

Boosting OLED Performance with Ab-initio Modeling of Roll-off and Quenching Processes.

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Abstract

Device-scale computer simulations support experimental R&D in the identification of microscopic bottlenecks in device performance. We present full ab-initio computation of the parameters required for simulation of roll-off and quenching in OLED stacks and illustrate how strategies to improve device design can be derived from computer simulations without relying on experimental input.

Keywords

OLED - virtual twin – computer-aided design - material development - predictive device simulations

Introduction

The nearly infinite variety of organic materials and the increasingly complex setup of OLED multilayer stacks renders the experimental optimization of OLED devices via trial & error fabrication, production and characterization a time-consuming and costly process[1]. Computer simulations can speed up the R&D process (i) by virtual screening of materials and system specifications, and (ii) by supporting experimental R&D with specific information on microscopic processes, providing fundamental understanding of what is going on in the device[2], [3]. Continuum models such as drift-diffusion are widely used in organic electronics R&D. However, these approaches fail to accurately account for all physical processes and effects, most notably Coulomb interactions, and are based on parametric models and therefore rely on input parameters extracted from experiment that are often hard to obtain with sufficient accuracy. In the past years, individual aspects of OLED devices were computed ab-initio with reliable accuracy, such as charge carrier mobility[4], [5]. However, the lack of ab-initio computational methods for other key features such as absolute energy levels and excitonic processes limited the application of computational approaches to full-stack design.

This work is a review of recent developments in the ab-initio computation of charge transport and excitonic processes for parameter-free simulations of full devices that enable a straightforward and systematic identification of performance bottlenecks, which allows the targeted development of compounds tailored for specific purposes and the optimization of layer architectures on the basis of a computer-aided design approach.

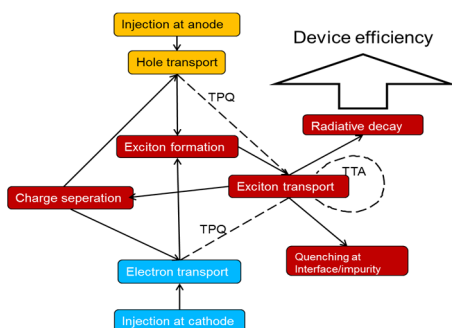


Figure 1: Microscopic processes to take into account when simulating OLED devices. Figure from [7]

Method

To maximize the impact of OLED simulations, we apply a kinetic Monte-Carlo (KMC) approach where each charge carrier or exciton is simulated as an individual entity, and relevant microscopic processes, as depicted in Fig. 1, are modeled explicitly. In KMC, every possible microscopic process, such as the hop of a charge carrier from molecule A to molecule B, the combination of two charge carriers into an exciton, or a quenching process, is associated with a site and state-specific rate that depends on the microscopic environment. Based on these rates, a single process is executed in each simulation step. By associating each executed step with an appropriate time interval, KMC simulations provide time-resolved particle and exciton trajectories.

While, especially in multi-layer OLED stacks, this approach is computationally more extensive than e.g. Drift-Diffusion simulations, it provides two key advantages: First, it allows the detailed analysis of charge carrier and exciton dynamics and therefore the identification of microscopic bottlenecks in OLED devices. Second, as we will demonstrate in this work, rates for microscopic processes can be computed from first principles without the use of parameters e.g. from experiment, enabling bottom-up virtual OLED design.

Rates of the processes depicted in Fig. 1 are highly material dependent and their computation is based on molecular quantities such as orbital energies, excitation levels, electronic couplings or transition dipoles. While quantum chemistry methods to compute these properties for single molecules are well established, the electronic structure of molecules changes when they are embedded in organic thin films, and quantities derived from vacuum quantum chemistry computations become inaccurate as they do not take into account the effect of the local environment of the molecules.

To enable reliable full-stack device simulations based solely on quantities derived from first principles, we follow a seamless bottom-up multiscale modeling approach generating a digital twin on the basis of the computation of relevant molecular properties with quantum chemistry methods, while taking into account environmental effects on a full-quantum mechanical level[4]–[7]. Including the actual OLED stack simulation, this results in four simulation steps, illustrated in Fig. 3:

Step 1 and 2: Customized force-fields and atomistic morphologies: To generate a digital replica of OLED devices in the computer, organic thin films and interfaces on the 10nm-scale with atomistic resolution are generated with Monte-Carlo based molecular modeling. The inter- and intra-molecular interactions are modeled using customized force-field functions automatically generated for every organic compound (Parametrizer). By mimicking physical vapor deposition in Deposit[8], experimentally observed features, such as inhomogeneities and anisotropies, are reproduced in these structures in good agreement with experiments [6], [9].

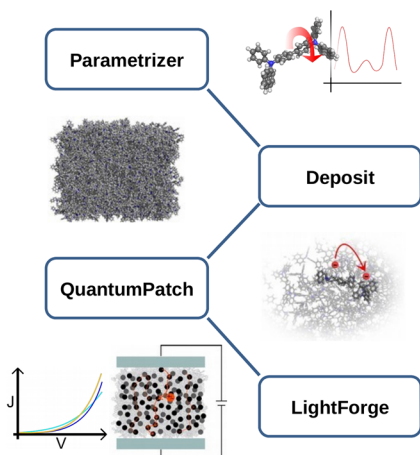


Figure 3: Multiscale workflow for ab-initio OLED simulations.

Step 3: Electronic structure of molecules in organic thin films:

The resulting atomistic morphologies are then analyzed at a fully quantum-mechanical level using the self-consistent QuantumPatch approach [4], [5]. Here, the properties of molecules (such as transport energy levels, excitation energies, transition dipoles, orbital overlap) are computed at high level of accuracy while taking into account the local electrostatic environment on a fully quantum-mechanical level. This allows an accurate computation of disorder effects dominating OLED performance.

Step 4: Simulation of charge transport and exciton dynamics:

Distributions of microscopic quantities such as hopping sites, site energies or electronic couplings are then expanded to generate a digital replica of a multilayer OLED stack. Rates for the individual microscopic processes (charge transport, exciton formation, radiative decay, quenching, etc.) are computed using state-of-the-art methodology. Based on these rates, system dynamics are simulated using a Kinetic Monte-Carlo protocol as implemented in LightForge, resulting in time-resolved particle (charge carriers & excitons) trajectories to be used e.g. for analyzing charge carrier mobilities, charge carrier balance or quenching.

A similar workflow has been used in various studies [7], [10], [11]. In this work, we apply this workflow to compute and validate molecular properties that are essential ingredients to OLED stack simulations from first principles, including parameters for charge

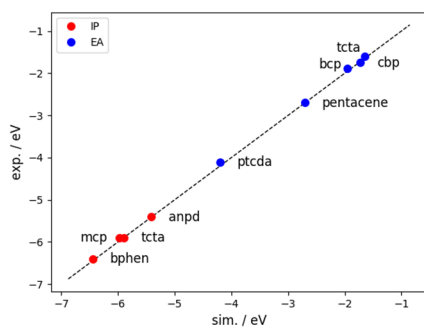


Figure 4: Comparison of computed and experimentally determined transport levels for holes (IP) and electrons (EA) in organic semiconductors (from Ref. [15]). Experimental values from [16]-[18]

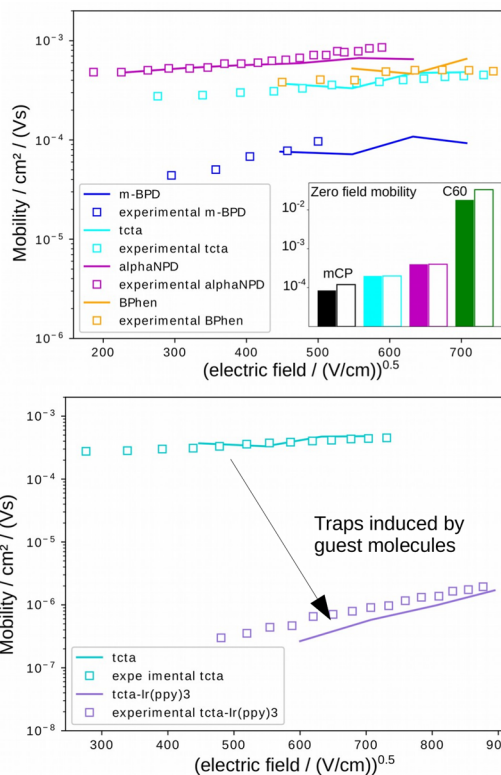


Figure 2: Simulated charge carrier mobility in comparison to experimental data [12]-[14]. Top: Electric field dependence of mobility and zero-field mobility (inset) of pristine C₆₀, Bphen (electron mobilities), mCP, alpha-NPD, TCTA and m-BPD (hole mobilities) materials shows good agreement for materials with mobilities ranging several orders of magnitude. Bottom: Field dependence of hole mobility in pristine TCTA and TCTA doped with 7% Ir(ppy)₃, compared to experimental data.

carrier transport (energetic disorder and electronic coupling), electronic transport levels (EA and IP) and exciton quenching rates (TTA and TPQ). We will further illustrate how OLED device simulations based on microscopic input can be used to analyze microscopic bottlenecks in device performance, and how virtual screening of system parameters can aid OLED R&D by identifying the sweet spot in the parameter space.

Results

Charge transport within the individual layers of an OLED stack has a strong impact on overall device performance. Therefore, we first validated the approach described above by computing charge carrier mobility in single organic layers and comparing to experimental data from the literature. The top panel of Fig. 2 shows charge carrier mobility computed with LightForge based on microscopic input derived using QuantumPatch and Deposit for the compounds C₆₀, Bphen (electron mobility), mCP, alpha-NPD, TCTA and m-BPD (hole mobility).

For these materials with mobilities spanning multiple orders of magnitude, field dependence and zero-field mobility (extracted by extrapolating field-dependence to zero field) show very good agreement with experimental data [12]-[14]. Comparison of the hole mobility of a guest-host system, TCTA doped with 7% Ir(ppy)₃, to the respective mobility of the pristine host layer is depicted in the bottom panel of Fig. 2. Again, we find good

agreement between computed and experimental mobility and observe the expected drop in mobility induced by energetically low-lying guest states.

The charge carrier mobility in pristine layers is determined by the electronic disorder, i.e. the relative differences of site energies within a single material, and the absolute values of transport levels (EA/IP) are not required for their computation. For the investigation of properties of mixed systems or interfaces, however, accurate computation of EA and IP becomes vitally important. Using QuantumPatch, we computed EA and IP values for nine materials by subtracting energies of charged and uncharged molecules, taking into account the response of surrounding molecules in the organic thin film. Details can be found in [15]. To allow direct comparison to experimental data from UPS measurements, theoretically predicted IP values (computed as the mean of a distribution) were corrected by the energetic disorder, and a global (material independent) linear correction to theoretically predicted values was applied. The comparison between computed and experimental transport levels (from [16]–[18]), displayed in Fig. 4, shows remarkable agreement.

Triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ) are responsible for limited efficiency and lifetime of OLED devices. Computer simulations can help researchers and device developers to understand and reduce the impact of TTA and TPQ, thereby improving both lifetime and efficiency. To aid this process, we developed a rate model for TTA and TPQ. Using the workflow described above, we computed distributions of microscopic TTA and TPQ rates for an emission system where TCTA was doped with the emitter Ir(ppy)₃. In order to validate our rate model, we performed virtual quenching experiments in LightForge KMC and compared them to experimental data [19]. In the TTA experiments, excitons were generated using a short laser pulse, and the rate model was fitted to the relative emission over time, providing a macroscopic quenching rate k_{TT} . Results of this virtual photoluminescence quenching experiment in comparison to the experimental data from [19] are displayed in panel a) of Fig. 5 (top: exp. data from [19], bottom: simulation). Reproducing this experiment virtually in KMC, we computed a macroscopic quenching rate of $k_{TT} = 8.5 \times 10^{-12}$ cm³/s, which compares very well with the experimental value of Reineke et al. of 7×10^{-12} cm³/s, derived at low exciton densities.

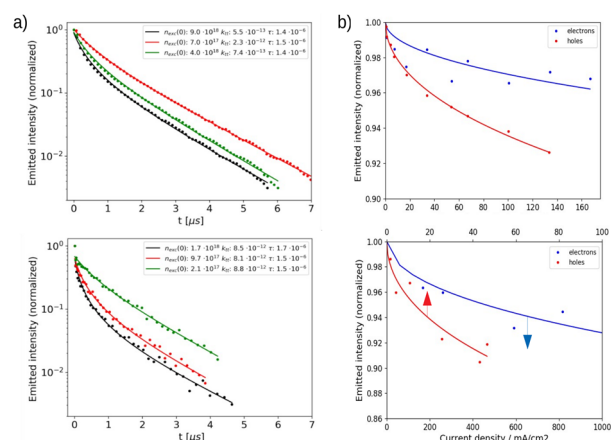


Figure 5: Analysis of quenching in the system TCTA:Ir(ppy)₃. a) experimental (top, from [19]) and simulated (bottom) photoluminescence for TTA analysis. b) experimental (top, from [19]) and simulated (bottom) relative emission at different current densities in the steady state to analyze TPQ. Panel a) taken from Ref. [10]

TPQ was analyzed using steady state conditions (constant illumination and constant current) and measuring relative emitted light over applied current (which determines polaron density).

Similar to the TTA analysis, a rate model was fitted, resulting in a macroscopic TPQ quenching rate k_P [19]. The results for the virtual TPQ experiment are displayed in panel b) of Fig. 5 (bottom) in comparison to experimental data from [19] (top). In the virtual experiment, we computed a TPQ k_P of 6.4×10^{-13} cm³/s for holes

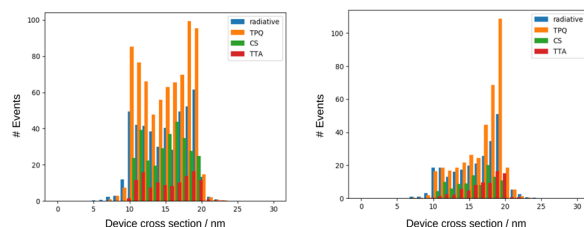


Figure 7: Occurrence of excitonic processes plotted over device cross section of the original (left) and modified device (right). The dominant processes are radiative decay (blue), triplet-polaron quenching (TPQ, orange) and separation of excitons into a hole and electron (CS, green).

(exp: 3.0×10^{-13} cm³/s) and 1.6×10^{-13} cm³/s for electrons (exp: 2.0×10^{-13} cm³/s).

For both TTA and TPQ, the extracted macroscopic quenching rates are within a factor of 2-3 compared with experimental data, which is a remarkable agreement considering that the microscopic quenching rates were computed using basic quantum chemistry.

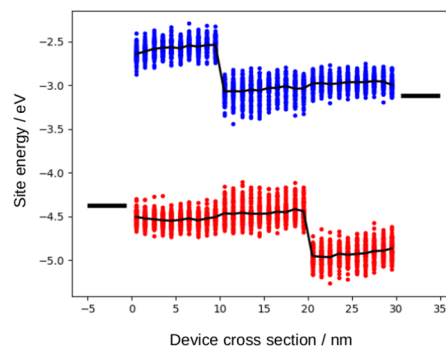


Figure 6: Energy profile of the device for electron transport (LUMO, blue) and hole transport (HOMO, red). Site energies are assigned according to a distribution that can be derived from first principles on atomistic morphologies.

Details on the TTA computation were recently submitted [10].

To exemplify the approach and highlight the insight that can be generated with ab-initio device simulations, we performed a parametric study of exciton dynamics including triplet-triplet annihilation and triplet-polaron quenching in common emission layers of OLED devices. We generated a digital twin of an emission layer between an ETL and HTL using a lattice morphology. HOMO and LUMO energies were assigned to the molecule sites according to Gaussian distributions. All excitonic parameters were distributed to the molecular sites based on values for TCTA:Ir(ppy)₃ that were computed from first principles using QuantumPatch and atomistic morphologies generated by Deposit. The energy profile of the device used in this study is illustrated in Fig. 6. For this device, we performed KMC simulations as implemented in LightForge at different electric fields of 1.2, 1.95 and 2.7 V/nm. Total current and the ratio of photon emission over exciton generation were tracked

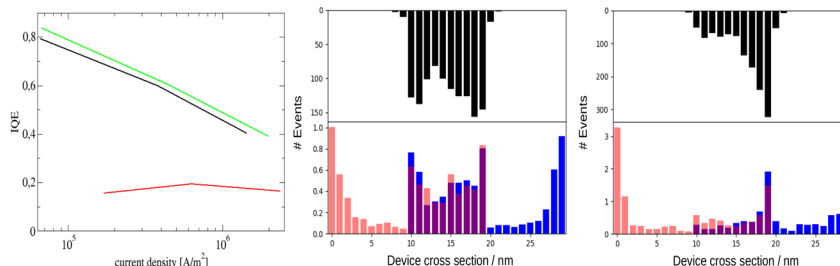


Figure 8: Left: Roll-off of original (black) and modified ((i) green, (ii) red) devices. Middle: Exciton quenching (black) and charge carrier (red: holes, blue: electrons) densities in the device. Right: Exciton and charge carrier densities in the modified (i) device.

to compute current dependent internal quantum-efficiency (IQE), as depicted in the left panel of Fig. 7.

As is observed experimentally in OLED devices, IQE decreases at larger currents (roll-off). To explain this behavior, we further analyzed excitonic processes. As illustrated in the left panel of Fig. 8, the most dominant processes are radiative decay and triplet-polaron quenching (TPQ). Comparison between these distributions at the lowest and highest applied electric field shows that the roll-off is mainly induced by TPQ processes occurring throughout the emission zone. This gives rise to the assumption that a targeted modification of charge carrier and exciton densities, e.g. by adapting relative energy levels of the guest-host system, may lead to an improved roll-off behavior. To test this hypothesis, we modified the system in two ways: i) We shifted the EA of the host material in the EML up by 0.2 eV, and ii) we shifted the EA of the dye down by 0.15 eV. The roll-off for both modified systems was computed and is included in the left panel of Fig. 8. While the second modification reduces IQE for all applied fields, the IQE improves with the first system modification. To further analyze this improvement, we computed time-averaged charge carrier and exciton densities in both devices, depicted in the middle and right panel of Fig. 8, and analyzed excitonic processes also for the second device, illustrated in the right panel of Fig. 8. The asymmetric shift of energy levels for holes and electrons leads to an asymmetric distribution of exciton density (which is approx. proportional to the quenching density in the Fig. 8).

We conclude that a targeted modification of energy alignment in guest-host systems can reduce TPQ and improve roll-off. The identification of the sweet spot in the parameter space (choice of energy levels, i.e. host materials) is quite time-consuming and costly experimentally, and computer simulations can support this process by providing understanding of what is going on in the device and pre-screening material combinations and device setups.

Conclusion

Identification of performance bottlenecks in device performance is the key towards the optimization of efficient and durable organic electronic devices. Ab-initio device simulations support experimental efforts by providing insight into microscopic processes that are hard to access experimentally, generating fundamental understanding of OLED devices and facilitating targeted R&D. The microscopic analysis of quenching processes that are responsible for two key bottlenecks in OLEDs, namely limited quantum efficiency (roll-off) and degradation, is therefore an essential step towards computer-based device design and allows researchers to derive design rules for efficient OLED devices. Incorporating charge carrier and exciton simulations based on first principles into the design cycle will

therefore increase device performance, speed up the design process, and allow shorter time to market.

Acknowledgements

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