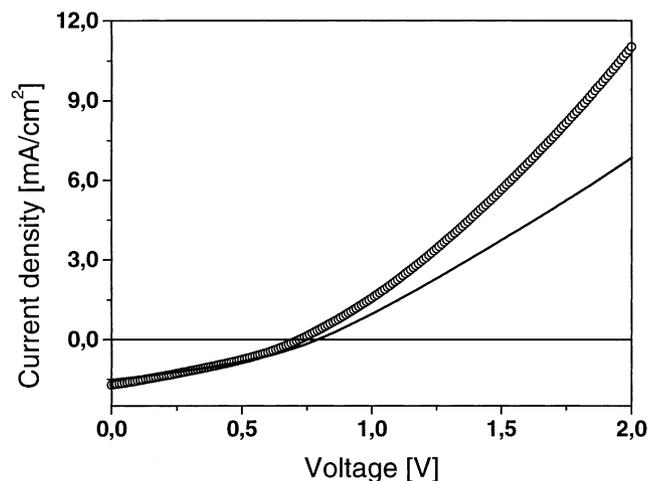Double Layer bilayer diffusion devices — these devices were produced as described above, but two

Fig. 4. I/V curves (illumination, 60 mW/cm^2, white halogen lamp) of bulk-heterojunction MDMO-PPV/PCBM devices. Single layer (open circles) and double layer (line) devices.

Table 1
Redox potentials of C_{60} and fullerene derivatives.

Compound	E^1_{Red} (V vs. NHE)
PCBM	-0.69
Azafulleroid	-0.67
Ketolactam	-0.53
C_{60}	-0.60

layers of pristine MDMO-PPV were cast instead of a single layer. These devices are denoted as DL (double layer) PPV/Diffusion Bilayer Fullerene.

The bulk heterojunction devices were also produced in two different thicknesses, single layer and double layer devices.

Single Layer bulk heterojunction devices — a layer of a MDMO-PPV:acceptor blend was cast by doctor blading a ~1%-wt. solution in toluene with a polymer/acceptor ratio of 1:1 (mol). These devices are denoted as PPV/(Fullerene) SL (single layer).

Double Layer bulk heterojunction devices — two layers of a MDMO-PPV:acceptor blend were cast by doctor blading a ~1%-wt. solution in toluene with a polymer:acceptor ratio of 1:1 (mol). These devices are denoted as PPV/(Fullerene) DL (double layer).

Photovoltaic parameters were determined under illumination with 60 mW/cm² white light from a halogen lamp. More than 80 devices were produced from each acceptor type to allow a statistical evaluation of the observed open circuit voltage. A box plot diagram was
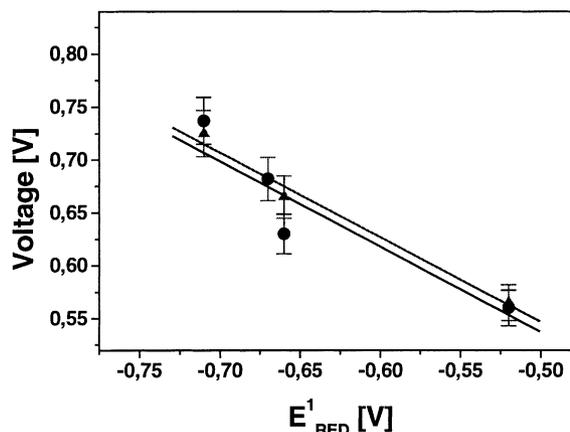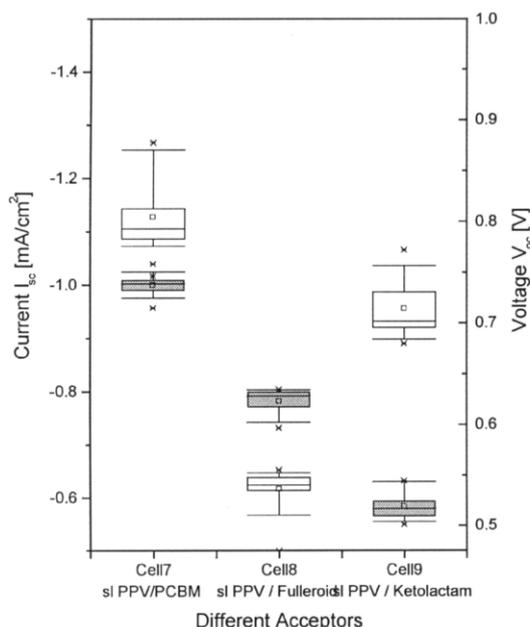

Fig. 6. V_{OC} vs. acceptor strength (1st reduction potential) for the bilayer diffusion (full grey triangles) and for the bulk heterojunction (full black circles) devices. It is important to note that the points present the mean average value calculated from all characterized devices. The slope of the fit is for both types of device S~0.8.

chosen to present the results from current/voltage (I/V) measurements for the V_{oc} (Fig. 3) [6].

3. Results and Discussion

Fig. 3. shows the results from the bilayer diffusion devices with the different acceptors, both for the single layer MDMO-PPV (Fig. 3a, and the thicker, double layer MDMO-PPV (Fig. 3b, devices. For both, the I_{SC} and the V_{OC} values a rather narrow distribution is
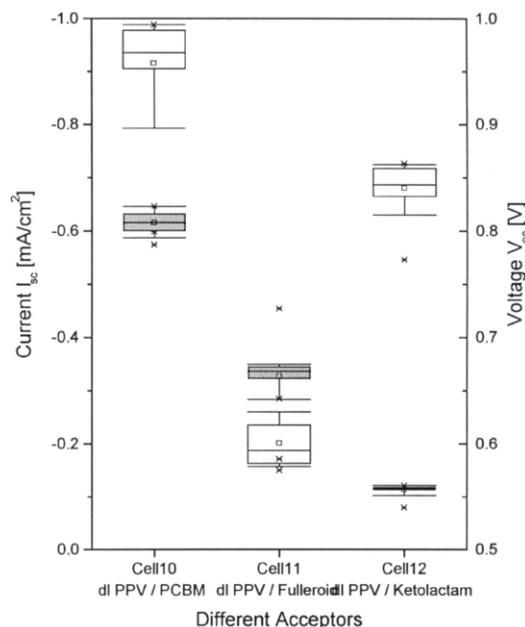

Fig. 5. I_{SC} and V_{OC} of blend bulk heterojunction devices with a single layer (a) and double layer (b) of the MDMO-PPV/acceptor blends. The transparent box plots represent the I_{SC} (left axis) while the shaded box plots represent the V_{OC} (right axis). The different acceptors are denoted at the x-axis. A description of the box plot is given by the caption of Fig. 3.

observed, proving the high reproducibility of the production process. While the variation in the I_{SC} is typically less than 15%, the V_{OC} is distributed within less than 7%. The same trend of the device characteristics with the acceptor strength is observed for both types of devices, (i.e. single layer or double layer of MDMO-PPV). Devices with PCBM as acceptor give the highest currents and voltages, followed by the fulleroid and the ketolactam. Generally, the I_{SC} is reduced for the double layer PPV devices, independently of the acceptor, while for the V_{OC} nearly identical values are observed for the single and double layer devices (see Fig. 4, devices containing PCBM as an example). These observations are in excellent agreement with the expectation of higher serial resistivities for increased film thickness, as expected for the double layer MDMO-PPV bilayer diffusion devices.

The most significant difference between the blend bulk heterojunction and the bilayer diffusion devices is the different trend of the I_{SC} with the acceptor strength. For the blend bulk heterojucntion devices (Fig. 5), the lowest currents are observed for devices with the aza-fulleroid acceptor followed by the ketolactam. The highest currents are again observed for PCBM. However, the trend for the V_{OC} with the acceptor strength follows exactly the observations made for the bilayer diffusion devices with nearly identical values for the two different device geometries. Again, lower currents are observed for the thicker (bilayer) devices, independent of the acceptor strength.

The different trends for the I_{SC} are attributed to different morphologies for the different production technique. For acceptors with a low tendency for phase separation, nearly identical values are observed for devices with comparable thickness. For PCBM and for the ketolactam, the bilayer diffusion geometry is at least comparable if not slightly higher in performance than the bulk heterojunction geometry. For the fulleroid, the bilayer diffusion is the more favorable geometry.

The trend of the V_{OC} with the acceptor strength is independent from the device geometry as well as from the device thickness. Obviously, both types of devices (blend bulk heterojunction as well as diffusion bilayer) follow the same diode principle and have the same origin of the V_{OC}. The strong linear correlation of the V_{OC} with the acceptor strength is verified in Fig. 6. The slope of the linear fits is $S \sim 0.8$ for both device geometries. Using the maximum observed V_{OC} values instead of the mean average values, the slopes of the linear fits are calculated with $S \sim 1$ [6]. This strong correlation proves that the V_{OC} of conjugated polymer/

fullerene solar cells is pinned to the reduction potential of the fullerene acceptor. Two mechanisms can give such an alignment: (a) Fermi level pinning vs. surface states of the fullerenes or (b) formation of a strong dipole layer due to partial charge transfer between the metal electrode and the fullerene. In comparison to observations in inorganic semiconductors we suggest Fermi level pinning [10] as the relevant mechanism, since the formation of dipole layers, well known for small molecules, [11] should not influence the V_{OC} that strongly.

4. Conclusion

We:

1. introduced the bilayer diffusion concept as an alternative to the use of polymer/fullerene blends for the preparation of bulk heterojunction solar cells. The bilayer diffusion devices reached at least comparable cell efficiencies and showed superior performance for donor/acceptor couples with problematic compatibility.
2. did not find a clear correlation between the acceptor strength and the I_{SC}. Conversely, we found a strong linear correlation between the acceptor strength and the V_{OC}. This observation is interpreted in terms of Fermi level pinning of the metal to surface states of the fullerene.

References

[1] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Science 258 (1992) 1474.
[2] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789.
[3] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Adv. Func. Mater. 11 (2001) 15.
[4] S.E. Shaheen, C.J. Brabec, F. Padinger, T. Fromherz, J.C. Hummelen, N.S. Sariciftci, Appl. Phys. Lett. 78 (2001) 1.
[5] J.C. Hummelen, B.W. Knight, F. Lepec, F. Wudl, J. Yao, C.L. Wilkins, J. Org. Chem. 60 (1995) 532.
[6] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, T. Fromherz, M.T. Rispens, L. Sanchez, J.C. Hummelen, Adv. Funct. Mat. 11 (2001) 374.
[7] D. Godovsky, L. Chen, L. Oettersson, O. Inganäs, M.R. Andersson, J.C. Hummelen, Adv. Mat. Opt. Electron. 10 (2000) 47.
[8] C.J. Brabec, F. Padinger, N.S. Sariciftci, J.C. Hummelen, J. Appl. Phys. 85 (1999) 6866.
[9] J.C. Hummelen, B. Knight, F. Wudl, unpublished results.
[10] L.J. Brillson, The Structure and Properties of Metal-semiconductor Interfaces, Surface Science Reports 2, North-Holland Publishing Company, 1982, p. 145.
[11] I.G. Hill, D. Milliron, J. Schwartz, A. Kahn, Appl. Surf. Sci. 166 (2000) 354.