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Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10 % Energy-Conversion Efficiency**

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There has been an intensive search for cost-effective photovoltaics since the development of the first solar cells in the 1950s.^[1–3] Among all alternative technologies to silicon-based pn-junction solar cells, organic solar cells could lead the most significant cost reduction.^[4] The field of organic photovoltaics (OPVs) comprises organic/inorganic nanostructures like dye-sensitized solar cells, multilayers of small organic molecules, and phase-separated mixtures of organic materials (the bulk-heterojunction solar cell). A review of several OPV technologies has been presented recently.^[5] Light absorption in organic solar cells leads to the generation of excited, bound electron–hole pairs (often called excitons). To achieve substantial energy-conversion efficiencies, these excited electron–hole pairs need to be dissociated into free charge carriers with a high yield. Excitons can be dissociated at interfaces of materials with different electron affinities or by electric fields, or the dissociation can be trap or impurity assisted. Blending conjugated polymers with high-electron-affinity molecules like C₆₀ (as in the bulk-heterojunction solar cell) has proven to be an efficient way for rapid exciton dissociation. Conjugated polymer–C₆₀ interpenetrating networks exhibit ultrafast charge transfer (~40 fs).^[6,7] As there is no competing decay process of the optically excited electron–hole pair located on the polymer in this time regime, an optimized mixture with C₆₀ converts absorbed photons to electrons with an efficiency close to 100 %.^[8] The associated bicontinuous interpenetrating network enables efficient collection of the separated charges at the electrodes. The bulk-heterojunction solar cell has attracted a lot of attention because of its potential to be a true low-cost photovoltaic technology. A simple coating or printing process would enable roll-to-roll manufacturing of flexible, low-weight PV modules, which should permit cost-efficient production and the development of products for new markets,

e.g., in the field of portable electronics. One major obstacle for the commercialization of bulk-heterojunction solar cells is the relatively small device efficiencies that have been demonstrated up to now.^[5] The best energy-conversion efficiencies published for small-area devices approach 5 %.^[9–11] A detailed analysis of state-of-the-art bulk-heterojunction solar cells^[8] reveals that the efficiency is limited by the low open-circuit voltage (V_{oc}) delivered by these devices under illumination. Typically, organic semiconductors with a bandgap of about 2 eV are applied as photoactive materials, but the observed open-circuit voltages are only in the range of 0.5–1 V. There has long been a controversy about the origin of the V_{oc} in conjugated polymer–fullerene solar cells. Following the classical thin-film solar-cell concept, the metal–insulator–metal (MIM) model was applied to bulk-heterojunction devices. In the MIM picture, V_{oc} is simply equal to the work-function difference of the two metal electrodes. The model had to be modified after the observation of the strong influence of the reduction potential of the fullerene on the open-circuit voltage by introducing the concept of Fermi-level pinning.^[12] It has also been shown that the V_{oc} of polymer–fullerene solar cells is affected by the morphology of the active layer^[13] and that it can be influenced by the electrochemical potential of the cathode (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), PEDOT:PSS).^[14] However, even an extended MIM model was found to be insufficient for a complete explanation of the V_{oc} of bulk-heterojunction solar cells. Recently, Gadisa et al.^[15] studied the correlation of electrochemical properties of six similar polythiophene derivatives and the open-circuit voltage of polymer–fullerene solar cells using [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as an acceptor and the same polythiophenes derivatives as donors. The authors attributed the variation of the photovoltage to variation of the oxidation potential of the conjugated polymer. Concluding the summary of the recent literature, there is no general consistent understanding of the origin of the open-circuit voltage of the bulk-heterojunction solar cell. In this work, the relation between the energy levels of the donor–acceptor blend and the open-circuit voltage of 26 different bulk-heterojunction devices is studied. A simple relation between the energy level of the highest occupied molecular orbital (HOMO) of the polymer and the V_{oc} is derived, which is used to estimate the maximum efficiency of bulk-heterojunction solar cells. Based on the model, the ideal material parameters for a conjugated polymer–PCBM device are determined. The results presented here can be used as a guideline for the selec-

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tion and synthesis of new active materials for bulk-heterojunction solar cells.

In Figure 1 the open-circuit voltage of different bulk-heterojunction solar cells is plotted versus the oxidation potential

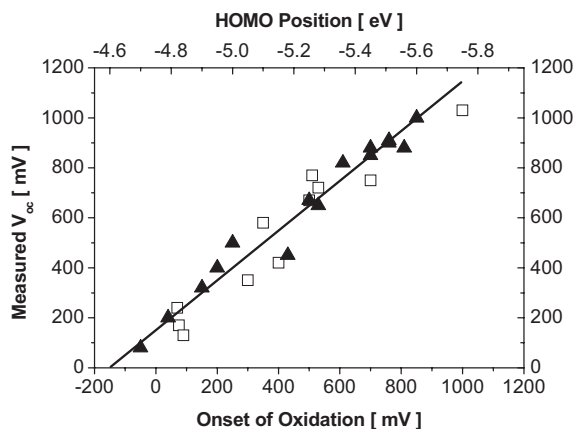


Figure 1. Open-circuit voltage (V_{oc}) of different bulk-heterojunction solar cells plotted versus the oxidation potential/HOMO position of the donor polymer used in each individual device. The straight line represents a linear fit with a slope of 1.

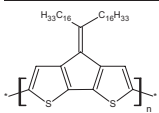
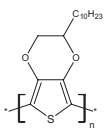
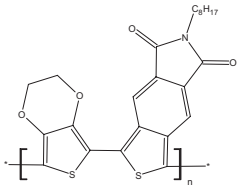
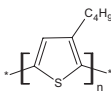
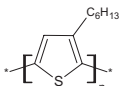
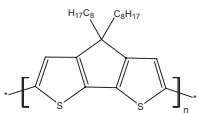
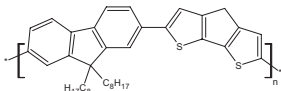
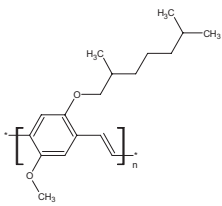
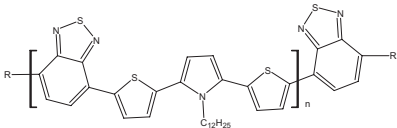
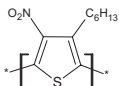
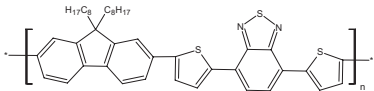
of the conjugated polymers used in these devices. The conjugated polymers corresponding to open squares are listed in Table 1. In addition, data points corresponding to polymer materials proprietary to Konarka (filled triangles) are added. The line representing a linear fit to the measured points has a slope equal to 1 and intersects the x -axis at -140 mV, which corresponds to a HOMO level of -4.6 eV. Figure 1 demonstrates that for a total of 26 different bulk-heterojunction solar cells, a linear relation between V_{oc} and the conjugated polymer oxidation potential is found; the open-circuit voltage of a conjugated polymer-PCBM solar cell can be estimated by

$$V_{oc} = (1/e)(|E^{\text{Donor}}_{\text{HOMO}}| - |E^{\text{PCBM}}_{\text{LUMO}}|) - 0.3 \text{ V} \quad (1)$$

where e is the elementary charge and using -4.3 eV for the PCBM lowest occupied molecular orbital (LUMO) energy. The value of 0.3 V in Equation 1 is an empirical factor which will be discussed below. It is interesting to note that PEDOT:PSS with a Fermi level of -5.0 eV can contact polymers with a wide range of HOMO levels. Although there may be an optimized doping level of the PEDOT:PSS layer for every conjugated polymer,^[14] even polyfluorene copolymers with a HOMO level of ~ -5.7 eV can be used as donors in efficient bulk-heterojunction solar cells when PEDOT:PSS is applied as the anode material.^[16,17] Based on this finding, the limiting efficiency of a bulk-heterojunction solar cell (given by the open-circuit voltage (V_{oc}) times the short-circuit current density (J_{sc}) times the electrical fill factor (FF) divided by the incident-light intensity) can be predicted solely as a function of the bandgap and the LUMO level of the donor.

As a practical limit to the efficiency, the external quantum efficiency (EQE) of the solar cell for photon energies equal to or larger than the bandgap energy of the donor and the FF are set to 65 %. Similar values have been found by several groups for optimized devices in the absence of recombination losses.^[8,18] In addition, any contribution to the short-circuit current from photons absorbed by the fullerene is neglected. Under these assumptions, the efficiency calculation requires only an integration of the Air Mass 1.5 (AM1.5) spectrum times the constant EQE for the J_{sc} and Equation 1 for V_{oc} . The result is shown in Figure 2 as a contour plot where the x - and y -axes are the bandgap and the LUMO level of the donor, respectively, and the contour lines indicate constant power-conversion efficiencies. The straight lines in Figure 2 define lines of constant donor HOMO levels of -5.7 and -4.8 eV. Calculations were performed for LUMO levels of the donor in the range of -3 to -4 eV assuming that an energy difference ΔE of 0.3 eV between the LUMO of the donor and the LUMO of the acceptor is sufficient for efficient charge separation.^[19] Figure 2 suggests that the energy-conversion efficiency of a bulk-heterojunction solar cell should be much more sensitive to changes of the donor LUMO level compared to variations of the donor bandgap. For example, for a LUMO level of -3.6 eV the calculated efficiency at a bandgap of 2.1 eV is ~ 5.8 %. Upon decreasing the bandgap, the efficiency increases to ~ 6.7 % at a bandgap of 1.8 eV and gradually decreases to ~ 5.8 % at a gap of 1.45 eV. A variation of the donor bandgap of 0.65 eV leads to a variation of only 1 % in the device efficiency. In contrast, a 0.65 eV variation of the polymer LUMO level results in efficiency changes between 3.5 and 8 % depending on the donor bandgap. For energy-conversion efficiencies exceeding 10 %, the donor polymer must have a bandgap < 1.74 eV and a LUMO level < -3.92 eV, assuming the FF and the average EQE remain equal to 0.65. For a 3.92 eV LUMO value, the calculated efficiency value is almost constant upon decreasing the donor bandgap down to 1.3 eV. The results presented here demonstrate the importance of the donor LUMO level in bulk-heterojunction solar cells. Besides a reduction of the bandgap, new donor materials must be designed to optimize the LUMO as this parameter dominantly drives the solar-cell efficiency. It is important to note that an optimized open-circuit voltage is a prerequisite to achieve certain device efficiencies; however, it is not sufficient. In addition, the charge-carrier mobility of electrons and holes in the donor acceptor blend must be high enough to allow efficient charge extraction and FF of 0.65. The relation between charge-carrier mobility and FF can be deduced from a model which has been reported recently.^[20] The main feature of this extended pn-junction model is that the photocurrent is dominantly field-driven. For devices with an active-layer thickness of several hundred nanometers, carrier mobilities of $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are required to prevent losses in the photocurrent in the absence of second-order recombination. Equally important is the successful description of the light-intensity dependence of the V_{oc} of bulk-heterojunction solar cells. Recently, Koster et al. suggested a complicated model

Table 1. Structures of different donor polymers used in bulk-heterojunction solar cells.

Structure	Name	HOMO [eV]
	Poly-[2,6-(4-dihexadecylmethylencyclopentadithiophene)]	−4.82
	Poly-[(1'-dodecyl)-3,4-ethylenoxythiophene]	−4.83
	Poly-[(3,4-ethylenedioxythiophene)-N-2'-ethyl-4,5-dicarboxylic-imide-benzo[c]thiophene]	−4.84
	Poly(3-butylthiophene)	−5.05
	Poly(3-hexylthiophene)	−5.1
	Poly[2,5-(7,7-dioctyl)-cyclopentadithiophene]	−5.15
	Poly[2,7-9,9-dioctylfluorene)- <i>alt</i> -2,6-cyclopentadithiophene]	−5.25
	Poly[(2-methoxy-5-[3,7-dimethyloctyloxy])paraphenylene vinylene]	−5.26
	Poly[N-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole]	−5.28
	Poly(3-hexyl-4-nitroxythiophene)	−5.45
	Poly[2,7-(9,9-dioctylfluorene)- <i>alt</i> -5,5''-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]	−5.75

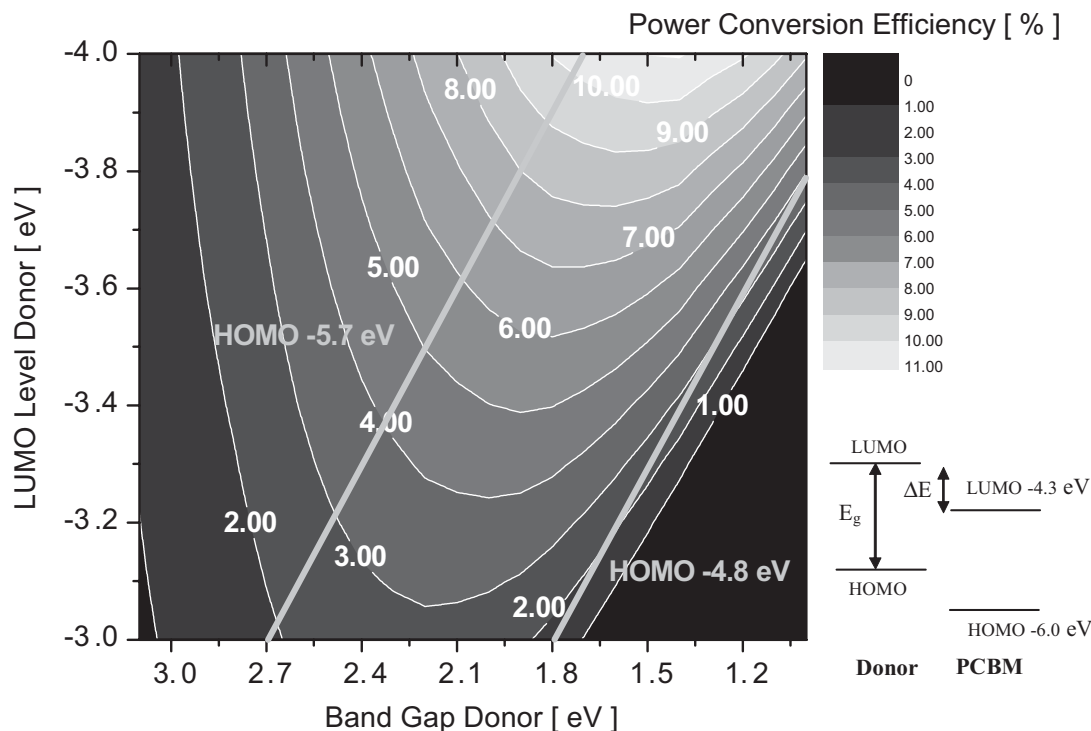


Figure 2. Contour plot showing the calculated energy-conversion efficiency (contour lines and colors) versus the bandgap and the LUMO level of the donor polymer according to the model described above. Straight lines starting at 2.7 eV and 1.8 eV indicate HOMO levels of -5.7 eV and -4.8 eV, respectively. A schematic energy diagram of a donor PCBM system with the bandgap energy (E_g) and the energy difference (ΔE) is also shown.

based on a MIM concept. The experimental findings presented here are in contradiction to the classical MIM picture, i.e., for more than 26 different material combinations, no influence of the contact work function on the V_{oc} is observed. These conceptual problems can be overcome by using the extended pn-junction model with a field-dependent photocurrent.^[21] Underlying the basic physics behind the model is the fact that all photovoltaic cells work essentially the same way: absorbed light is transferred into photogenerated charge carriers, which are separated by a junction later. The junction guarantees that separated charge carriers do not recombine before reaching the contacts. In contrast to classical solar-cell materials like Si or Ge, however, the quantum efficiency for charge generation in pristine organic semiconductors is low, typically in the range of 1%. It is therefore a necessity to blend semiconductors with appropriate electron affinities and work functions^[19] to increase the quantum efficiency for charge generation. This so-called donor-acceptor principle is successfully applied in liquid-electrolyte and solid-state dye-sensitized solar cells as well as in polymer/fullerene solar cells. A consequence of this approach is the presence of a charge-generating junction that is identical to the charge-separating junction. In other words, the energy-level differences between the polymer and the fullerene form the junction for the photovoltaic action. The V_{oc} and the built-in potential V_{BI} are determined by the difference between the HOMO of the donor and the LUMO of the acceptor. It is trivial to note that this is

the theoretical maximum value for the V_{BI} in bulk-heterojunction systems. As discussed above and shown in Figure 1, deviations between the theoretical maximum V_{BI} and the V_{oc} on the order of 0.3 V are found. In Figure 3, the current-voltage curve of a poly(3-hexylthiophene) (P3HT)/PCBM bulk-heterojunction solar cell acquired in the dark (solid line) and field-driven photocurrent (dotted line) and

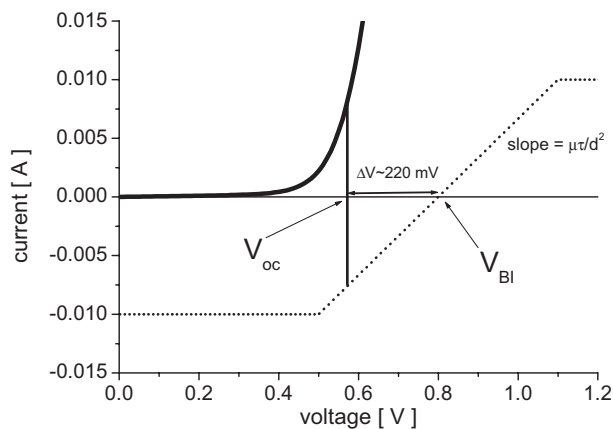


Figure 3. Current-voltage curve of (P3HT)/PCBM solar cell measured in the dark (solid line) and field-driven photocurrent (dotted line). The built-in potential V_{BI} is given by $E_{LUMO}(\text{PCBM})$ minus $E_{HOMO}(\text{P3HT})$ (-4.3 V $- (-5.1$ V) = 0.8 V). μ : charge-carrier mobility; τ : charge-carrier lifetime; d : active-layer thickness.

the idealized field-driven photocurrent (dotted line) are plotted. The superposition of both curves gives the current-voltage curve under illumination.^[20] The open-circuit voltage of the solar cell is defined as the voltage which compensates the current flow through the external circuit (indicated by the vertical line in Fig. 3). Figure 3 shows that a reduction of V_{oc} is caused by the dark current-voltage curve of the diode, which is determined by the ideality factor n and the reverse dark current I_0 of the diode. This loss has been found to be typically on the order of 200 mV. In addition, a smaller part of the V_{oc} loss (~100 mV or less) originates from the fact that the photocurrent in bulk-heterojunction devices is dominantly field-driven. The open-circuit voltage depends on the slope ($=\mu\tau/d^2$) of the field-driven current around V_{BI} , where μ is the charge-carrier mobility, τ is the charge-carrier lifetime, and d is the active-layer thickness. A steeper slope moves the V_{oc} closer to V_{BI} , which is typically observed for thin-film devices where the electric field is maximized across the active layer.

The highest energy-conversion efficiencies derived above are in the range of 10 % for single-bulk-heterojunction solar cells. This number appears achievable, although the donor material comprising all the required material properties has probably not yet been prepared. To go beyond 10 % efficiency, one could try to increase the external quantum efficiency of the device by improved light management and/or improving FF by optimizing the electrical design. This would shift the efficiencies in Figure 2 to higher values, but would not change the shape of the contour plot. Upon optimizing the open-circuit voltage of a bulk-heterojunction solar cell, the maximum efficiency in Figure 2 would move to smaller bandgaps. This may be achieved by reducing the losses resulting from a non-perfect diode, as discussed above. In addition, upon reducing the required difference between the LUMO levels of the donor and the acceptor (e.g., by developing materials with very small exciton-binding energies), the energy-conversion efficiency of the bulk-heterojunction solar cell would approach the classical single-bandgap solar cell that has been discussed under various assumptions before.^[3]

In conclusion, it has been demonstrated that the open-circuit voltage of bulk-heterojunction devices using PCBM as acceptor is determined by the HOMO level of the donor and the LUMO level of the acceptor molecule. Together with earlier investigations on the role of the LUMO level of fullerene acceptors, this work confirms that the MIM model is not applicable to bulk-heterojunction devices. The observed deviation of V_{oc} from V_{BI} (HOMO donor minus LUMO acceptor) is related to the working principle of the bulk-heterojunction solar cell and can be minimized by optimizing materials, the active-layer thickness, and the charge-carrier mobility. Based on the presented findings, a relation between energy-conversion efficiency of a bulk-heterojunction solar cell, bandgap, and the LUMO level of the donor was derived. In addition, the model derived in this work can be used as a guideline for the material selection and material development for bulk-heterojunction solar cells.

Experimental

In this study, commercially available compounds and polymers which were prepared for Konarka to be tested in solar cells by companies, universities, or other research institutions were investigated. The chemical structures, which are public and not proprietary to Konarka, are listed in Table 1. The electron-acceptor material PCBM was purchased from NanoC.

Solar cells were prepared as small area (0.25 cm²) sandwich devices. The hole conductor PEDOT:PSS (H. C. Starck) was doctor-bladed from an aqueous solution on a pre-cleaned, patterned indium tin oxide (ITO)/glass substrate. The blend polymer/PCBM solution was doctor-bladed on top of the PEDOT:PSS. The devices were finalized by the deposition of a 1 nm thick LiF layer and a ~100 nm aluminum layer as top electrodes. LiF and aluminum were thermally evaporated at a pressure <10⁻⁵ mbar (1 mbar 100 Pa). The geometry of the electrode was defined by a shadow mask. Device preparation was performed under ambient conditions, except for the evaporation of the top electrode. Devices were characterized in a dry-argon atmosphere. Current-voltage characteristics were measured using a Keithley 2400 SMU while the solar cells were illuminated by an ORIEL Solar Simulator at 80 mW cm⁻² (AM1.5D) white light. The electrochemical properties of all polymers were studied by cyclic voltammetry (CV). Electrochemical experiments were carried out on thin films at room temperature in a glove box under argon atmosphere using a computer-controlled Jaisle 1002 T-NC potentiostat. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF₆, 98 %, Aldrich, ~0.1 M) in anhydrous acetonitrile (Aldrich). Platinum foils were used as the working electrode (WE) as well as the counter electrode (CE). Polymer films were deposited on the WE by drop-casting. As a reference electrode (RE), a silver wire coated with AgCl was used. After each measurement, the RE was calibrated with ferrocene (oxidation potential $E^0 = 400$ mV versus normal hydrogen electrode (NHE)), and the potential axis was corrected to NHE according to the difference between E^0 (ferrocene) and the measured $E^{1/2}$ (ferrocene). The oxidation onset potentials were determined as the position where the oxidation current starts to differ from the baseline. To evaluate the accuracy of our measurement procedure, several polymers were also characterized by the more precise method, electrochemical voltage spectroscopy (EVS) [22]. An excellent agreement between CV and EVS measurements was found, and therefore only oxidation potentials extracted from CV measurements are used in this study. Measured onset potentials were corrected to NHE and recalculated to electron volts versus vacuum level using a potential value of -4.75 eV for NHE [23,24]. The LUMO level of PCBM was also determined by a CV measurement. The onset of the first reduction of PCBM was found to start at a potential of -4.3 eV with respect to vacuum.

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