

## Chapter 7

# Conclusions and Outlook

*I have investigated the diverse ways in which molecular and morphological features on the microscopic and mesoscopic scale jointly condition the density of states of charge carriers and charge transfer states in organic semiconductors. Using particle-based descriptions with atomistic or coarse-grained resolution, the underlying computational framework has enabled quantitative insight into the energetics of organic heterostructures, grain boundaries, partially ordered polymeric and amorphous mesophases relevant in organic solar cells, light-emitting diodes and transistors. Long-range interactions in particular have proven fundamental to the study of organic semiconductors, relating the energetics on a molecular and supramolecular level to device-level characteristics. In this final chapter, I will retrace the derived structure-property relationships and design rules for organic electronic devices, outlining challenges in the understanding and modelling of organic semiconductors.*

**Impact of Mesoscale Order at Organic–Organic Interfaces** The functionality of organic solar cells relies on suitably tailored energy level profiles with appropriate interfacial offsets and bending that ideally favour charge generation and prevent recombination. The qualitative features of the resulting profiles were, however, subject of discussion, as computational studies strived to understand the functionality of highly efficient devices. We could show how microscopic simulations successfully access these energy profiles if mesoscopic ordering, probed by long-range electrostatic interactions, is properly accounted for. The resulting level profiles are thus subject to an order criterion: Flat level profiles across thin films—as a frequent experimental finding—only result for pronounced in-plane structural coherence over a length scale that well exceeds the thickness of the film. This link to the mesoscopic organization in crystalline thin films is an intriguing consequence of the quadrupolar structure shared by the vast majority of organic semiconductors. The action of the associated long-range fields sets this class of materials apart from disordered soft matter on the one hand, which lacks the structural coherence to generate these fields, and inorganic

semiconductors on the other hand, which exhibit strong screening mechanisms that compensate them.

**Role of Molecular Architecture, Packing and Orientation** From a comparative study of various small-molecular materials, we could show how molecular architecture and orientation control the energy level alignment across thin films. The molecular architecture, which can be of a donor, donor-acceptor, or acceptor-donor-acceptor type, establishes an energy hierarchy for the face-on, edge-on and tip-on orientations. The computational approach captures both the absolute and relative change of level positioning upon reorientation of the molecular crystals with excellent accuracy, as seen from the comparison with photoemission spectra. Meanwhile, molecular packing into, for example, brickwork versus herringbone structures, was found to be less relevant in thin films, as the energetics are then determined by the competition between in-plane and out-of-plane interaction directions. The polarity of the latter is only weakly influenced by crystalline repacking. Previous studies of bulk energetics, by contrast, have attributed a stronger role to crystalline packing modes. For bulk (i.e., 3D-infinite) systems, where orientation is of course undefined, this should indeed be the case. The good agreement between thin-film levels and experimentally determined energies indicates, however, that a bulk description should by no means be used to assess out-of-plane energy level alignment. We have nevertheless found molecular packing and architecture to play a decisive role at *in-plane* grain boundaries, where they determine which molecular subunits are exposed at the interface, and hence govern the formation of either energy barriers or energy traps at the grain boundary. To retain efficient charge transport, energy barriers should be preferred as the charge migration across the boundary is then limited by barrier gap diffusion rather than by the escape time from energetic traps.

**Merits of the Acceptor-Donor-Acceptor Architecture** Based on the relationship between molecular architecture and orientation, we could rationalize the success of the acceptor-donor-acceptor (ADA) architecture for molecular donor materials, used in the world-record system C<sub>60</sub>/D5M. The electrostatic layout of these ADA compounds leads to a destabilization of hole carriers in the absence of long-range ordering. In the case of long-range coherence in a thin-film setup, however, the face-on orientation of the D5M component corresponds to the lowest-ionization-energy configuration, then characterized by an only slightly (rather than strongly) negative electrostatic contribution. This face-on mode thus combines a sizeable photovoltaic gap and adequate interface polarity with strong optical absorption (due to the favourable alignment of the transition dipole moment) and fast out-of-plane transport (due to the favourable alignment of the  $\pi$ - $\pi$ -stacking direction) required for efficient charge separation and extraction. These advantages not only extend to C<sub>60</sub>/D5M, for which the face-on configuration has indeed been verified, but to ADA compounds in general. The ADA paradigm therefore appears a promising approach for the development of new donor materials. Similarly, the DAD pattern, if synthetically realizable, could be used for the synthesis of new non-fullerene acceptors with strong absorption profiles.

**Calculation of Open-Circuit Voltages Across Planar Heterojunctions** By computing the densities of states across planar donor-acceptor heterojunctions—with an account of both molecular orientation and thermal broadening—we calculated the charge-density-dependent open-circuit voltage from the quasi Fermi level splitting. The thus obtained voltages prove in excellent agreement with experimental voltages for typical steady-state charge densities at open-circuit conditions. The difference between the open-circuit voltage  $V_{oc}$  and mean of the photovoltaic gap  $\Gamma$  is largely effected by the thermal broadening  $\sigma$  of the densities of states [1]. For crystalline organic semiconductors,  $\sigma$  ranges between 40 and 100 meV. As a result, we found the difference between  $V_{oc}$  and  $\Gamma$  to range in between 0.7 and 0.9 eV. This exceeds the voltage gap of around 0.5 eV estimated from photoemission spectra [2]. It remains to be seen whether this discrepancy might be due to a systematic underestimation of the photovoltaic gap by photoemission techniques, where the onsets of the HOMO and LUMO peaks are used: The latter are not only subject to thermal broadening, but also, due to the measurement process, vibrational broadening and shifts. This way, for instance, energetic disorder strengths of 250 meV have been extracted for pentacene—far larger than what is physically plausible for such a high-mobility system. Meanwhile, the 0.7–0.9 eV are consistent with the 0.5–0.6 eV difference between CT energies and  $V_{oc}$  reported by optical measurements [3] when taking into account the CT binding energy. Indeed, our computed CT energies confirm this empirical relationship, yielding a slightly lower gap of 0.4–0.5 eV. The microscopic origin of this gap remained, however, impervious to our simulations, as explicit dynamics of charge-carrier and charge transfer state recombination would have to be addressed.

**Pathway for Charge Splitting and Detrapping** We have proposed a mechanism for electron-hole splitting at donor-acceptor interfaces that harvests mesoscale fields during the initial steps of charge separation, crucial in organic solar cells. To this end, we have shown how the in-built interface polarity results from the asymmetric stabilization (or destabilization) of electrons and holes on either side of the interface, as dictated by molecular architecture and orientation. Interface roughness then creates a field gradient that assists charge splitting and enables minority-carrier detrapping if the interface is poled correctly. Due to their mesoscopic origin, the charge splitting fields persist both in the case of fine intermixing and domain interpenetration. The resulting push-out mechanism can in principle be engineered such that the charge transfer (CT) state becomes isoenergetic with the photovoltaic gap—thus providing a route for barrier-less electron-hole separation. The molecular orientation and degree of interface roughness control the amount by which the CT-state energy is increased or decreased. The largest push-out forces can be realized in low hole- and electron-energy configurations of the donor and acceptor, respectively—at the cost of a decreased photovoltaic gap. We have rationalized that operation just above an isopolar point, characterized by flat electrostatic level profiles, is most desirable. Realization of such a scenario may however be challenging, in particular in systems where both the donor and acceptor component are strongly polar and can thus render charge generation ineffective if arrested in a negative-polarity orientation. Still,

this electrostatic charge splitting pathway with its direct link to interface structuring could explain why some photovoltaic systems display a temperature-independent [4–6] rather than the expected temperature-activated charge generation behaviour [7].

**Vice and Virtue of Low-Energy Configurations** We have attributed a key role to lowest-energy configurations at interfaces: These configurations not only appear to categorically determine the open-circuit voltage in organic solar cells, but also (see above) facilitate charge splitting and detrapping. Beyond low-energy orientations, low-energy packing modes are also more likely to promote energy barriers at grain boundaries, preferred over energy traps. In solar cells, however, they imply a reduced photovoltaic gap, which linearly enters both the CT-state energy and open-circuit voltage. In many cases the Frenkel exciton energy still leaves room for increasing the CT-state energy (and hence voltage) without stalling device functionality nor impeding charge push-out effects. An open question is therefore whether precise morphological tuning can indeed harvest what energetically resembles a passed-up opportunity. Even in bulk heterojunctions, the device characteristics continue to be pinned by these lowest-energy configurations—despite the “traditional” picture of bulk heterojunctions suggesting the coexistence of a variety of donor-acceptor interfaces with different orientations, in-plane extensions, degrees of intermixing, and hence different energetics [8]. Nevertheless, the open-circuit voltage of bulk heterojunctions is usually on the order of 0.1 eV smaller than in the planar setup, and still correlated with a *single* CT energy extracted from absorption and electroluminescence. This energetic similarity of bulk and planar heterojunctions remains enigmatic; to identify its origin, more details would have to be known about the microscopic structure of these junctions. In particular, the “centro-symmetric” layout of bulk morphologies may have to be reassessed, as in-situ growth studies [9] and ellipsometric characterizations [10] indicate that donor-acceptor mixtures are not only well phase-separated, but in fact macroscopically ordered with respect to the substrate. In view of this residual preferential ordering, future computational studies will hopefully resolve to which degree mesoscopic interactions persist in both planar and bulk heterojunctions.

The derivation of quantitative structure-property relationships and design principles summarized above were made possible by the development of new computational methods targeting the morphological and electronic properties of organic semiconductors with a systematic link to the molecular structures. Most importantly, the presented long-range polarized embedding technique provided quantitative access to the energetics of charges and CT states. Built on a perturbative approach, the method is efficiently parametrized from first principles and applicable to large atomistic models incorporating thousands of molecules at an affordable computational expense. Beyond organic heterostructures and grain boundaries, it enabled, for example, the study of the formation of low-energy states and spatial energetic correlations in large models of polymeric mesophases incorporating long-range conformational disorder.

The method as applied here is, however, not yet suited to investigate the energetics of states with a strongly quantum-mechanical character, such as non-integer CT states. An extension of the scheme to incorporate a quantum-mechanical description

of the embedded state is currently under development. On the quantum level, many-body Green's functions approaches are the method of choice due to their accuracy and computational efficiency: The GW-BSE formalism, for example, significantly improves on time-dependent density functional theory by accounting for a dynamically screened Coulomb interaction in the self-energy operator (GW) and an excitonic electron-hole interaction described by the Bethe-Salpeter equation (BSE) [11].

Highly relevant for the modelling of devices, a further extension of the embedding approach should target the description of metal-organic interfaces, notably injection barriers: The effect of image charges on contact potentials can be modelled directly [12], whereas charge equilibration across the interface probably has to be addressed by coupling the particle-based description to a Poisson-Fermi solver [13].

An additional challenge lies in how accurate energy calculations can be integrated efficiently into explicit simulations of charge-carrier and exciton dynamics using kinetic Monte-Carlo techniques. Encoding long-range interactions into the single-particle energy landscapes already implies a possibly inappropriate approximation to many-body polarization effects, since these result both in an effectively reduced *attraction* between charge carriers of the same polarity and reduced *repulsion* of charge carriers of opposite polarity not captured by the single-particle approximation. Within monodisperse systems, the associated charge concentration effects could be modelled using an effective distance-dependent dielectric function. However, whether a similar approach would hold for more complex polydisperse systems and heterostructures is uncertain. Yet more complicated is the incorporation of long-range electrostatics and polarization into systems with partially delocalized carriers, where explicit propagation of the wave functions via surface hopping techniques becomes necessary [14]. Such an extension is highly relevant as the degree to which polarization leads to an additional localization of charge carriers is still unresolved.

Meanwhile, morphology simulations continue to present one of the greatest challenges in the modelling of organic semiconductors due to the inherent large length and time scales that even in experiments occasionally result in kinetically arrested non-equilibrium structures [9]. Obtained using diverse approaches, the morphologies studied in this work retained their strictly model-like character, hence limiting the range of studies for which they are suited: Many relied on preassembled and experimentally determined input structures, others only provide a phenomenological description of complex morphological features such as grain boundaries or rough interfaces. Finally, those that do provide atomistic details are prone to finite-size effects that may impact the energy landscape of electronic states, here identified even for amorphous mesophases of dipolar molecules.

Predictive modelling of at least local structuring should, however, be possible. Crystal-structure prediction techniques could, for example, be applied to organic-organic interfaces to resolve molecular packing and orientation. For non-local structuring, particularly relevant in the complex organization of bulk heterojunctions, strictly predictive approaches remain elusive. The most promising simulation strategies thus combine bottom-up with top-down modelling protocols: The former provide

the link to the molecular detail, whereas the latter capture supramolecular features such as lamellar ordering or domain formation. On the mesoscopic, top-down level, both field- [15] and particle-based approaches [16] coupled to an atomistic, bottom-up description are conceivable. The polymeric mesophases studied in this work [17] give an impression of what can be achieved with such approaches, hopefully providing a baseline for future method development.

## References

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