How Fermi level pinning impacts the energy level alignment at interfaces with organic semiconductors

Norbert Koch [a),b)]

[a)] Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany
[b)] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Renewable Energies, 12489 Berlin, Germany
norbert.koch@physik.hu-berlin.de

In excitonic solar cells, e.g., comprising organic semiconductors, an electron donor / electron acceptor interface is required to dissociate the strongly bound electron-hole pair (exciton) that results after photon absorption. Consequently, the alignment of the frontier energy levels at the donor/acceptor interface critically impacts the device efficiency. Specifically, the open circuit voltage of the cell depends on the maximum possible energy separation of the quasi-Fermi-levels of holes and electrons in the donor and acceptor material, respectively. For organic-based cells, this is often approximated by the difference in ionization energy of the donor and electron affinity of the acceptor – the "photovoltaic gap" of the interface [often synonymously used are the levels of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)]. For a given material, the ionization/affinity levels can be retrieved from, e.g., direct and inverse photoelectron spectroscopy [1], where the energy difference between the respective onsets is also termed charge transport gap. For solar cells made of organic semiconductors, it is commonly observed that the measured open circuit voltage is smaller than the photovoltaic gap by approximately 500 meV, i.e., a substantial energy loss supposedly occurs.

To understand the origin of this energy loss, and to provide guidelines for device improvement, it is important to understand the fundamental mechanism that determined the energy level alignment at interfaces that are ubiquitous in solar cells, including the donor/acceptor interface but also those between electrodes and the respective semiconductor materials. It is worth noting that photoelectron experiments reported in the past by different groups often returned a different energy level alignment for a given organic donor/acceptor material pair, which certainly should be unsettling for device engineers. It will turn out that Fermi-level pinning and its consequences for charge density re-distribution is an overarching mechanism that is operative for these cases.

This presentation will first provide a generalized picture of how the levels between generic electrodes and organic semiconductors align, contrasting the weak and the strong electronic coupling regime, focusing on Fermi-level pinning. It is found that in the weak coupling regime charges are transferred between electrode and semiconductor to establish electronic equilibrium across the interfaces. These interfacial charges diffuse away from the interface and result in a situation of gradual electrostatic potential shifts within the semiconductors, i.e., energy level bending – in full analogy to band bending in (inorganic) covalent semiconductors [2]. The

distance of the Fermi-level from the frontier energy levels of the semiconductor in thick layers is then a function of amount of transferred charge and the width of the HOMO level distribution (e.g., brought about by structural disorder). In the strong coupling regime, all charge required to establish equilibrium is transferred between the electrode and organic semiconductor monolayer, so that in abrupt "interface dipole" and "flat bands" result [2].

For intrinsic donor/acceptor interfaces, in the absence of strong electronic coupling – which is most often the case for organic semiconductor pairs, the electrostatic potential across the interface changes only marginally – if at all. This situation, however, can be significantly altered when at least one of the two semiconductors is Fermi-level pinned by the "effective work function", i.e., the electrochemical potential of charges within the bulk. Since organic semiconductors feature Debye lengths typically exceeding the film thickness in devices, the Fermi-level position (and thus the work function) can indeed be imposed by the contact to an electrode. Thus one can create situations where the donor is Fermi-level pinned by the work function of the acceptor film and *vice versa*. This then requires charge transfer across the organic heterojunction, and electrostatic potential gradients result, even for material pairs that would not undergo any charge transfer in the absence of contact with electrodes [3]. The full wealth of varying energy level alignment situations for one and the same material pair will be discussed. Consequently, device engineering has to fully take into account the effect of adding the electrodes to a solar cell comprising an organic donor/acceptor interface, otherwise correlations between assumed electronic structure and device performance remain highly uncertain.

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[3] M. Oehzelt, K. Akaike, N. Koch, G. Heimel, Sci. Adv. 1 (2015) 1501127