Tuning ETL Mobility by Disorder Passivation

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Abstract

In organic electronics (OE) application a high degree of control of material parameters such as transport levels and charge carrier mobilities is required to build a balanced device. We demonstrate that electron mobility of the prototypical electron transport material TPBi can be tuned freely by mixing it with a secondary electron transport inert material. We can in particular increase electron mobility in TPBi by up to a factor of 10 by diluting TPBi. This increase is due to a reduced electrostatic disorder in the mixed morphology. Using our predictive ab-initio based modeling tools we can find the optimal mixture to maximize or pinpoint electron mobility in TPBi.

Author Keywords

Tuning OLED performance; Virtual Design of OLEDs; Multiscale OLED simulations; Design rules of OLED materials and devices.

1. Introduction

Reducing exciton quenching persists to be a major challenge in OLED devices. In order to minimize loss processes that limit efficiency and cause degradation, it is essential to balance the charge and exciton density in the device. One promising path towards balanced OLEDs is to tune charge carrier mobility in hole and electron transport layers (HTL/ETL).(1) However, especially ETLs often suffer from low mobility due to a large energy disorder induced by the large polarity of the materials.(2–4) Low ETL mobility not only makes it difficult to create a balanced stack, it also increases driving voltage of the device.(5)

One approach to increase mobility is to reduce electrostatic disorder by reducing the polarity of the compounds via molecular design. Chemical modifications, however, often change other key molecular properties such as the HOMO and LUMO energies.(6-8)

In this work we investigate an alternative approach and analyze the impact of mixing ETL materials with guest materials with low polarity and a LUMO which makes it inert for electron transport. Reducing local energy disorder increases mobility, while a decrease in connectivity limits percolation pathways. As charge mobility in disordered organic semiconductors scales as $\mu \propto \exp(-\sigma^2)$ we expect the reduction of the disorder due to the additional material to overcompensate for the worse percolation.(9)

To disentangle the opposed effects of disorder and percolation when introducing non-electron-trapping guest material (further termed (disorder)-passivator) into polar ETLs, we follow a seamless bottom-up multiscale modeling approach. We compute concentration dependent charge carrier mobilities in TPBi doped with α-NPD which exhibits significantly lower electrostatic disorder than TPBi, based solely on first principles. We demonstrate that we can enhance electron mobility in TPBI by up to a factor of 10, and identify the (material specific) sweet spot in the parameter space.

2. Method

In order to translate microscopic molecular properties to the device level, we follow a simulation workflow to construct a digital twin of the device down to the electronic scale. Thereby, properties computed with quantum chemistry methods are ultimately mapped to charge transport simulations on the device level. This approach was recently applied to investigate individual aspects of OLED devices from ab-initio with reliable accuracy, such as charge carrier mobility or quenching in emission layers (12,14–20).

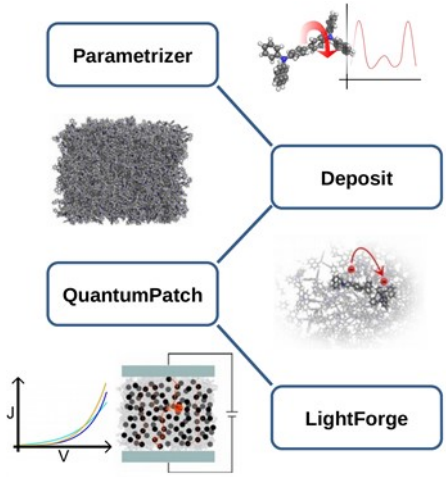

Figure 1: Multiscale workflow used for the ab-initio charge transport simulations.

The workflow depicted in fig. 1 consists of three distinct steps: 1) Following the Deposit approach, (10–14) thin-film morphologies of O(1000) molecules and with atomistic resolution are generated by mimicking physical vapor deposition: Molecules are added to the simulation box one at a time and relaxed into their thermally equilibrated state using Monte-Carlo based basin hopping with simulated annealing. During the deposition process, bonds and angles were kept fixed, while rotations around single bond dihedrals were modeled using customized intramolecular interactions derived from DFT computations on various single molecule configurations. The intermolecular interaction is modeled using Lennard-Jones and Coulomb forcefields with ESP charges from DFT. 2) Using the QuantumPatch method, we analyze the electronic structure of the thin films to compute transport energy levels and electronic couplings (11–14). Specifically, we iteratively and self-consistently relax the electronic structure of a subset of molecules while taking into account environmental effects, i.e. the unique electrostatic environment of each molecule, exclusively on a quantum chemical level (ab-initio). Based on the computed energy level shifts of calculated molecules, energy levels of all molecules in the thin film morphology can be computed a) using a Gaussian disorder model or b) using an atomistic electrostatics energy

model based on the electrostatic potential and explicit configuration of each molecule. 3) We simulate charge transport on a microscopic level in expanded amorphous morphologies with kinetic Monte Carlo (15–18) using Marcus rates (21) with site-specific pairwise energy level differences and electronic couplings derived from QuantumPatch. Reorganization energies are set to 200 meV.

3. Results

Following the workflow described above, we constructed digital twins of TPBi, doped with α-NPD acting as "passivator" material (by reducing electrostatic disorder) at concentrations of 0, 25, 40, 45, 55 and 70%. Subsequently, the electronic structure of each resulting thin film morphology with atomistic resolution consisting of 2000 molecules was analyzed using QuantumPatch. For the morphologies at different concentrations in the order stated above, we computed the LUMO disorder to be 169, 146, 134, 132, 129 and 119 meV respectively.

Based on the morphologies from Deposit, energy disorder and distributions of electronic couplings, we performed kinetic Monte-Carlo (kMC) simulations for all systems using the kMC package LightForge. Accurate, extended systems for transport simulations are obtained by periodic extension and subsequent calculation of the electrostatic potential on the extended system. For a parameter sweep we use systems with the, less accurate but more flexible, corresponding Gaussian distribution of LUMO energies on geometrically extended systems of 40x40x40 nm³. EA levels of TPBi and passivator were set to 2.25 eV and 1.9 eV respectively, asserting that charge transport occurs only on TPBi. To consider bulk mobility (i.e. to neglect injection effects at electrodes) no electrodes were attached to the sample. Instead, 20 electrons, corresponding to an electron density of 3.125e-4 1/nm³, were distributed randomly in a periodic sample and the electron mobility was computed by measuring drift velocity under an applied voltage in 15 independent simulations.

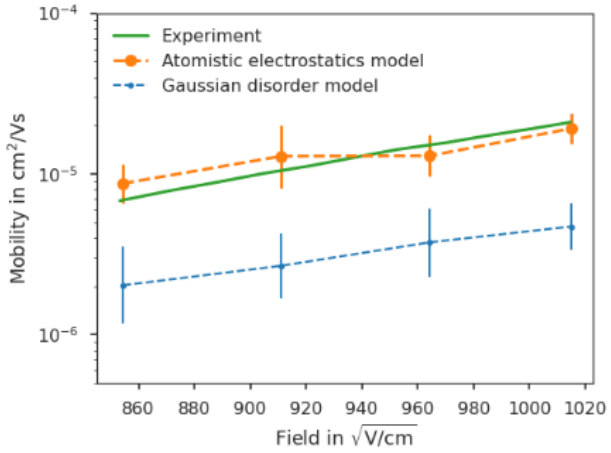

Figure 2: Comparison between simulated mobility using a Gaussian disorder model (blue) and an atomistic electrostatics energy model (orange) with experimental data from Zhang, *et al.*(2) Using the atomistic electrostatics model we find a very good match between simulation and experiment. Simulations using the Gaussian disorder model underestimate mobilities by a factor of four.

For the pristine TPBi layer, mobility was computed at various applied fields. Fig. 2 shows the simulated mobility vs. experimental data from Zhang, *et al.*(2). For the simulation based on the accurate energy model (orange) we find a very good match to experimental data and the Gaussian disorder model (blue) underestimating the mobility by a factor of four while reproducing the experimental trend.

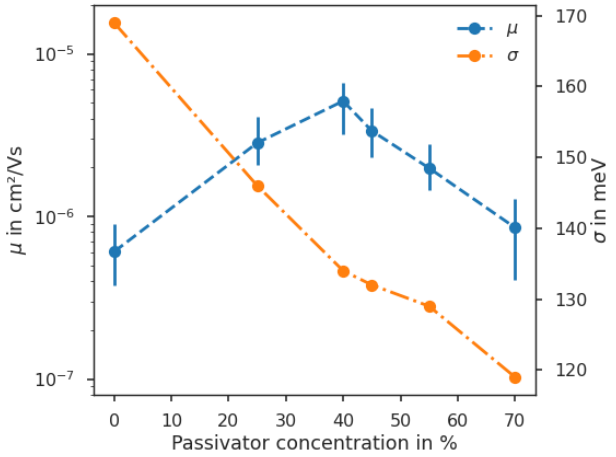

Figure 3: Energy disorder (orange) and charge carrier mobility (Gaussian model) (blue) in dependence of the passivator concentration. As disorder decreases with increased passivator concentration we find an increase in mobility, while mobility is decreased by reduced connectivity between TPBi molecules, leading to an optimum at 40% passivator concentration.

Passivator concentration dependent mobilities were computed at a field of 0.03 V/nm and are displayed fig. 3 (left y-axis), along with the energy disorder (right y-axis). We find a significant disorder decrease of 35 meV between pristine TPBi and TPBi doped with 40% passivator, leading to an increase in mobility by a factor of 10. Upon further increase of the passivator concentration, mobility decreases despite a further decrease of energy disorder. We therefore conclude this decrease to arise from diminished connectivity between TPBi molecules at lower concentrations.

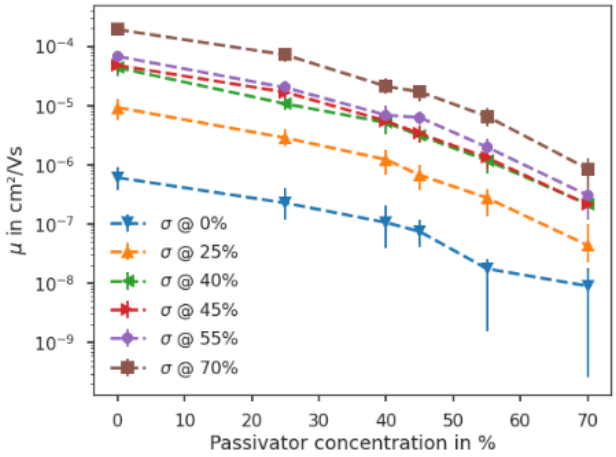

Figure 4: Mobilities (Gaussian model) in dependence of passivator concentrations for different disorders (kept constant) show an expected decrease of mobility with increased passivator concentration for all disorders due to limited connectivity.

To disentangle the impact of connectivity and disorder, we conducted mobility simulations at various passivator concentrations, while keeping disorder constant at various values.

The results are depicted in fig. 4. As expected, there is a continuous decrease of mobility, when passivator concentration is increased (if disorder is kept constant).

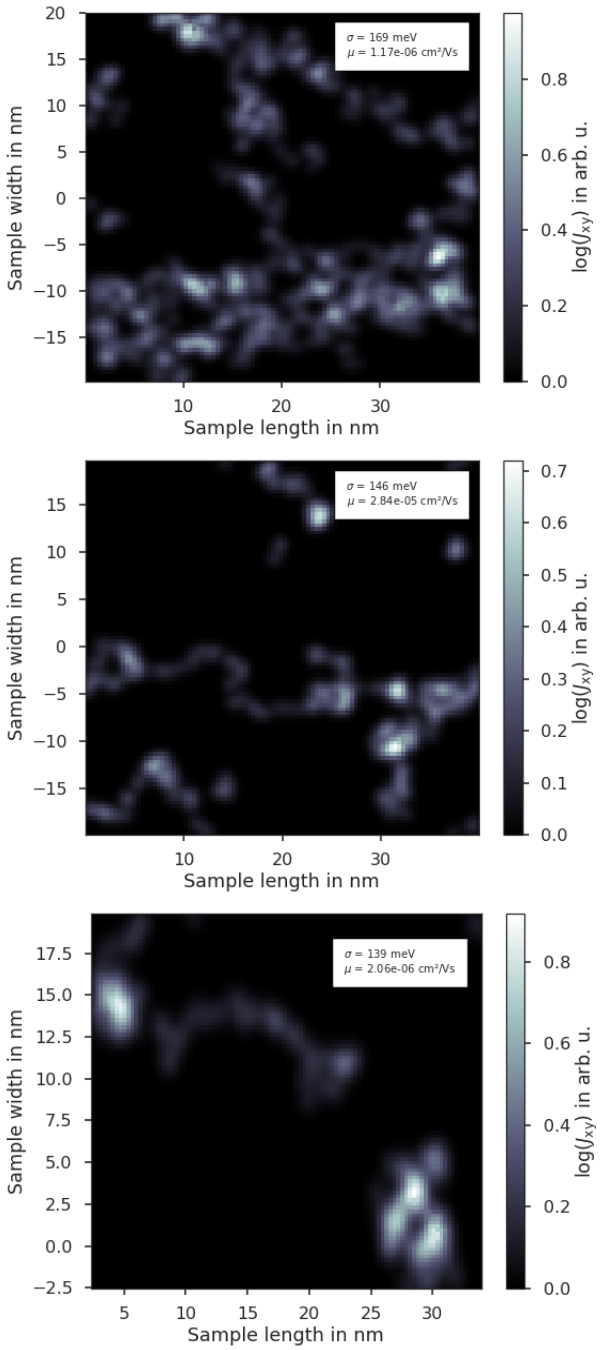

Figure 5: Projection of net bond-hops per molecule on the x-y plane (field applied in x-direction), for TPBi with 0% (top panel), 25% (middle panel) and 70% (bottom panel) passivator concentration. Insets show the disorder of the LUMO energies and electron mobilities. The middle panel exhibits the highest mobility of the shown system, although less paths are contributing to the transport.

Ultimately, we analyzed intermolecular hopping in the transport simulations at different passivator concentrations. Fig. 5 shows a projection of net-bond hops per molecule on the x-y plane, where x is the transport direction. We observe a qualitative thinning of conduction paths with increasing passivator concentration, which we attribute to the reduced number of connections between TPBI molecules in the diluted samples. Although there appear to be less conduction paths in the system with 25% passivator concentration compared to the system without passivator, mobility is increased due to decreased disorder in the conduction path (analogous to traffic on many gravel roads vs one highway).

4. Conclusion

In OE applications a high degree of control of material parameters such as transport levels and charge carrier mobilities is required to build balanced devices. In this work we used computer simulations to tune mobility in ETLs by adding transport inert guest molecules with low polarity. By systematically varying individual material parameters, which are not accessible individually in experiment, we disentangled the impact of two microscopic mechanisms with opposing effects on electron mobility. We were able to find optimal guest concentrations for a given mobility target by balancing the disorder and connectivity reduction with increased passivator concentrations. Tuning the passivator concentration allows for targeted design of OLED layers.

As the ratio of disorder and connectivity reduction for any passivator concentration are material specific, the experimental screening for both good passivator molecules and their optimal concentrations would be overly time-consuming and costly in the design of novel materials. This study therefore demonstrates how parameter-free computer simulations from first principles can aid experimental R&D of OLED materials and devices by efficient screening of materials and device parameters. Furthermore, by connecting fundamental chemistry and device design, these multiscale simulations provide fundamental understanding of how entangled microscopic properties impact device performance. This approach therefore enables material and device designers to investigate the impact of specific molecular properties on layer and device performance and to derive structure-function relationships between chemical structure and the performance in the device, leading to design rules for organic materials and devices.

5. Acknowledgements

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