



Multi-scale calculation of the electric properties of organic-based devices from the molecular structure



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ABSTRACT

A method is proposed to calculate the electric properties of organic-based devices from the molecular structure. The charge transfer rate is obtained using non-adiabatic molecular dynamics. The organic film in the device is modeled using the snapshots from the dynamic trajectory of the simulated molecular system. Kinetic Monte Carlo simulations are carried out to calculate the current characteristics. A widely used hole-transporting material, N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) is studied as an application of this method, and the properties of its hole-only device are investigated. The calculated current densities and dependence on the applied voltage without an injection barrier are close to those obtained by the Mott-Gurney equation. The results with injection barriers are also in good agreement with experiment. This method can be used to aid the design of molecules and guide the optimization of devices.

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1. Introduction

Understanding the relationship between the molecular structure and device characteristics is important to material design and device optimizations. For organic semiconductors, the charge transport properties, which are crucial to the performance of devices [1–4], are affected by factors such as the molecular structure, molecular packing, temperature, the carrier density and the electric field [5–10]. It has been shown that the last two factors are highly non-uniform inside organic electronic devices [11–16], which means that the charge carrier transport needs to be investigated at the device level in order to reveal the physics inside these devices. In contrast to the band transport in inorganic semiconductors, the charge transport in organic ones is often described by a hopping process [5,6]. For this reason, analytical methods derived from the band theories may be inappropriate to investigate the physics inside organic electronic devices. On the other hand, the kinetic

Monte Carlo (KMC) method has gained much popularity in the simulation of these devices over the past few years [17–20]. However, in these works, the molecular structure and packing have often been neglected when modeling the device. Instead, they are usually represented by lattice sites, where molecules are assumed to align perfectly and have isotropic charge transport properties [16–20]. The lack of connection between the results and the molecular structure in these device models means that they are ineffective in aiding material design.

Incorporation of molecular packing in device models is not an easy task. In organic light-emitting diodes (OLEDs), the thickness of organic layers can be several tens or hundreds of nanometers [21–23]. For organic field-effect transistors (OFETs), the channel length is usually larger than one micron [24–26]. Directly modeling systems of these sizes for device simulations is still difficult [27]. Although it has been shown that the properties of organic semiconductors can be considered in some degree in device models by using parameters that are obtained by fitting experimental or simulation data [20,28], the information of molecular packing is largely lost when modeling the device, the influence of which on the calculation results is not understood.

For organic semiconductors, the energetic disorder has a great influence on the charge transport process [5,6]. Recently, Tummala et al. [29] have studied several organic systems, and found that the degree of the dynamic disorder is close or comparable to that of the

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static disorder. This suggests that the time snaps along one dynamics trajectory of one organic system may be used to construct a larger one to represent an amorphous system. The idea is similar to the concept of “time average” in molecular dynamics (MD) simulations in respect to that of “ensemble average”. In fact, the amorphous structures of P3HT and ADN have been modeled using this approach, and the charge transfer rates were obtained using non-adiabatic molecular dynamics (NAMD) simulations [30,31]. The calculated mobilities in these works are close to those from the time-of-flight (TOF) measurement [30–33].

Following these works, here, a method is proposed to calculate the electric properties of organic electronic devices from the molecular structure. The current densities of the hole-only device of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB), a widely used hole-transporting material [34], is calculated as an illustration. MD and Born-Oppenheimer molecular dynamics (BOMD) are used to simulate the amorphous packing structure. The charge transfer rate is calculated from NAMD simulations. The obtained molecular packing structure and the charge transfer rate are then used to construct the hole-only device. The current characteristics are calculated through KMC simulations. The current densities of the hole-only device with a small or no injection barrier is found close to those obtained by the Mott-Gurney equation. The results in the presence of an injection barrier are also found reasonable by comparing with the data of a hole-only device of NPB from experiment.

2. Computational methods

Here, we use a multi-scale approach to calculate the electric properties of an organic electronic device. We'll use a hole-only device as an illustration. The simulation is comprised of three steps. First, an amorphous system is modeled using molecular dynamics simulations. Then NAMD simulation is used to obtain the charge transfer rate. Finally, the hole-only device is constructed and the current densities are calculated. We denote the systems in the above three steps as level-1, level-2 and level-3, respectively. The flowchart of the calculation is shown in Fig. 1.

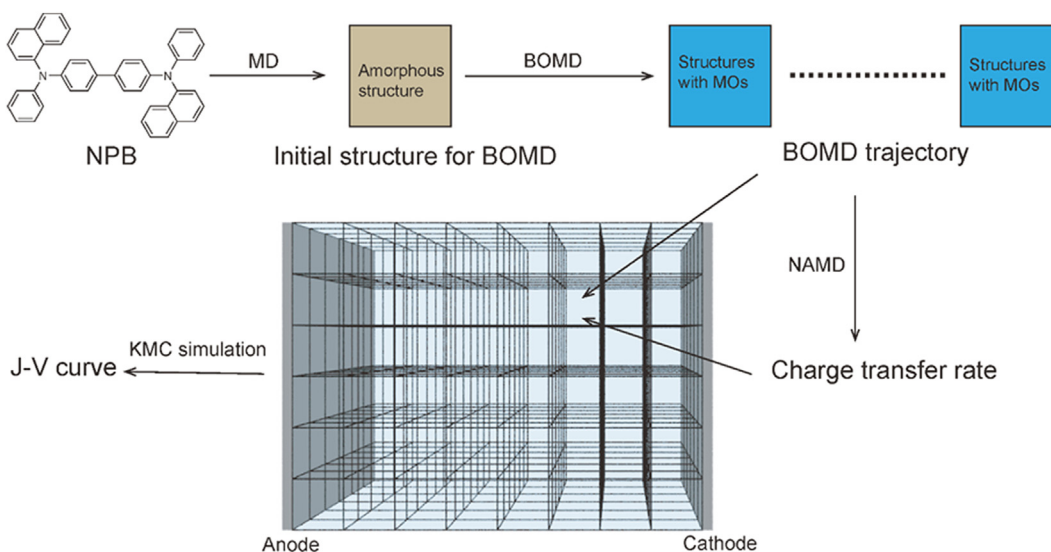


Fig. 1. Flowchart of the calculation of the electric properties of an organic electronic device.

2.1. Generation of the amorphous structure

The amorphous structure will be generated by allowing the molecular structure to relax under NPT conditions from a loose configuration. The initial molecular packing structure is generated using the Packmol package [35]. Eight NPB molecules (624 atoms) are randomly packed inside a cube with a size of $2.7 \text{ nm} \times 2.7 \text{ nm} \times 2.7 \text{ nm}$. The corresponding density is 0.40 g/cm^3 .

The general AMBER force field (GAFF) [36] is used for energy minimization and molecular dynamics. The force field parameters are generated by the Antechamber package from Amber tools 12 [37]. Atomic partial charges are determined by restrained electrostatic potential (RESP) fitting scheme [38] at the b3lyp/6-31g(d) level. The DFT calculations are performed using Gaussian 03 package [39]. Validation of the force field parameters for the studied material can be found in Figs. S1–S3.

Energy minimization of the system is performed by the GRO-MACS 4.6 package [40]. A molecular dynamics simulation is then carried out for 500 ps under NVT conditions. The time step and the temperature are 1 fs and 298 K, respectively. Following this, an NPT simulation is performed for 1000 ps. The density of the system rises fast within the first 30 ps, then slowly reaches 1.13 g/cm^3 , lower than that of the crystal structure of 1.22 g/cm^3 [41]. Finally, an NVT simulation is carried out for 500 ps. The change in density and cell vectors during the MD simulations can be found in Fig. S4.

2.2. Calculation of the charge transfer rate

The CPMD package [42] is used to perform Born-Oppenheimer molecular dynamics. Vanderbilt ultrasoft pseudopotentials [43] and PBE functional [44] are used. The energy cutoff of the plane-wave basis is 30 Rydberg, and the calculation is carried out at the gamma point only (at the center of the Brillouin zone).

Geometry optimization is first applied on the final structures from MD simulations. The system size is $1.9 \text{ nm} \times 1.9 \text{ nm} \times 1.9 \text{ nm}$. A BOMD simulation is then carried out for 3 ps under NVT conditions to allow the structure to further relax. The time step is 1 fs. It has been verified that for the studied system, reducing the time step to 0.5 fs doesn't result in a significant difference in the molecular structure during a trajectory of 1 ps, as is shown in Fig. S5. Berendsen temperature control is used, and the time constant is

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