Low exciton binding energies from computational predictions

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Outlook

7.1 Worm’s eye view

The central aim of this theoretical and computational research project is to find strategies for lowering exciton binding energies in organic photovoltaic (OPV) materials. Interesting directions for future research based on some of these strategies, are listed below.

A next step in the research described in Chapters 3 and 4 may be to study the flexibility of the polymer side-chains and of the tails of the PCBM analogues in which the permanent dipoles are incorporated. As was pointed out in Chapter 3, only a modest rotation of the dipoles is needed to reduce the charge-transfer (CT) exciton binding energy significantly. In a bulk heterojunction (BHJ) it is possible that the (interface) morphology is influenced by these dipoles, which may have consequences for their rotational freedom. To obtain information about the rotational freedom that these dipoles have in a BHJ and their possible influence on the morphology of the blend, studies analogous to the ones described in Chapters 3 and 4 can be performed, but now with snapshots of (coarse-grained) Molecular Dynamics (MD) simulations of polymer/PCBM blends with installed dipoles in their side-chains/tails. These snapshots can be used to calculate rotational barriers of these side-chains/tails within their environment. In addition, the snapshots reveal the morphology changes when dipoles are incorporated in the donor and acceptor molecules.

Another interesting direction for future research based on the studies described in Chapters 3 and 4 may be to study the time scale needed for dipole alignment and to compare this time scale with the typical time scales of the steps of the OPV working mechanism. Considering the typical time scales of $\sim 150$ fs for the electron transfer step between donor and acceptor and for the creation of free charges from the inter-molecular charge-transfer (CT) state, the dipoles have to rearrange themselves within a few hundred fs in order to align favourably around the created local and CT excitons. Since molecular vibrations take place on time scales of ps, dipoles might not have enough time. Considering the typical time scales of several ns for the recombination of free charges, the dipoles have to rearrange themselves within a few ns in order to align favourably around the charge-separated (CS) state and thus to reduce Coulomb interactions between free charges. Based on the time scales of molecular vibrations, this is likely to happen. In order to make sound predictions of the time scales needed for dipole alignment and also to obtain information about of the rotational freedom that dipoles have in a BHJ, force fields especially
developed for the molecules of interest are required to perform the necessary MD simulations.

In order to make a connection between composition and local environment of the molecules and the bulk dielectric response of the material, approaches are needed that model the dielectric constant of molecule-based materials by including the effects of position, orientation and packing of the molecules. Heitzer et al.\textsuperscript{3,4} report about a first-principles approach that can model the dielectric response of molecule-based materials by taking into account these effects. They conclude that large packing density and alignment of the $\pi$-system parallel to the applied electric field lead to a high dielectric constant. So controlling the molecular ordering may be the key to design high dielectric constant molecule-based materials.\textsuperscript{3,4} An interesting direction for future research would therefore be to apply approaches like the one developed by Heitzer et al.\textsuperscript{3,4} to several molecules that are described in this thesis in order to predict their bulk dielectric response and to discover which molecular orderings lead to a high dielectric constant, which can then possibly be obtained via synthetic chemical means.

Several other interesting research directions related to the studies described in this thesis but focusing more on the fundamental understanding of the charge separation mechanism, are listed below.

An interesting issue that was outside the scope of the research described in this thesis is comparing the relative (electron transfer) rates of the various steps of the OPV working mechanism and of the possible competing processes. Strong couplings may be possible between certain excited states, which can then act as efficient decay channels. Several studies\textsuperscript{5-7} have already been performed in this direction. Often Marcus theory\textsuperscript{8} is applied to obtain a theoretical estimation of the electron transfer rate (Chapter 2, section 2.11.1).

Presently, the role of the lowest charge-transfer (CT\textsubscript{1}) state in the charge separation process is still unclear.\textsuperscript{9-11} It is proposed that delocalised and higher energy electronic CT\textsubscript{n} (n>1) states are needed for long-distance electron transfer to overcome the CT exciton binding energy.\textsuperscript{12} Charge delocalisation over several molecules might affect the CT state energy in such a way that it will not act as an intermediate trapped state between the initial excited and final CS state. Studying the effect of charge delocalisation on the excited state energies and the energies of the CT and CS states is only possible by using a large donor-acceptor complex, \textit{e.g.}, two PCBM molecules and a short oligomer consisting of three monomeric units of a typical donor-acceptor co-polymer. In this way, the energies of the delocalised and higher energy CT\textsubscript{n} states with respect to the energy of the lowest CT\textsubscript{1} state can be determined. By calculating the electronic couplings between certain excited states, insight can be obtained in the role of the CT\textsubscript{1} state and of delocalised and higher energy CT\textsubscript{n} states in the charge separation mechanism.

As the last example indicates, treating ever larger systems at the electronic structure theory level is of great importance to make progress in the fundamental understanding of the charge separation mechanism via computational modelling. Some envisaged future developments in Theoretical Chemistry could contribute to this grand challenge in the
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research field of OPV. Firstly, it has been estimated that the progress in the microprocessor technology will continue in the next decades. In combination with the development of linear scaling Quantum Chemical methods and the application of fast Graphical Processing Units (GPUs), this leads to a reduction in the computational cost.\(^\text{13}\) In this way more accurate and much larger calculations become computationally within reach. Secondly, future progress in Density Functional Theory (DFT) (Chapter 2, section 2.6) – which is nowadays often used to describe large systems – is expected to lead to better approximations to the exchange-correlation functional for describing excited states with long-range CT character. This will improve the description of electron transfer processes in OPV devices using DFT and therefore will make this method more suitable to apply in studying the grand challenges of the OPV research field.

7.2 Bird’s eye view

OPV can only become a competitive technology in the energy market when basic requirements are fulfilled, like reasonable power-conversion efficiency (PCE), lifetime and cost.\(^\text{14}\) To reach these requirements, research focusing on all these aspects is carried out in academia, at research institutes and in industry. Currently, in all these areas challenges and unanswered questions can be found. An overview of the current status and of the expected future research in these areas, is given below.

Concerning the first requirement, different strategies can be envisaged to increase the PCE of OPV devices, like increasing the dielectric constant, controlling the (interface) morphology, \textit{e.g.}, by using donor-acceptor block co-polymers, and optimising molecular properties, \textit{e.g.}, the relative alignment of frontier molecular orbital energies.\(^\text{15}\) Strategies usually focus on one or several loss processes that limit the performance of OPV devices. Losses can originate from high local and CT exciton binding energies, limited absorption, bad morphology of the active layer, large charge carrier recombination, inefficient charge transport, and non-optimised offsets between donor and acceptor energy levels.\(^\text{16}\) In future, progress is expected in both the understanding of the fundamentals of charge separation and in the application of this knowledge to the optimisation of material and device design.\(^\text{15}\)

Even if in future the PCE of \textit{lab sized} solar cells will increase sufficiently to become practically useful, this does not imply that the PCE of \textit{module sized} solar cells will then also be sufficient.\(^\text{17}\) There still remains a significant drop in the efficiency on a module scale. According to Li \textit{et al.},\(^\text{18}\) the PCE of lab sized solar cells should increase above 15% in order to have an acceptable module efficiency around 10-12%. Rivière \textit{et al.}\(^\text{19}\) show that currently commercially available modules have PCEs in the range of 1.5-2.5%. They conclude that the final module performance strongly depends on the number of well performing and non-limiting cells and the active layer thickness, which is associated with the homogeneity of the deposition process.\(^\text{19}\) In this area of research, one of biggest
Challenges is to identify the possibilities to translate lab efficiencies to module efficiencies by discovering and reducing the causes of main loss.\textsuperscript{17}

Concerning the second requirement, the material stability towards oxygen and water must improve.\textsuperscript{17} The first solar cell devices were stored in inert atmosphere in order to prevent degradation due to exposure to sunlight, water and oxygen. Increased understanding of the photochemical processes in organic layers has been achieved since then, like the insight that the molecular structure has a strong impact on the photochemical stability. Other device designs may also help to improve the device stability.\textsuperscript{20} In conventional BHJ solar cells low work function metals are applied as top contact (Chapter 1, Fig. 1.2). Under ambient conditions these low work function metals form non-conductive oxides, which leads to a fast degradation of the solar cell. To prevent fast oxidation of these electrodes, the solar cell is often encapsulated in expensive packing materials that show very low oxygen and water permeability. In an inverted device design this issue is solved because the hole and electron blocking layers are reversed. The top contact is now made of a high work function metal like silver or gold, which is air stable. Inverted solar cells show substantially improved stabilities under ambient conditions.\textsuperscript{21}

According to Dennler \textit{et al.},\textsuperscript{22} OPV modules should have a lifetime of 7 years to become competitive. Currently the lifetimes of square meter sized panels on average is 5 years under outdoor conditions.\textsuperscript{23} In order to increase the device stability, a deeper understanding of the interactions with water and oxygen at all the interfaces in BHJ solar cells is needed, together with an improved stability towards oxygen and water both at the material and device architecture level.\textsuperscript{17}

Concerning the third requirement, according to Brabec,\textsuperscript{14} cost reduction in developing OPV devices is expected when roll-to-roll printing techniques – applied in the industrial process – instead of spin coating techniques – mainly used in the laboratory process – are applied in the production process. It turns out that the average PCE of printed OPV devices is slightly lower than that of spin coated OPV devices. In order to increase the efficiency of printed OPV devices, more research is needed to improve the printing processing techniques to obtain smoother and more homogeneous layer structures. When printing techniques are used, large-scale production of OPV devices may become feasible, which in turn may lead to a fall in the prices of the materials and thus in cost reduction.\textsuperscript{14}

According to Krebs \textit{et al.},\textsuperscript{24} the total cost for developing OPV devices is mainly determined by the cost of the materials. So a further cost reduction may come from: elimination of expensive components such as indium-doped tin oxide (ITO) as the transparent anode, reduction in the costs for the electron blocking layer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and for the active donor and acceptor materials through upscaling by the chemical suppliers, increase in the manufacturing speed, and possibly from developing in-line coating systems where all layers are coated in the same pass through the machine.\textsuperscript{24}
7.3 Future perspective for organic photovoltaics

According to Green et al., a convincing market advantage is essential to commercialise a new solar cell technology. From the different classes of organic solar cells that currently exist, the organic-inorganic hybrid perovskite solar cell has the highest PCE and therefore its convincing market advantage may be its high PCE in combination with its low manufacturing cost. At the moment this solar cell technology also has its drawbacks, like its large fluctuations in device performance, its reliance on the environmentally hazardous heavy metal Pb, and its instability under ambient conditions, which requires expensive encapsulation to protect the solar cell for degradation. There is a possibility to replace Pb with the less toxic element Sn, however, easy oxidation of Sn$^{2+}$ to Sn$^{4+}$ lowers the photovoltaic performance. In the present market, the toxicity of Pb is not expected to be a major obstacle for large-scale applications since CdTe solar cells were also able to gain a considerable market share.

Despite the convincing market advantage of the perovskite solar cell that makes this organic solar cell technology currently the most promising, one can argue that also for polymer-based organic solar cells there is a sunny future. Currently, a lot of questions have so far been unanswered about the charge separation mechanism in this class of organic solar cells. Koster et al. showed that organic solar cells can in potential have PCEs of more than 20% by increasing the dielectric constant. So by new materials development and comprehensive understanding of the photovoltaic principles there still remains a lot to gain. In the future a substantial rise in the PCE of polymer-based organic solar cells may therefore be expected.

Based on the before mentioned considerations, it is tempting to conclude that one should not focus on improving polymer-based organic solar cells anymore. However, it is misleading shorthand to draw this conclusion. Both solar cell technologies are promising and have the possibility to gain a reasonable market share in future, since both technologies have their own convincing market advantages and drawbacks. It is unlikely that solely one renewable energy technology will be leading on the energy market in future. Instead, a situation in which several renewable energy technologies gain a reasonable market share is more likely, since diverse (new and existing) application possibilities are thinkable for which a certain solar cell or energy technology may turn out to be the most suitable. For example, organic solar cells may become dominant in low-cost and light-weight consumer or building integrated applications where importance is attached to environmental impact and toxicity issues.

In conclusion, putting effort in improving several kinds of promising renewable energy technologies is the best way to prepare a diverse landscape of possible energy technologies for the future. In this way full replacement of fossil fuels in all kinds of application areas is likely to happen.
7.4 References


Chapter 7