

## Chapter 7

# Conclusion and Outlook

In this thesis, we have combined, implemented and extended different theoretical methods developing a multiscale model for organic semiconducting materials. We have investigated the influence of both molecular and morphological structure on resulting electronic states, charge transfer properties and charge transport in BHJ-OSCs.

Primarily, we give a detailed overview of the variety of computational methods used for modelling molecular and mesoscopic properties within the multiscale approach. The focus here is on calculations of electronic structure, molecular dynamics and charge carrier dynamics.

As the starting point of the calculations, we focused on the influence of different quantities in the Marcus rate expression. We examined the impact on the charge carrier mobility in subsequent kinetic Monte Carlo simulation. We find the tendency of lower charge transfer properties in force-field generated structures compared to DFT-optimised structures based on acceptor dimers. The calculated charge transfer integrals depend sensitively on the choice of method, e.g. on the functional and especially on size of the basis set. This sensitivity is particularly evident in the distributions of the charge transfer integrals of all pairs in the entire morphology, which differ significantly in both mean values and shape. We provide scaling schemes for DIPRO-based charge transfer integrals in combination with semiempirical methods, DFTB and DFT to match computational demanding CDFT results. We obtain different scalings for electrons and hole transfer. If the wavefunction evaluation does not converge, we propose a geometric parametrisation of the charge transfer integral as a backup method. A more promising approach applies the wavefunction overlap in the parametrisation of charge transfer integral.

CDFT is the method of choice to model the intramolecular charge transfer integral. The proposed partitioning scheme of polymer chains into  $\pi$ -conjugated segments in combination with intramolecular and intermolecular charge transfer enables the description of charge transport in amorphous morphologies containing organic polymers. We adapt this procedure for two different polymers P3HT and PBDT-TS1.

We see general trends for a reduction of the internal reorganization energy with increasing system size in both acceptor molecules and donor polymers. Our investigations of the influence of the environment indicate a reduction in the reorganization energy of the embedded charge transfer complex compared to standard calculations on isolated molecules since a complete relaxation is hindered sterically. The incorporation of outer-sphere and polarisation effects in a self-consistent manner using the Thole model is essential. These contributions to the site-energy difference significantly alter the energy landscape and the charge carrier mobilities in kinetic Monte Carlo simulations.

We calculated the Marcus, Jortner and Weiss-Dorsey rates associated with these transfer integrals and reorganization energies for the entire morphology, and pointed out the importance of the site-energy difference. We discussed the limited applicability of Marcus rates in case of large driving forces, especially at the donor-acceptor interface and compared Marcus rates to Jortner and Weiss-Dorsey rates. We apply the multiscale model to two amorphous materials P3HT and PPDI, as well as to two blend morphologies simulating hole and electron transport in organic bulk heterojunction solar cells, e.g. P3HT:DIPBI and PBDT-TS1:PPDI. We analysed the influence of different parametrisation schemes of the transfer rates on obtained quantities as the charge carrier mobility, site-occupation probabilities, local currents, pathways of low local resistance. The latter method enables the identification of packing motives that promote efficient charge transport.

Application of Jortner and Weiss-Dorsey in kMC simulations allows differentiating distinct electron transport mechanisms in P3HT:DIPBI and PBDT-TS1:PPDI, which are imposed by the underlying blend morphologies. Electron transport occurs predominantly along charge transport channels of DIPBI aggregates inside the investigated P3HT:DIPBI morphology, whereas in the PBDT-TS1:PPDI we observe a trap-and-release mechanism for the hopping between small, isolated PPDI clusters embedded in amorphous PBDT-TS1.

Using the developed screening for perylene diimide acceptors, we examined thirteen classes of molecules concerning their chemical structure, e.g. conformations, chirality and stability. These allowed the elucidation of spectral differences in bulk, thin-film and solution. For each component, the preferred packing motifs could be determined and correlated with charge transfer properties. The investigated acceptors show excellent electron transfer capabilities, of which PDTTI, in particular, stands out for an application in future OSC devices due to its suitable aggregation behaviour. In sum, the developed screening thus provides a link between the molecular structure and material properties that allow at least a rough assessment of the applicability as organic semiconductors.

We have elaborated how the chemical modification of the chromophore in six metal-organic complexes bearing tetra-dentate ligands with Pt centres induces spectral changes in absorption and photoluminescence. The manipulations of the complex structure allow to tailor the character of the lowest triplet state and thus to modify the wavelength of the phosphorescence emission. The analysis of stacking motifs with associated binding energies shows which complexes tend to form aggregates. We identify the mechanism underlying the red-shift of phosphorescence in aggregates compared to monomer emission, making both species clearly distinguishable. We observe high charge transfer rates along the stacking direction of Pt aggregates and can identify the preferential directions of charge transfer with organic components in OLED.

As we have demonstrated in this thesis, the theoretical investigation of BHJ-OSC and OLEDs requires the linking of a variety of methods on different time and length scales into a multiscale procedure. The choice of a bottom-up approach allows the generation of a realistic device morphology, in which quantum mechanical calculations are the basis for the development of a classical atomistic model, and this is extended to a classical coarse-grained representation. We showed that the top-down approach is applicable to extract bulk-properties from the morphology using quantum mechanical calculations on single molecules, pairs and aggregates. The kMC simulations elucidate charge transport processes in devices by linking molecular properties at the quantum level with the morphological structure. Hence, the multiscale model gives insight into the conductive connectivity of domains based on the evaluation of electronic couplings, the energetic landscape, site occupations, local electronic currents and mainly charge carrier mobilities.

Considering the enormous number of modelling steps required to obtain the charge carrier mobilities, one can hardly expect a quantitative agreement with experiment. Therefore, the task is rather to detect factors for increasing the efficiency of OSCs with the help of the multiscale model and to derive design rules for novel donor/acceptor materials, and optimise OSC-BHJ manufacturing processes.

Given the multitude of theoretical methods available to researchers, one might assume that most of the challenges in simulating organic semiconductors have been overcome to predict charge transfer parameters for organic solids reliably. Unfortunately, this is not the case, as we have repeatedly noted. There are still several difficulties in predicting macroscopic properties based on computational methods, and therefore the increased interplay between theory, simulation, and experiment remains essential. For example, the direct comparison of absolute mobilities with the experiment is still rarely possible for several reasons. One reason is that the transport mechanism is unknown for novel materials, which is, however, the prerequisite as a starting point for modelling. Especially in the transition region between band transport and hopping regime, this can lead to erroneous descriptions. Instead, it requires the accurate consideration of electron-phonon interactions in the modelling for charge carrier localisation and propagation, in order to include dynamic effects on electronic couplings, on-site energies and structural disorder in theoretical studies. Within the framework of an ideal theory, the exact mechanism of charge carrier transport would be the result of the investigations, instead of the input. Another point is that experimental studies have their own unique challenges to overcome. For example, mobility measurements of the same system can yield different results, due to minute differences in preparation.

In general, there are still open questions regarding how intermolecular and intramolecular interactions determine the device morphology. There are still open questions, e.g. whether the main limiting factor for charge transport are small electronic coupling elements or high energetic disorder and why charge transport maintains a dispersive character even at moderate energetic disorder. Even though CG and MM models for polymers are available to simulate liquid-crystalline phases and amorphous melts, a systemic understanding of the polymer self-assembly process is still missing. The restricting bottlenecks remain (i) the insufficient accuracy of selected computational methods due to the discrete, limited degree of resolution, (ii) the need for extended simulation times (microseconds) and lengthscales (micrometres) to study self-assembly processes in the morphology, and (iii) the unaccounted error propagation in the course of the transition from one level of theory to another. The latter case arises mainly, when QM calculations are employed in the parametrisation of FFs or when CG models are generated on the basis of MM simulations. Difficulties in the generation of the microscopic, amorphous morphology can lead to a non-equilibrium distribution of the atomically resolved structures and then be transmitted to the distribution of the charge transport parameters. Deviations in the structural distributions can potentially lead to discrepancies between experiment and theory.

Finally, despite the number of challenges, one of the great advantages of theory-driven research is identifying trends and thus establishing a link between the structure and function of a material. The assessment and development of suitable descriptors for material properties based on known materials make it possible to investigate the influence of chemical modifications or even design new systems in computer-assisted screening studies. Furthermore, detailed knowledge about the donor-acceptor interface is necessary to deduce the structure-property relationship and propose design strategies to enhance the total PCE in future OSCs.

