

Internal electric field in organic-semiconductor-based photovoltaic devices

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The authors performed transient photocurrent measurements under applied bias and electroabsorption spectroscopy on devices based on a pristine poly(phenylene vinylene) derivative as well as its mixture with 1% of a methanofullerene electron acceptor. Combining both techniques allows us to directly determine the internal electric field and to conclude on its implication on the photovoltaic performance of the devices. The electric field is identified as the driving force of the photocurrent, hence indicating the maximum obtainable photovoltage. Acceptor concentrations as low as 1% shift the energetic alignment of the top electrode to the reduction potential of the acceptor, reducing the internal electric field. © 2006 American Institute of Physics.

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In recent years organic semiconducting materials have triggered steadily increasing attention both in academic and industrial researches. Their optical and electronic properties make them attractive materials for a wide range of applications. Moreover, polymeric semiconductors offer advantageous low-cost manufacturing properties allowing printing, coating, and processing on large areas. Today, conjugated polymers, such as derivatives of poly(phenylene vinylene) (PPV), are widely used in both polymer light emitting diodes^{1,2} and in photovoltaic devices.^{3,4} As photoexcitation leads to bound electron-hole pairs (excitons), the charge generation efficiency in pristine conjugated polymers is generally small.⁵ For efficient exciton dissociation, these materials are blended with electron accepting species, e.g., C₆₀ buckminster fullerene or its more soluble derivatives. The difference in the electron affinities of the two components has to be large enough to overcome the exciton binding energy in the polymer. The applicability of the metal-insulator-metal (MIM) picture,⁶ according to which the maximum photovoltage of the device equals the difference in the work functions of the electrodes for these two component solar cells, remains under debate.⁷ An alternative model^{8,9} suggests that the offset between the highest occupied molecular level (HOMO) of the polymer and the lowest unoccupied molecular level (LUMO) of the acceptor indicates the upper limit for the open circuit voltage (V_{OC}) created in such a device (illustrated in the inset of Fig. 1). Whereas this offset in energy levels enables efficient charge generation it also introduces a loss mechanism to the device as V_{OC} is reduced.¹⁰ This has been identified as a major limiting factor of the power conversion efficiency shown by organic photovoltaic devices.^{11,12}

The strength of the internal electric field (V_{int}/d , d is the thickness of the photoactive layer) and its influence on the photovoltaic performance of organic bulk heterojunction solar cells are still under discussion. In this letter we present direct measurements of both V_{int} as well as the transient photocurrent under various applied bias voltages and correlate

V_{int} present in the active layer with the photovoltaic performance of PPV based organic semiconductor devices. We studied devices containing an active layer of a pristine PPV derivative or its blend with small amounts of a soluble methanofullerene electron acceptor.

The samples were prepared in sandwich geometry using glass slides covered with indium tin oxide (ITO) (purchased from Merck, Inc.) as substrates. After a substrate cleaning procedure, ITO was covered with a layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) (BAYTRON-PH, purchased from H. C. Starck) by spin coating. This intermediate layer is known to improve the performance of both polymer light emitting diodes and organic solar cells.¹³ The PEDOT:PSS film was dried prior to the deposition of the

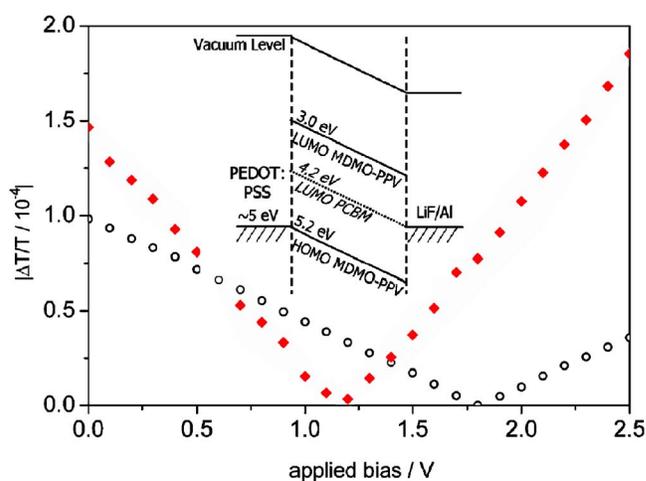


FIG. 1. (Color online) First harmonic electroabsorption response at 570 nm (100 K), ac amplitude of 1 V. (♦) represent ITO-PEDOT:PSS-MDMO-PPV/PCBM (100:1)-LiF/Al and (○) represent ITO-PEDOT:PSS-MDMO-PPV-LiF/Al. The inset shows a schematic diagram of the relevant energy levels under short circuit conditions in MDMO-PPV/PCBM based diodes. Due to our experimental results energetic alignment between the highest occupied molecular level (HOMO) of MDMO-PPV and PEDOT:PSS as well as between the lowest unoccupied molecular level (LUMO) of PCBM and LiF/Al is assumed.

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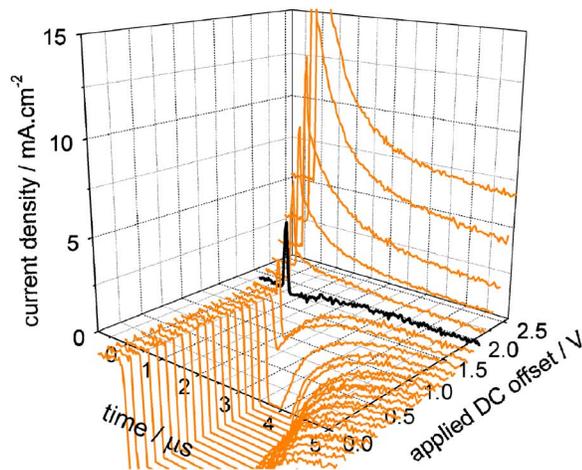


FIG. 2. (Color online) Transient photocurrents of an ITO-PEDOT:PSS-MDMO-PPV-LiF/Al device under various applied bias offsets.

active layer. This consisted either of pristine poly [2-methoxy-5-(3',7'-dimethyloxy)-1-4-phenylene vinylene] (MDMO-PPV) (Covion GmbH) or its blend with 1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C61 (PCBM) (Nano-C, Inc.) in the ratio 100:1 (w/w). The films were cast from chlorobenzene solutions. LiF/Al top electrodes were deposited via thermal evaporation. Introducing a nominally 0.7 nm thick LiF layer, between the active layer and the Al electrode, light emission of organic light emitting diodes¹⁴ as well as V_{OC} of photovoltaic devices are typically enhanced.⁷

Electroabsorption (EA) spectroscopy¹⁵ is a well established technique offering a direct way to study the electric field inside the device. In order to probe the internal electric field, an ac voltage (V_{ac} , frequency f) is applied in addition to a dc voltage (V_{dc}). The electric field induced change in the transmission ($|\Delta T|/T$) at frequency f is then given by

$$\frac{|\Delta T|}{T}(h\nu) \propto (V_{dc} - V_{int})V_{ac}, \quad (1)$$

where V_{int} is proportional to the internal electric field. The EA response is therefore zero when an externally applied bias (V_{dc}) cancels V_{int} [Eq. (1)]. It is necessary to carry out the EA experiments at sufficiently low temperatures (in our case approximately 100 K) and low electron acceptor concentrations to rule out disturbing effects due to current flow through the device.¹⁶ The studied semiconducting polymer (MDMO-PPV) is used as a model system because it is known for its high purity and very low concentration of free charge carriers, making it compatible with a MIM picture.¹⁷ As a consequence, the electric field is homogeneously distributed inside the semiconductor film. The photovoltaic performance of the devices is studied with transient photocurrent measurements under applied bias.¹⁶ Pulsed laser excitation (3 ns) using the 532 nm line of a neodymium doped yttrium aluminum garnet laser was employed. Due to its high amount of photons delivered over a short period of time, deterioration of the sample is avoided. By using filters of various optical densities we observed that 0.3 mJ pulses saturate V_{OC} sufficiently long for the measurements. The laser pulse induced transient photocurrents were recorded on devices biased by an external voltage offset. The photogenerated charge carriers are extracted by the overall dc bias present in the semiconducting layer. Therefore, when this

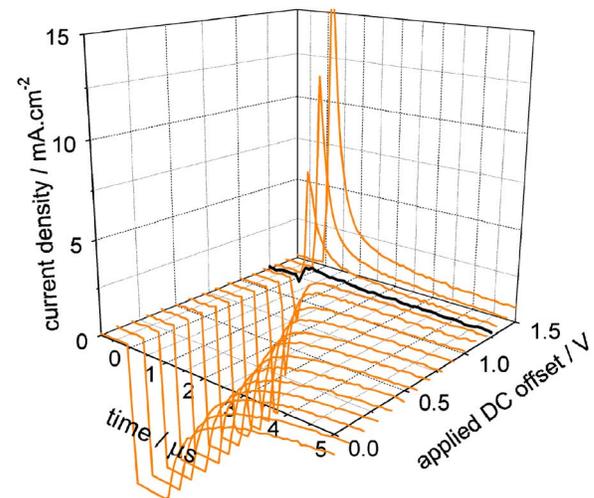


FIG. 3. (Color online) Transient photocurrents of an ITO-PEDOT:PSS-MDMO-PPV/PCBM (100:1)-LiF/Al device under various applied bias offsets.

electric field is compensated externally, i.e., flat-band conditions are established, the created charge carriers cannot leave the device and recombine inside the photoactive layer. We refer to this compensation voltage as V_{BI} in the following.¹² The transients were recorded by a Tektronix TDS754C oscilloscope, the offset voltage applied by an Agilent 33250 A function generator.

The inset of Fig. 1 schematically shows the relevant energy levels of the investigated devices under short circuit conditions. In Fig. 1, the EA responses of the devices based on pristine MDMO-PPV films are compared with results obtained from devices where 1% of PCBM is added to the photoactive layer. V_{int} is given by the external dc bias necessary to cancel the EA response, around +1.2 V in the case of MDMO-PPV/PCBM blends and roughly +1.8 V for the pristine polymer. The same trend is observed for the transient photocurrent measurements under applied bias. As shown in Fig. 2, roughly +2 V have to be externally applied to cancel the photocurrent induced by the laser pulse in pristine MDMO-PPV based samples with LiF/Al electrodes. Adding PCBM to the active layer, V_{BI} is reduced to about +1.2 V (Fig. 3). In addition to the current response related to the bias voltage, which occurs in the time scale of several microseconds, an additional short term response (“spike”) immediately after the laser pulse can be seen. This feature is significantly more pronounced in the case without PCBM (Fig. 2). We attribute this spike to a creation of charge carriers close to the electrodes. Whereas devices based on MDMO-PPV films with PCBM have efficient exciton dissociation sites in the bulk, in the pristine polymer charge carriers are generated close to the electrode.¹⁸ The data on the pristine MDMO-PPV films can be meaningfully interpreted in terms of a MIM picture. V_{int} found for devices with LiF/Al electrodes is close to the band gap of MDMO-PPV (Ref. 19) and coincides with the onset of detectable light emission. Hence we interpret the data in terms of an almost Ohmic contact between PEDOT:PSS and MDMO-PPV on one side^{12,20} and LiF/Al on the other side. Therefore, the Fermi levels of the contacts align with the HOMO and the LUMO of MDMO-PPV, respectively. Adding small amounts of PCBM changes this picture. EA measurements on conjugated polymers doped with C_{60} have shown that due to electron transfer to

the C_{60} the Fermi level of the low work function electrode is pinned close to the LUMO of the acceptor.²¹ In our devices, which contain about 1% of PCBM, V_{int} is determined to be +1.2 V. Again, pinning of the Fermi level to the LUMO of PCBM is the reason for this value. By space charge limited current measurements, a V_{int} of +1 V was found for ITO-PEDOT:PSS-PCBM-LiF/Al devices.²² The difference of 0.2 V between these pristine PCBM based devices and our results is attributed to the different matrix conditions. Energy values are sensitive to the environment and may be altered when PCBM is embedded into MDMO-PPV. According to previous work done by our group, we estimate the LUMO of PCBM to be approximately 4.3 eV.^{22,23} Correlating V_{int} found by EA spectroscopy with transient photocurrent measurements under applied bias, we identify the overall dc field inside the photoactive layer as the driving force of the photocurrent in the solar cell. V_{BI} indicates the voltage where the photocurrent goes to zero, i.e., the zero crossing of the photocurrent determined by subtracting current-voltage (I - V) curves in the dark from I - V curves under illumination.¹² As V_{int} determined by EA spectroscopy is found to be equal to V_{BI} , this voltage is identified as the maximum photovoltage possibly deliverable by an organic solar cell since it indicates the voltage at which the photocurrent equals zero. V_{int} in MDMO-PPV/PCBM bulk heterojunction solar cells with LiF/Al top electrodes is given by the potential offset between the oxidation potential of MDMO-PPV and the LUMO of PCBM, even if its concentration is as low as 1%. This is well below the percolation threshold.

In conclusion we state that we have directly measured V_{int} in organic semiconductor devices and identified this value as the maximum photovoltage theoretically deliverable by the device. Furthermore, we found evidence that V_{int} is determined by the energy offset between the HOMO of MDMO-PPV and the LUMO of PCBM.

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