Tailored heterojunctions for efficient thin-film organic solar cells: a photoinduced absorption study.

<u>R. Schüppel¹</u>, K. Schmidt², C. Uhrich^{1,*}, K. Schulze¹, D. Wynands¹, J. L. Brédas², E. Brier³, E. Reinold³, H.-B. Bu³, P. Bäuerle³, B. Männig^{1,*}, M. Pfeiffer^{1,*}, M. K. Riede¹, K. Leo¹

¹ Institut für Angewandte Photophysik, Technische Universität Dresden, Germany

² Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, Georgia, USA

³ Institut für Organische Chemie II und Neue Materialien, Universität Ulm, Germany

After the introduction of the donor-acceptor heterojunction concept [1] providing an efficient mechanism for charge separation in organic materials, the challenging field of organic photovoltaics became a quickly growing research community. Within the last years, the reported device efficiencies have been steadily increased. Nevertheless, the predicted maximum of the power conversion efficiency η_{PCE} of blended single layer structure devices (10-11%) is still not reached [2,3]. In general, three major strategies are discussed that lead to an increase of η_{PCE} . Without weighting these strategies, as a first measure, the absorbed part of the sun spectrum should be extended up to the infrared. This basically increases the photocurrent of the device. Second, the open circuit voltage of the devices should be increased by minimizing the loss of free energy of the charge carrier compared to that of the excitonic state. Third, the fill factor of the device needs to be optimized, i.e. a maximized efficiency of the charge separation as well as an optimized transport to the electrodes including charge collection at the contacts has to be achieved.

An appropriate device design is one of the possible routes to fulfill the above-mentioned criteria. The usage of doped transport layers [4] increases the conductivity and allows to position the absorbing layer freely within the device with respect to thin film optics of the stack. For extending the absorption range, a general limitation appears on single cell devices. Since the excitons that are generated by the absorption of light rapidly relax down to the energetically lowest singlet state, the open circuit voltage is in general limited by the optical band gap of the absorbing material. For inorganic solar cells, where free electrons are directly generated, this consideration is known as the Shockley-Queisser limit [5]. In organic solar cells, efficient charge carrier separation necessarily requires a step of the ionization potential and the electron affinity to overcome the exciton binding energy. Compared to the relaxed excitons, the energy of the free charge carriers is lowered and the maximum achievable open circuit voltage is further reduced. This has to be taken into account to estimate the optimum band gap of the absorbing layers. Concepts like stacked devices, e.g. tandem cells [6] or even multiple cells [7], are connected in series and thus, adding up the open circuit voltage of the single cells with possibly different absorption range.

In this talk, we focus on the optimization of the open circuit voltage in single cell devices. Recently, we have demonstrated an open circuit voltage of 1V and a power conversion efficiency of 3.4% in thin film solar cells utilizing a new acceptor-substituted oligothiophene (DCV5T) with an optical gap of 1.77 eV as donor and C_{60} as acceptor [8]. The open circuit voltage is nearly doubled compared to the well known phthalocyanine:fullerene devices due to an optimized optimized donor-acceptor offset. Stimulated by this result, we systematically studied the energy and electron transfer processes taking place at the oligothiophene:fullerene heterojunction along a homologous series of these oligothiophenes (DCVnT) using photoinduced absorption. The observed transitions were unambiguously identified by TD-DFT calculations and

^{*} now at: Heliatek GmbH Dresden, Germany

cation spectroscopy in solution. The heterojunction is modified by tuning the HOMO level using different oligothiophene chain lengths, while the LUMO level is essentially fixed by the choice of the acceptor-type end-groups (dicyanovinyl) attached to the oligothiophene [9]. Thus, we can directly address the origin of the open circuit voltage, with the aim to reflect the possible approach of increasing this quantity.

As a major result, we identify the triplet recombination of charge carriers as an additional limiting factor for high open circuit voltage devices. With increasing the effective energy gap of the donor-acceptor pair (by increasing the ionization energy of the donor), the photoinduced electron transfer followed by dissociation of the electron-hole pair is eventually replaced by recombination into the triplet state and further, by energy transfer while electron transfer is surpressed (DCV3T) [10]. Consequently, we present a modified picture of charge carrier generation and recombination at the donor-acceptor heterojunctions, where triplet states are involved.

Temperature-dependent photoinduced absorption spectroscopy as well as variation of the acceptor material point towards an thermally activated generation of free charge carriers [11], while the recombination into the triplet state depends critically on the relative position of the energy levels of triplet state and charge separated state. Thus, we focus on the question of tailoring heterojunctions to provide a maximized free energy of the charge carriers without recombination into a triplet state, i.e. we discuss the trade-off between efficient charge carrier dissociation and a high open circuit voltage. We conclude that an open-circuit voltage between 1.0 and 1.1 V present an optimum for the material system studied here, as higher voltages can only be achieved with concomitant losses in charge separation efficiency.

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