DOI: 10.1002/adfm.201500703

Computational Modelling of Organic Semiconductors: From the Quantum World to Actual Devices

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Organic semiconductors are already present in commercial technology, primarily as active elements in display applications. They carry further promise in a variety of applications, including solid-state lighting, electronics and simple circuitry, sensors, memories, and last but not least organic solar cells. A detailed understanding of the relevant (opto)electronic processes in organic semiconductors is vital for improving their performance in the aforementioned applications and for paving the way to entirely new ones. Since the early days of the field, simulations have crucially contributed to our understanding of these materials. With steady improvement in computational tools, in combination with growing computational resources, one can safely predict that the role of computer simulations will keep growing in the years to come.

We are confident that the enormous potential of computer-based simulations for rationalizing the observed properties of organic materials and devices is made obvious by the various contributions in this Special Issue. A possibly even more important aspect is that the available computational tools have reached a level where they allow predictions of properties of new materials or device structures even before their experimental realization. In this way, simulations help guide rational design processes that form the basis for future progress of the field. Consequently, also the "design aspects" of computational modelling for organic electronics are addressed in several of the following contributions.

Simulating organic semiconductors and organic electronic devices is intrinsically a multi-scale problem. At the shortest length- and time-scales, it involves calculations at the quantum-level. Traditionally, this has been the largest area of computational modelling of organic materials, which is reflected in the number of corresponding contributions in the present Special Issue. Here it is illustrated that a variety of methodological advances over the past few years has significantly improved the quantitative reliability of the available methods. For understanding an actual device, however, one needs to go significantly further. Consequently, molecular dynamics using classical force fields plays an important role for describing the structure, dynamics, and even growth of extended molecular ensembles, often in conjunction with parametrized coarse-grained methods that allow the treatment of even more extended model systems. For understanding the dynamics of charges and excitons, or to analyze the formation of heterogeneous phases, statistical approaches including Monte-Carlo techniques can be applied. As illustrated in two of the following contributions, such methods have nowadays the capacity of treating complete devices, including the electrodes. The last element in the outlined multi-scale modelling chain is the drift-diffusion approach, which builds on effective materials parameters to allow the efficient modelling of highly complex devices, in operation, at typically moderate computational costs.

The multi-scale nature of simulating the transport in an organic device is elegantly reviewed in the Feature Article by Kordt et al. Starting from the molecules described at the quantum-level, the authors discuss the entire modelling chain until a full device can be simulated. This yields a multi-scale scheme that "can be used to predict [organic light-emitting device] OLED properties without fitting parameters, starting from chemical structures of compounds."

In fact, the accurate description of transport properties is a considerable challenge already at the quantum-level. This becomes apparent in the Feature Article by Ortmann et al., in which approaches to model the charge carrier dynamics from "ballistic motion to incoherent hopping" are discussed, with a particular focus on the accurate description of electron–phonon coupling and how to account for disorder. The role that static and thermal disorder, as well as domain interfaces and grain-boundaries, play for electronic transport in organic semiconductors is central to the Feature Article by Mladenović and Vukmirović. There, the authors discuss the interplay between materials imperfections and charge-carrier localization that eventually determines the transport properties.

A further challenge when simulating organic semiconductors is the quantitatively accurate description of optical excitations and their dynamics, which is again intrinsically a quantum-mechanical problem. One of the challenges in this context is the reliable simulation of charge-transfer excitons, which is of immediate relevance for the performance of organic solar cells. This topic is addressed in the paper by Niedzialek et al., where the authors compare the results of different ab initio techniques with experiments, to show the potential and limitations of the available approaches. To gain deeper insight into the charge separation process, Pittalis et al. model the coupled electronic and nuclear dynamics following the photo-excitation of a well-defined dyad molecule. This allows them to assess the role of vibronic effects and molecular morphology. A further level of complication arises when simulating excitations in extended periodic solids (as opposed to molecular dimers or small clusters). This topic is addressed in the paper by Sharifzadeh et al., who use many-body perturbation theory calculations to simulate excitations in TIPS-pentacene in order to describe the delocalization of excitons and how it is affected by the solid-state structure.

The last quantum mechanics topic addressed here is the treatment of omnipresent dispersive interactions, which has been a serious limiting factor in the simulation of molecular materials for several decades. Fortunately, especially in this area, tremendous progress has been made recently, which is briefly reviewed in the Highlight by Tkatchenko. This article also addresses the origin of collective van der Waals interactions and stresses the importance of a full many-body treatment of vdW interactions in complex materials.

Leaving the quantum—but not the atomistic—modelling world, D'Avino et al. use molecular-dynamics calculations based on classical force fields to simulate nucleation and growth at organic/organic interfaces. They describe also the growth of defective islands and multilayers and model the impact of thermal annealing at an atomistic level.

With the goal of modelling entire devices, Coehoorn et al. develop a 3D Kinetic Monte Carlo method in which they include charge transport as well as the relevant excitonic processes to simulate phosphorescent OLEDs. This provides significant insight into the origin of quantum-efficiency roll-off and helps developing rules for OLED-stack design. In a similar effort, Gagorik et al. use Monte Carlo simulations of the carrier dynamics in isotropic bulk-heterojunction solar cells to study the impact of charge delocalization on the device efficiency.

At the long time- and length-scale limit of the multi-scale modelling chain, Bartesagi and Koster use a drift-diffusion based approach to explain the relationship between the power-conversion efficiency of conjugated polymer/fullerene-derivative solar cells and the actual film morphology. The latter is characterized by the coexistence of fullerene "blobs" and a finely mixed donor/acceptor matrix, where photocurrent originates from the interfacial regions of the two phases as well as from the donor/acceptor matrix.

Last but not least, Vanzo et al. model the dielectric properties of organic thin films of nanometer thickness, applying a microelectrostatic approach and the model of intra-molecular charge redistributions. Polarization and depolarization effects in molecular crystals of less than cubic symmetry are analyzed, with a particular focus on surface effects.

Naturally, computational modelling cannot stand alone, but must be performed in close dialogue with experimental investigations. This is well reflected in the current Special Issue, with the majority of the papers describing joint modelling and experimental efforts. This combination indeed appears to be the most promising approach for further advances in the field of organic semiconductors and for making a larger number of their applications technologically and even commercially viable.

Finally, it should be noted that this Special Issue is associated with the Symposium on "Computational Modelling of Organic Semiconductors: From the Quantum World to actual Devices" held at the 2014 E-MRS spring meeting and comprises contributions from selected (mostly invited) speakers from this event.

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