



## Estimation of charge carrier mobility in amorphous organic materials using percolation corrected random-walk model



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### ABSTRACT

A computationally simple yet predictive multi-scale simulation scheme is introduced to estimate zero-field charge mobilities for amorphous OSC materials. A percolating charge model is utilized to describe inhomogeneity of hopping trajectories of carriers in amorphous media. The prediction scheme is composed of the following stages: quantum chemical calculation of Marcus inner sphere reorganization energies, molecular dynamics simulations of the amorphous condensed phase bulk structure, automated quantum chemical calculations of the electronic coupling for dimer pairs in the amorphous solid, and calculation of the Marcus theory charge hopping rates and an estimated bulk mobility using the Einstein relation, corrected for the inhomogeneous hopping network of the solid. Comparisons with independent experimental measurements of hole mobility for ten OSC compounds show that this approach gives good correlation between predictions and measurements suitable for ranking systems, and useful quantitative agreement. This low-cost model with minimal complexity is well-suited for incorporation into a virtual materials discovery framework for advanced OSC solutions.

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Organic semiconductor materials (OSCs) are under widespread development for application in current and next-generation technologies including organic light-emitting diodes (OLED), organic photovoltaics (OPV) and organic thin-film transistors (OTFT). For OLED, OPV and OTFT, charge transport of electrons and holes in multiple OSC layers is important to determine device properties. As such, availability of reliable prediction schemes for energetic properties of OSCs as well as their charge transport characteristics play vital roles in reducing interfacial loss in devices based on layered OSCs and maximizing their real-life performance [1]. The organic materials comprising the active layers in these devices are selected or designed according to specific molecular and condensed phase properties. Previously, the development of new OSC materials largely depended on chemical intuition, combined with

tremendous experimental effort toward synthesis, purification, characterization and testing of a limited number of candidate systems, with variable success. Atomic-scale simulation can provide an efficient and low-cost approach to systematically explore the chemical design space and advise experimental efforts for OSC materials [2–4].

Quantum chemical simulation can calculate intrinsic properties that are critical for organic optoelectronic applications much faster, at lower cost than experimental measurements, with predictive reliability. These properties include redox potentials, HOMO and LUMO energy levels, Marcus theory inner sphere reorganization energies ( $\lambda$ ) and singlet and triplet excited state energies. This predictive capability has been harnessed through the automation of intrinsic OSC property workflows, enabling the analysis of large libraries of candidate materials. In order to exploit favorable intrinsic properties, the OSC material must also exhibit good electronic coupling ( $H_{ab}$ ) and charge mobility in the condensed phase. The *in silico* prediction of OSC charge mobilities is complex and poses significant challenges. Estimation of charge transport rate

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constants for weakly interacting disordered molecular solids can be described by Marcus theory [5], which enables the deduction of transport rates between molecules once their relative configuration is determined. Charge mobility calculations involve structure and property predictions at multiple length scales and time, in going from individual molecules, to donor-acceptor pairs, to a realistic condensed phase structure [6]. Percolating paths of charge carriers through molecular solids can be discussed by analyzing shapes and distributions of HOMO and LUMO over nearest neighboring molecular pairs [7,8]. There is also considerable progress being made in developing full physics toolkits for simulating OSC carrier mobility [9]. Yet there is pressing need for models that can rank and evaluate candidate OSC materials quickly and accurately to the level where it can be used for routine analysis in materials discovery framework.

In this work, a simple scheme for estimating charge mobility in weakly interacting amorphous OSCs is demonstrated which strives toward minimal complexity while simultaneously providing meaningful predictive capability. The treatment is based on quantum chemical calculations of the Marcus theory donor-acceptor hopping rates for dimers extracted from a force-field molecular dynamics (MD) derived amorphous condensed phase structure. This leads to an isotropic random-walk charge mobility, which is then tempered using a factor from a percolation model to directly reflect the inhomogeneity of the conduction network in an amorphous solid. The method is validated through the calculation of hole mobilities for ten well-known hole transport OSC systems (structures shown in Fig. 1): mCP (1,3-bis(N-carbazolyl) benzene), NPB (N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine), CzC (9-(4-tert-butylphenyl)-3,6-ditryl-9H-carbazole), 2TNATA (4,4',4''-tris[2-naphthyl (phenyl) amino] triphenylamine), TCTA (Tris(4-carbazoyl-9-ylphenyl)amine), TPD (N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine), spiro-TPD (N,N'-bis(3-methylphenyl)-N,N'-diphenyl-9,9-spirobifluorene-2,7-diamine), o-BPD (N,N'-di(biphenyl-2-yl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine), m-BPD (N,N'-di(biphenyl-3-yl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine), and p-BPD (N,N'-di(biphenyl-4-yl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine). Comparison with experiment shows the simple method described here gives discrimination and suitable quantitative agreement; which should be very useful for providing simple mobility estimates for ranking and evaluating synthetic targets in the development of OSC materials; complementing more advanced and costly charge mobility treatments.

The foundation of this work is the donor-acceptor dimer charge hopping rate described by Marcus theory [5]. Within a single component phase, the charge hopping rate between neighboring molecules in the solid is described by the following equation:

$$\kappa = \frac{2\pi}{\hbar} \left( \frac{H_{ab}^2}{\sqrt{4\pi\lambda k_B T}} \right) \exp \left[ -\frac{(\Delta G + \lambda)^2}{\sqrt{4\pi\lambda k_B T}} \right] \quad (1)$$

Here,  $\Delta G$  is the free energy difference for charge transfer,  $\lambda$  is the Marcus reorganization energy, and  $H_{ab}$  corresponds to the intermolecular electronic coupling.

Fig. 2. presents the steps in the mobility estimation calculation presented in this work. It consists of four stages: (1) quantum mechanical calculation of inner-sphere reorganization energy, (2) classical molecular dynamics (MD) simulation of the bulk amorphous structure, (3) quantum mechanical calculation of individual dimer electronic coupling and charge hopping rates, and (4) estimation of the amorphous OSC bulk mobility based on a percolation-theory corrected diffusion model.

All of the quantum chemical calculations and classical MD simulations in this work were carried out using the Schrödinger Materials Science Suite [10]. Density functional theory (DFT)

calculations of the Marcus theory reorganization energies ( $\lambda$ ) and electronic coupling constants ( $H_{ab}$ ) were performed using Jaguar (Version 8.42) [11]. MD simulations were carried out using the Desmond MD [12] program (Version 3.8).

As presented in the equation above, within Marcus theory, charge transfer in a molecular homodimer has an exponential dependence on the reorganization energy. For charge transport in organic solids, the intramolecular reorganization energy is the dominant contribution, over medium polarization effects (inner- and outer-sphere reorganization energy, respectively). For the hole-transporters considered here, hole reorganization energies are calculated as the sum of the difference between the vertical and adiabatic ionization potential for a neutral molecule and the difference between the vertical and adiabatic electron affinity of the oxidized species:

$$\lambda_{h,calc} = (E_0^1 - E_1^1) + (E_1^0 - E_0^0) \quad (2)$$

where  $E_b^a$  denotes the DFT energy for the system with charge  $a$  at the minimized geometry for the system with charge  $b$ . Table 1 shows the inner sphere hole reorganization energy ( $\lambda_{h,calc}$ ) for the OSC systems considered here, calculated using the hybrid B3LYP density functional [13] along with MIDI! double- $\zeta$  polarized basis set [14].

Although local charge transfer rates computed for a few dimer pairs may suffice to analyze the charge transport of organic crystals [15], estimating charge mobility in amorphous OSC materials requires a physically reliable model of the disordered film structure. Molecular dynamics (MD) simulations based on empirical force-fields can be used to obtain a well-equilibrated amorphous structure of organic solids allowing extensive sampling of local dimer charge hopping rates throughout the system.

Relaxing models of high- $T_g$  organics through MD simulation require simulation times of 30–100 ns to reach thermodynamic equilibrium. In this work, we increased the speed of MD simulations by running the trajectories on general-purpose graphics processing units (GPU). To get the lowest energy conformations of each molecule, we used conformational search algorithm provided by Schrödinger Materials Science Suite [10] along with OPLS2005 force field [16,17] to collect the 10 lowest-energy conformations of each molecule. Then the simulation box for MD simulations was built by populating the box with Boltzmann distribution of conformers at 298.15 K. Molecules were initially placed in cubic grid with random rotation with low density applying van der Waals scale factor of 0.8 or larger for non-bonding atoms. Once the simulation boxes were built, MD simulations were carried out using the OPLS2005 force field to describe the interatomic interactions. Equilibrium structures for the amorphous bulk OSC materials were obtained by first minimizing the periodic 64-molecule box followed by running an NVT-ensemble MS simulation for 6 ns followed by a NPT simulation for 60 ns to bring it to an equilibrated density. The initial starting 64-molecule configuration was assembled from the lowest energy molecular conformations. Trajectories from the last 10 ns were collected to confirm convergence and estimate the final mass density. The standard deviation for density was less than 1% of the final averaged density for all compounds. The final amorphous bulk structure for 2TNATA is shown in Fig. 3 as an example. The average density for each of the hole-transport test systems is reported in Table 1. Predicted densities of the all compounds fall near the range of measured thin film densities for most common OSC materials (1.05–1.3 g/cm<sup>3</sup>) [18].

The MD-equilibrated structure is used as input for the charge coupling calculations. A critical parameter in the Marcus hopping rate expression is the electron coupling between donor and

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