

Modeling Charge Transport in Organic Photovoltaic Materials

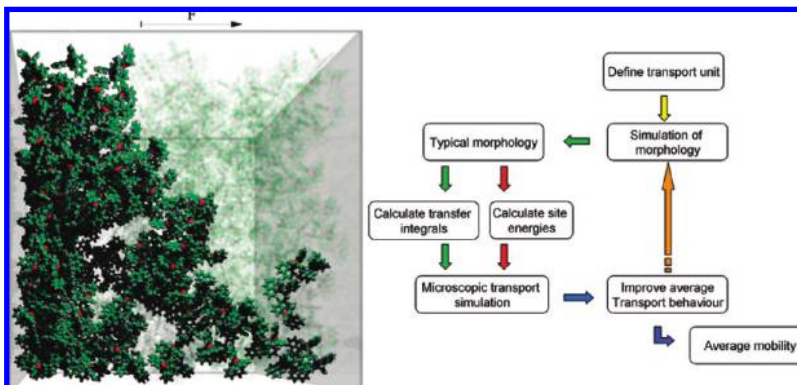
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RECEIVED ON JULY 30, 2009

CON SPECTUS

The performance of an organic photovoltaic cell depends critically on the mobility of charge carriers within the constituent molecular semiconductor materials. However, a complex combination of phenomena that span a range of length and time scales control charge transport in disordered organic semiconductors. As a result, it is difficult to rationalize charge transport properties in terms of material parameters.



Until now, efforts to improve charge mobilities in molecular semiconductors have proceeded largely by trial and error rather than through systematic design. However, recent developments have enabled the first predictive simulation studies of charge transport in disordered organic semiconductors.

This Account describes a set of computational methods, specifically molecular modeling methods, to simulate molecular packing, quantum chemical calculations of charge transfer rates, and Monte Carlo simulations of charge transport. Using case studies, we show how this combination of methods can reproduce experimental mobilities with few or no fitting parameters. Although currently applied to material systems of high symmetry or well-defined structure, further developments of this approach could address more complex systems such as anisotropic or multicomponent solids and conjugated polymers.

Even with an approximate treatment of packing disorder, these computational methods simulate experimental mobilities within an order of magnitude at high electric fields. We can both reproduce the relative values of electron and hole mobility in a conjugated small molecule and rationalize those values based on the symmetry of frontier orbitals. Using fully atomistic molecular dynamics simulations of molecular packing, we can quantitatively replicate vertical charge transport along stacks of discotic liquid crystals which vary only in the structure of their side chains. We can reproduce the trends in mobility with molecular weight for self-organizing polymers using a cheap, coarse-grained structural simulation method. Finally, we quantitatively reproduce the field-effect mobility in disordered C60 films. On the basis of these results, we conclude that all of the necessary building blocks are in place for the predictive simulation of charge transport in macromolecular electronic materials and that such methods can be used as a tool toward the future rational design of functional organic electronic materials.

Introduction

A key consideration in the application of molecular semiconductor materials to optoelectronic

applications such as photovoltaic energy conversion is their low charge carrier mobilities. Even in the best cases, charge mobilities of organic semi-

conductors are, at $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, several orders of magnitude lower than those of inorganic photovoltaic materials ($\sim 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The low mobilities arise from the localization of electronic states on individual molecules or segments of molecules. Relatively weak intermolecular interactions mean that charge transport is best described by hopping transfer rather than band transport.

Low charge mobilities in molecular semiconductors influence organic photovoltaic device performance in several ways: (i) Low mobilities allow bimolecular charge recombination to compete with charge collection, reducing photocurrent. This limits the thickness of the photoactive layer. (ii) High resistivity of the semiconductor layers decreases the device fill factor. (iii) The local charge mobility (influenced by the order in molecular packing) appears to influence the efficiency of charge pair separation following exciton dissociation.

At the present time, mobility is often treated as a constant parameter as in classical semiconductor device physics treatments (e.g. ref 1). These treatments have the advantage that several modeling tools are available, and have been used to fit experimental results with reasonable success. However, this classical semiconductor approach fails to explain a number of observations, such as the large variation in the short circuit current,² the high order of charge recombination,³ the non-ideal diode behavior of devices in the dark, and the consistently low fill factors of devices under illumination. Some approaches have incorporated a charge density dependent mobility, which goes some way to explain some of these phenomena and can be explained in terms of disorder.⁴ However, such approaches still leave no scope to deal with inhomogeneity of molecular packing.

While the prediction of charge carrier mobility from the chemical and physical structure of the molecular material is desirable, this goal is complicated by the following factors: (i) disorder in the conformation, conjugation length, separation, and relative orientation of the charge transporting units;^{5,6} (ii) the multicomponent nature of most molecular photovoltaic materials;⁷ and (iii) inhomogeneity in molecular packing.⁸ This means that a knowledge of chemical structure alone is insufficient to indicate charge mobility.

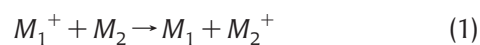
In this Account, we present a framework for the simulation of charge carrier mobility in molecular solids as a function of their chemical and physical structure, which combines several levels of simulation on different time and length scales. We first define certain fundamental principles of charge transport in molecular semiconductors and present methods to model the processes of molecular packing, intermolecular charge transfer, and charge transport. We then demonstrate

how combinations of these methods can explain the relationship between chemical structure and charge transport in the case of several important molecular semiconductors. Finally, we identify the main objectives for optimizing and modeling charge transport in organic photovoltaic materials. The ultimate objective of this work is to help build tools for the rational design of organic photovoltaic materials and devices.

Fundamentals

To simulate charge transport we need to create a simulation volume containing sites where charges can be localized, to calculate the rates of charge transfer between any pair of sites under given conditions (temperature, applied electric bias), and to simulate the motion of charges in a way that best mimics the experiment. Clearly, this involves a number of different types of calculation and different methodologies.

In this Account, we restrict attention to systems where intermolecular charge transfer can be treated as a hopping process, that is, a transition from the charge being localized entirely on one molecule or segment (M_1) to its being localized entirely on the other (M_2). The process is a charge transfer reaction of the sort



In the diabatic approximation, the electronic Hamiltonian of such a two level system, neglecting external environment, is

$$H = \begin{pmatrix} E_1 & J_{12} \\ J_{12}^* & E_2 \end{pmatrix} \quad (2)$$

where E_i represent the energy of each diabatic state and J_{12} is the electronic transfer integral between the states. The rate of incoherent electron tunneling from one state to another is determined by the square of this matrix element. In this work, we use semiclassical nonadiabatic Marcus theory, discussed below, to calculate the transfer rates. The motion of a single charge through a molecular assembly is modeled as several sequential uncorrelated charge transfer events of this sort; the motion of multiple charges is represented by several simultaneous sequences of such transitions.

A key characteristic of charge transport in disordered molecular solids is the wide range of intermolecular charge transfer rates (see Figure 4 below for an example), which leads to the phenomenon of dispersive transport.⁹ In extreme cases, the charge transfer time for the slowest events in the assembly exceed the time scale of the experiment. This effect means that different methods which would return the same measure of charge mobility in an ideal semiconductor can return very different measures in a disordered organic semiconductor.

Methods that have been used to measure charge mobility in molecular semiconductors include direct probes such as time-of-flight (ToF); probes of injected current such as space-charge-limited dark injection, charge extraction under linearly increasing voltage (CELIV), steady state current density–voltage response, and admittance spectroscopy, all of which probe injection efficiency as well as mobility and are generally probes of nonuniform electric field distributions; field effect transistor (FET) measurements, which probe the mobility at high charge carrier densities; and probes of the most mobile fraction of charges such as time-resolved microwave conductivity (TRMC). In addition, local mobility can be inferred from the dynamics of transport limited processes such as charge recombination.⁴ This rich variety of methods provides a sound basis for testing models of charge transport.

Previous Modeling Approaches. Previously, several approaches have been proposed to simulate hopping transport in disordered molecular media. Most important among these is the Gaussian disorder model (GDM).¹⁰ The GDM encompasses the description of the charge transfer reaction (eq 1) for individual charge transfer events, and sample configurational and energetic disorder from characteristic Gaussian distributions. However, although successful at reproducing the general features of observed charge transport phenomena, the GDM offers no power to predict transport behavior from knowledge of the chemical and physical structure.

Variants of the GDM sought to include known physical influences on the site energy disorder such as the charge–dipole interaction in doped molecular solids,¹¹ quadrupolar interactions,¹² and local ordering. A first attempt to use quantum chemical methods to calculate the effect of chemical structure on the hopping rate distributions¹³ nicely demonstrated both the chemical origin of dispersion in hopping rates and the importance of torsional interactions in molecular solids. In the studies described herein, we extend the approach of those authors by including simulations of molecular packing.

Multiscale Models. In any experiment, a range of dynamic scales is involved in the transport process: the rate of intermolecular charge transfer (ps–ns), the rate of molecular vibration (fs–ps) and of conformational change (ps–ns or longer), and the time scales for charge transit across a device (ns– μ s or ms). In addition, very different length scales are involved ranging from intramolecular distances (10^{-10} m) to device thicknesses (10^{-7} – 10^{-5} m). The wide range of time and length scales means that no single method can adequately address the problem. Instead, a combination of methods each addressing processes on different time scales must be used.

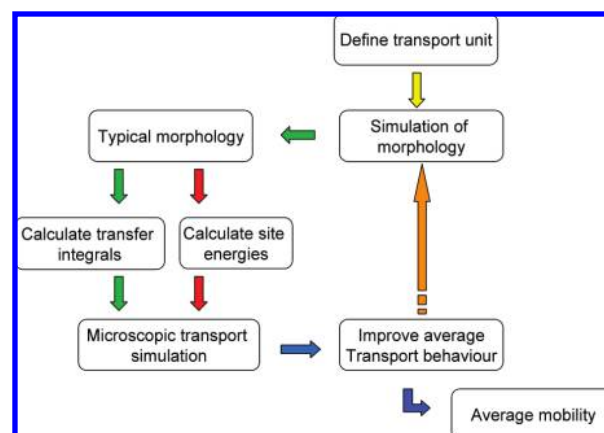


FIGURE 1. Generic flowchart for the multiscale simulation of charge transport in a (disordered) molecular assembly.

In this work, we use a combination of three methodologies: (1) molecular modeling methods to simulate the position and orientation of the transport units; (2) quantum chemical calculations for the intermolecular charge transfer rates; and (3) Monte Carlo simulation of a charge mobility measurement, to simulate the experimental data from which mobility is estimated. The generic approach is illustrated in Figure 1.

Simulation of Molecular Packing. Atomistic molecular dynamics (MD) refers to methodologies that simulate the motion of atoms within each molecule in response to the electrostatic, electronic, inductive, and dispersive forces due to the other atoms and molecules in the ensemble. Atoms are repeatedly moved in response to these forces until the statistical–mechanical properties of the ensemble reach a dynamic equilibrium. Representative configurations or “snapshots” of the molecular assembly may then be sampled and used as the matrix for a charge transport simulation. In the case of assemblies of “small molecules” where the charged state is delocalized over the entire molecule, the position and orientation of the conjugated molecular core should be recorded. In the case of conjugated polymers, where a polaron occupies only a fraction of the molecular chain, some definition of conjugation length must be applied to split the chain into segments, each of which could accommodate a charged state. For example, a certain degree of torsion between monomers could serve to delineate conjugated segments.¹⁴ If changes in molecular configuration and conformation are slow compared to the rate of charge transport through the assembly, static representations of the configuration of charge transport sites can be used as the matrix for transport simulations. If not, then the molecular configurations should be updated according to the evolution of the MD simulation during the course of the transport simulation.

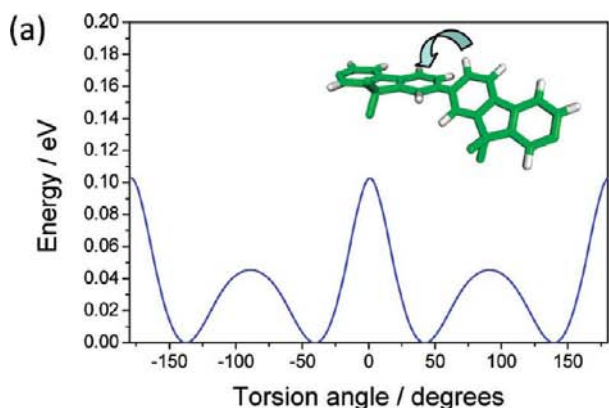


FIGURE 2. (a) Torsional potential energy for a dimer of fluorene in vacuum. (b) Frequency plots of the intermonomer torsional angles adopted by neighboring monomers in solvated octamers of dimethylfluorene (red) and dioctylfluorene (black), obtained from 500 ps MD simulation runs. At $\theta = 0$, the bridging carbon atoms are on the same side.

Fully atomistic MD is computationally intensive and in practice is limited to relatively small or simple systems for short time scales on the order of nanoseconds. Various approximations can be made to reduce computational effort and enlarge the size of assemblies addressed, for example, a united atom approach or coarse graining.¹⁵

Until now, MD has not been widely used for organic semiconductors, and existing force fields seldom describe π -conjugated systems correctly: in general, the delocalized electron density tends to planarize the core. To supplement extant force fields for our materials, relaxed potential energy scans are carried out around a particular degree of freedom of a minimal representative structure to yield an improved potential energy function for that mode. In many semiconducting polymers, the torsional degree of freedom influences conformation most strongly and therefore needs to be accurately modeled.

Both intramolecular conformation and intermolecular packing are strongly influenced by the side chains, which otherwise have negligible electronic function. An example is shown in Figure 2. The potential for intermonomer torsion in a dimer of fluorene calculated using AM1 with form checked and barrier heights calculated by HF//MP2/cc-pvdz (Figure 2a) shows four minima, separated by (relatively low) potential barriers of ~ 0.1 eV. The side chain free dimer shows no clear preference for the bridging carbon atoms to lie on the same or opposite sides. However, when this torsional potential is used within a MD simulation of chloroform solvated fluorene octamers with long (octyl) side chains, a clear preference is observed for side chains to lie on the same side of the back-

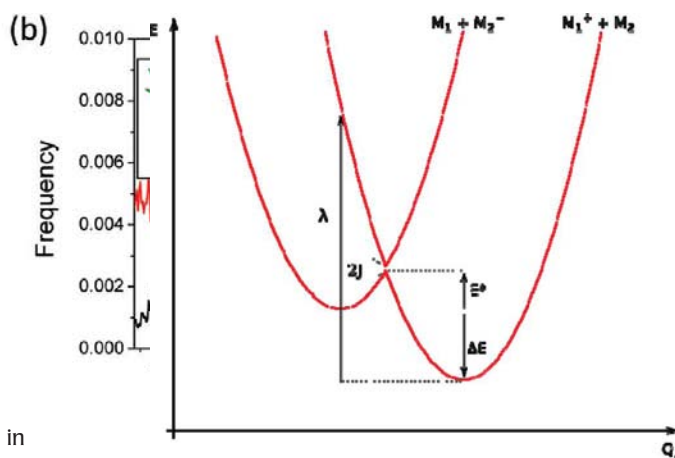


FIGURE 3. Potential energy surfaces of the reactants and products of the charge transfer reaction as a function of a single reaction coordinate Q_r . The Marcus rate represents the product of the probability of reaching the intersection and the rate of reaction once there.

bone. In contrast, the octamer with short (methyl) side chains adopts all four torsional minima equally.

Accurate simulation of molecular packing structures with MD requires reliable structural information both for validation of results and for the definition of suitable starting configurations. In the case of ordered systems, structural information can facilitate the use of fairly crude, but potentially informative, coarse grained approaches. Such an approach is described below.

Calculation of Charge Transfer Rates. The mechanism of charge transfer between molecules depends upon the exact form of the charge transfer Hamiltonian (eq 2). In the limit where the electronic states on different molecules are very strongly coupled, charge transport is bandlike.¹⁶ At the opposite limit, charge transfer is described by a hopping mechanism. All the systems discussed herein are treated in the hopping regime. In this limit, the hop rate can be calculated with semiclassical nonadiabatic Marcus theory:¹⁷

$$\Gamma = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta E + \lambda)^2}{4\lambda k_B T}\right) \quad (3)$$

where k_B is Boltzmann's constant, T is the temperature, λ is the reorganization energy, and ΔE is the change in energy between the initial and final state of the charge transfer reaction, $\Delta E = E_2 - E_1$. Although the difference in free energies should be considered, it is common to neglect entropic effects in molecular solids.¹⁸ Figure 3 depicts J , ΔE , and λ on a potential energy surface plot.

For the hopping approximation to be valid, the system needs to be strongly localized in one of the two states in Figure 3, that is, $J \ll \lambda$. It is also assumed that J is constant with

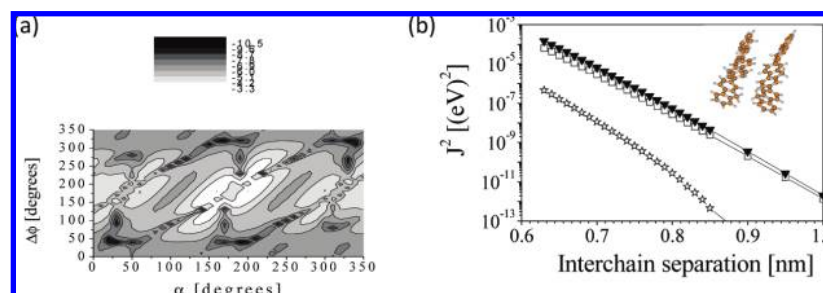


FIGURE 4. (a) Logarithm of $|J|^2$ for two parallel trimers of fluorene separated by 0.65 nm as a function of the azimuthal angle (α) and torsion angle (ϕ) defining the relative orientation of the backbones. Variations in orientation affect $|J|^2$ by more than 7 orders of magnitude. (b) $|J|^2$ as a function of separation of the trimers, for some different relative orientations. Adapted with permission from ref 27. Copyright 2007 American Chemical Society.

respect to variation in Q_r ¹⁹ and that the vibrational modes of the reactants and products can be treated classically.²⁰

The parameters controlling the Marcus rate, λ , J , and ΔE can each be calculated with quantum chemical methods. A comprehensive review can be found in refs 16 and 21.

The reorganization energy λ is the sum of contributions from the energetic relaxation of the molecules M_1 and M_2 , λ_{inner} , and from the relaxation of the surrounding medium, λ_{outer} . λ_{inner} can be estimated from calculations on individual gas-phase molecules.²² λ_{outer} is commonly neglected because it is difficult to quantify the relevant dielectric response on the time scale of charge transport. However, it has been shown to be small in certain cases.²³

Whereas λ_{inner} only has to be calculated once for a given material system, ΔE and J have to be calculated for every pair of neighboring molecules and normally make the largest computational demand of the simulation. J is most accurately calculated by projecting the individual orbitals of M_1 and M_2 onto the orbitals of the pair $M_1 + M_2$.²⁴ In cases where J is large, more efficient, approximate methods can be used.²⁵ Figure 4 illustrates the large variation in J that can result from variations in molecular separation and orientation.

The energetic driving force ΔE contains contributions from the nuclear relaxation and electronic polarization of both M_1 and M_2 , and the surrounding molecules.²³ The former can be approximated from the calculations on the gas phase molecules M_1 and M_2 . A reasonable approximation to the contribution to ΔE from electrostatic interactions between the molecules in the initial and final state can be made using a distributed multipolar analysis of the calculated charge densities on each molecule.²⁶ Rigorous treatment of polarization effects is computationally costly, and in the examples given below it is neglected. The final contribution to ΔE is from the effect of any applied electric fields.

Simulation of Charge Transport. Given the positions of molecules, and the rates of charge transfer between them, the

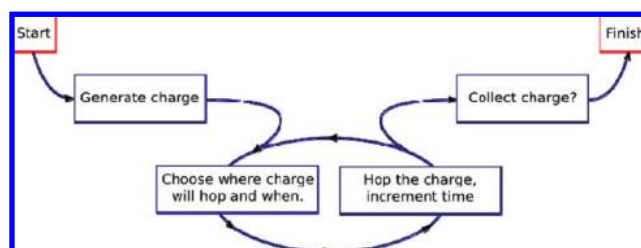


FIGURE 5. Schematic of the kinetic Monte Carlo simulation of transport for a single charge.

motion of charges through a solid can be simulated. One approach is to solve a master equation directly, but, to make the calculation tractable, low charge densities and steady-state must be assumed.¹³ A more flexible approach is to use a kinetic Monte Carlo (KMC) algorithm.

A schematic of the KMC algorithm is given in Figure 5 for the simulation of a single charge. A charge is generated according to the experiment being modeled: for example, to simulate a time-of-flight experiment, the charge is “photogenerated” in a generation layer near the top of the molecular film. The algorithm then iteratively chooses where the charge will hop and at what time, and executes the hop. At each step, the current is updated and a check is made as to whether the charge should be collected, for example, if it has reached the counter-electrode in the time-of-flight experiment. Current transients are averaged over many simulation runs for different realizations of the molecular assembly and different starting conditions. This KMC method relies on the use of an adaptive time step, which makes the simulation efficient for dispersive charge transport. Other advantages are the capability to treat high charge densities by limiting multiple occupation of charge transport sites and the capability to treat Coulomb interactions exactly. These methods have been integrated into the open-source code “ToFeT” [<http://tofet.org>] and used to simulate ToF and field-effect mobilities.

Case Studies of Charge Transport Simulations

We now present results of several simulation studies of charge transport in molecular semiconductors. The selected studies use different degrees of approximation in the simulation of the molecular packing, and together they demonstrate both the critical influence of molecular packing on charge transport and the complexities in its simulation.

Demonstration of Effects of Positional Disorder and Chemical Structure: AIQ3. The first study concerns the molecular semiconductor tris(8-hydroxyquinoline) aluminum (AIQ3), which is an electron transport material and green light emitter in organic light emitting diodes. AIQ3 is interesting because its measured electron mobility is around 2 orders of magnitude larger than its hole mobility (Figure 3b); most organic semiconductors show a higher hole mobility, attributed to the higher symmetry (fewer nodes) of the HOMO relative to the LUMO. In this study, we compare the simulated electron and hole time-of-flight (ToF) mobilities in an AIQ3 crystal with those in a disordered assembly of AIQ3 molecules. The disordered assembly is generated via a crude coarse grained method, where rigid copies of the relaxed AIQ3 molecule are moved within the potentials of their neighbors, as modeled with the Dreiding force field. While this method cannot be expected to reproduce the conformation of amorphous AIQ3 accurately, the comparison of crystalline and disordered cases allows us to make some simple observations about the effect of disorder on transport.

In each case, crystalline or disordered, J and ΔE between neighboring gas-phase molecules are calculated with density functional theory.²⁸ The resulting standard deviation in ΔE is 0.2 eV which is consistent with the large dipole moment of AIQ3 and similar to values predicted by the GDM.

The ToF experiment is simulated as described by ref 28, and the calculated electron and hole mobilities for a crystalline and disordered film of AIQ3 are shown in Figure 6a. In the case of the crystalline film, the mobility is high and sensitive to orientation of the electric field within the crystal. Disorder reduces the mobility by over 2 orders of magnitude and slightly increases the dependence on electric field. Although the field dependence of the mobility in the disordered sample is still small compared to both experiment (Figure 6a) and predictions by the GDM and its variants,^{10,11} this inaccuracy is not unexpected given the small size of our samples (~1100 molecules).

The lower mobility for the disordered film is readily rationalized in terms of the higher incidence of very low transfer

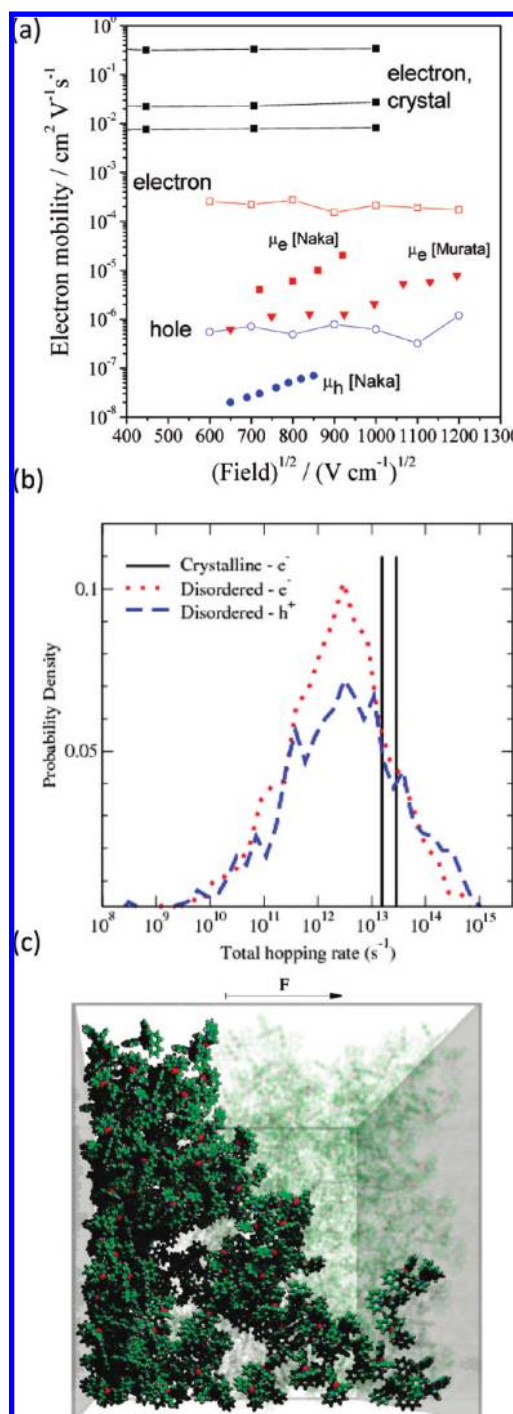


FIGURE 6. (a) Simulated time-of-flight mobilities (open symbols) for electrons (red) and holes (blue) in disordered films of AIQ3, in comparison with experimental data (filled symbols) and with simulated electron mobilities in the three principal crystal directions (black squares). (b) Frequency plot of electron (red) and hole (blue) transfer integrals for disordered film in comparison with that for electrons in the crystal (black). (c) Image of the disordered simulation volume, where all molecules that are visited during 2000 repeats of the simulation are colored green. Reprinted with permission from ref 28.

rates, illustrated in Figure 6b, and the resulting dispersive character of the charge transport. Analysis confirmed that the main

cause of the disorder in transfer rates was the variation in ΔE , resulting largely from the strong dipole moment of the AIQ3 molecule, rather than the variation in J . A high incidence of low charge transfer rates indicates a significant population of sites that either act as charge traps or are effectively inaccessible. The effect of this is illustrated in Figure 6c, where a large fraction of the film is shown to be inaccessible. Such “filamentary” transport could have significant implications for solar cell design.

A second key observation is that the simulated electron mobility exceeds the hole mobility, following experimental observation. This is unusual in conjugated molecular solids. However, for AIQ3, the LUMO is *more* symmetric than the HOMO, being delocalized over two lobes of the molecule rather than one. As a result, electrons experience *less* disorder than holes in both J and ΔE .

Although the method used to simulate molecular packing was relatively crude, this study demonstrates the potential impact on transport of packing disorder. In order to estimate the influence of disorder quantitatively, a more realistic representation of the disordered molecular assembly is required. In the next section, this is done using fully atomistic molecular dynamics.

Demonstration of Effects of Side Chains on Molecular Packing: HBC. This case study addresses the hole transport properties of a discotic liquid crystal, hexabenzocoronene (HBC). In the discotic mesophase, the molecules self-organize to form columns with strong π -orbital interactions within columns and insignificant interactions between columns. Such materials are of interest for devices such as solar cells, where improved vertical mobility is desired. Hole mobilities in HBC derivatives are high, such that they must be inferred from TRMC measurements, and show a clear dependence upon the side chain type.²⁹ Atomistic MD methods developed at Mainz were applied to simulate the structures formed by HBC molecules with different side chains.³⁰ Here, we show how the degree of order in intracolumnar packing, as modeled by MD, can explain the observed trend in TRMC mobility with side chain type.

HBC derivatives with three different types of side chain (Figure 7a, inset) were studied. Snapshots of molecular arrangements within stacks of each type of HBC in the discotic mesophase were taken from atomistic MD simulations.^{30,31} Simulation and structural measurements both showed that packing order is maximized for long aliphatic side chains while more bulky dodecylphenyl and branched hexyldecyl side chains lead to greater disorder in the intermolecular spacing and tilt angle (Figure 7a).

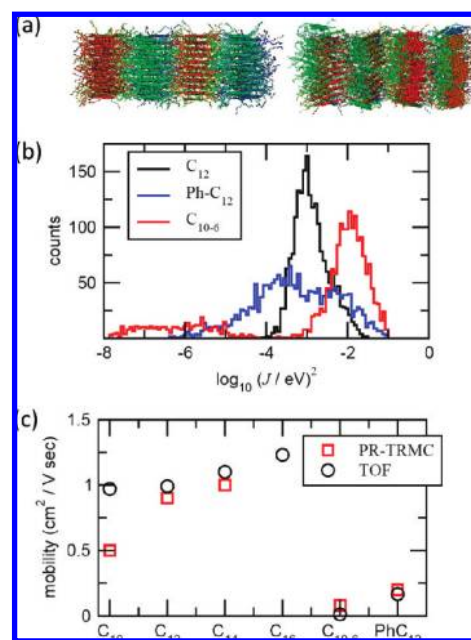


FIGURE 7. (a) Side view of snapshots of a MD simulation of stacks of HBC in the discotic mesophase, for the cases of unbranched dodecyl side chains (left) and branched hexyl-decyl side chains (right). (b) Frequency plot of $|J|^2$ for the dodecyl (black line), phenyl-dodecyl (blue line), and branched hexyl-decyl (red line) side chain. (c) Simulated ToF mobility (circles) at an applied field of 10^5 V cm^{-1} , in comparison with measured TRMC mobility (squares) for HBCs with different side chain. Reprinted with permission from ref 32.

The distribution of nearest-neighbor hole transfer integrals in MD generated stacks of each of the three types of molecule is shown in Figure 7b. The unbranched dodecyl side chain which leads to the highest degree of order in intermolecular separation and tilt also leads to the narrowest distribution of transfer integral, while the bulky and branched side chains lead to wider distributions with a significantly larger fraction of low transfer integrals. In this case, where transport is one-dimensional, low transfer integrals *must* trap charges and so are expected to affect the charge carrier mobility profoundly. Simulated ToF mobilities are shown in Figure 7c in comparison with the results of TRMC measurements.³² Since TRMC probes the motion of the fastest charge carriers, the good agreement between simulation and experiment indicates that the MD simulations represent relatively well ordered clusters of molecules within the films.

A Coarse Grained Approach to Polymer Packing: P3HT. The previous study was greatly simplified by working with a molecule that is known to pack into a columnar arrangement. For three-dimensional disordered molecular assemblies, predicting structure is still too challenging for methods available today. However, structural information can be used to identify preferred packing motifs and the most sig-

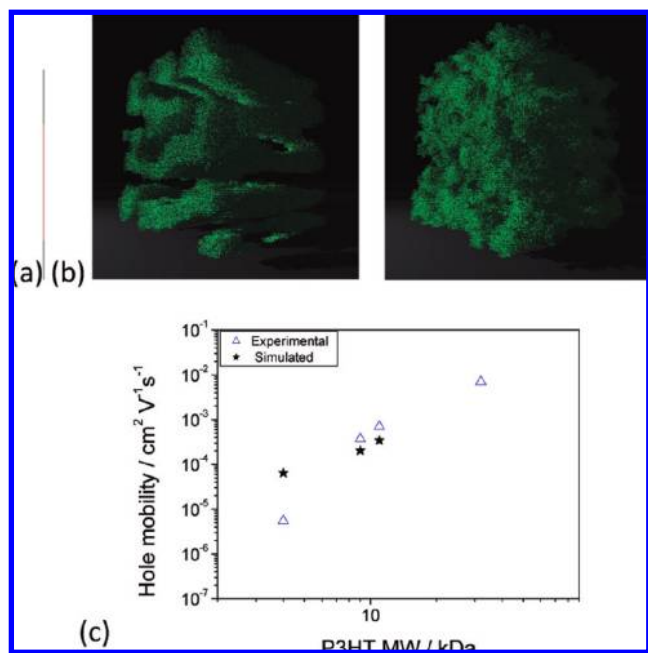


FIGURE 8. (a) Schematic of the lamellar structure adopted by P3HT. (b) Simulated structures obtained by coarse grained method for short (~ 40 repeat units) (left) and long (~ 160 repeat units) (right) chain lengths. (c) Simulated low-field limit time-of-flight mobility (filled stars) in comparison with measured FET mobilities (open triangles) from ref 5.

nificant degrees of freedom, and so to construct simplified, coarse-grained models of the molecular packing. Here, we show how such an approach can rationalize the molecular weight dependence of hole mobility in regioregular polythiophene.

Regioregular poly-3-hexylthiophene (P3HT) is an important organic semiconductor on account of both its high FET hole mobility and its success as the donor component in organic solar cells. The conjugated backbone shows strong planarity and adopts a lamellar structure where chains fold within two-dimensional sheets. These lamellae readily stack together, giving structures with strong intersheet π -stacking interactions and high charge mobilities in the π -stacking direction (Figure 8a). Interestingly, studies on the effect of molecular weight (MW) on P3HT hole mobility have shown that, as P3HT MW increases up to ~ 40 kDa, the hole mobility increases even though the crystallinity of the film *decreases*.⁵

To explore this phenomenon, we develop a coarse grained model of the packing of P3HT, where we represent the polymer as a jointed chain which is constrained to move on a square lattice within a two-dimensional sheet. Each link in the chain represents approximately four thiophene units, a lower limit to the typical conjugation length. Chains move within sheets by reptation, via a Metropolis Monte Carlo algorithm. The relative values of the intrasheet and intersheet interac-

tion energy between monomers are chosen in accordance with reported interaction energies³³ for coplanar and cofacial thiophene units. In agreement with experiment,⁵ short chains form more ordered structures (because of the more favorable intersheet interaction) whereas long chains form less ordered structures (which are more entropically favorable) (Figure 8b).

Figure 8c shows simulated ToF hole mobilities in the coarse-grained structures in comparison with experimental FET mobilities as a function of MW. Simulation details are given in ref 34. Simulated hole mobility increases with increasing MW, in agreement with the experimental observations and despite the reducing crystalline order. This result supports the hypothesis that transport in the vertical direction through organic films is limited by the transfer rate between ordered domains, even when these domains are directed parallel to the substrate.²⁷ In the case of low MW, crystalline domains form with strong internal order but with few direct interconnections. For higher MW, chains still interact strongly in the intersheet direction on a local scale, but these domains are well linked by polymer chains.

This study nicely demonstrates the importance of heterogeneity in determining the macroscopic charge transport properties. The model is limited, however, by the stylized rectangular geometry. In particular, the factors that control packing in the intercrystalline regions need to be better understood.

To study the effect of heterogeneity on transport in detail, we next focus on a highly symmetric molecule where the growth of heterogeneous films can be simulated with relative accuracy and ease.

Microscopic versus Macroscopic Effects in C60 films. In this section, we present results of a multiscale simulation of transport in disordered films of C60. C60 is widely studied as an electron transporter in organic FETs and as an acceptor in solar cells. It is known to crystallize into a close-packed lattice, as expected from its spherical symmetry, but most studies are carried out on vacuum deposited films which contain both crystalline and disordered regions. The study is motivated partly by the existence of (conflicting) experimental data on the correlation between crystal grain size and FET electron mobility.^{35,36} The symmetry of the molecule imparts three simplifications for our study: first, the intermolecular potential is determined primarily by the intermolecular spacing and is known;³⁷ second, the symmetry prevents any substantial electrostatic contribution to energetic disorder, allowing energetic disorder to be disregarded; and third, the transfer integral is determined only by the intermolecular

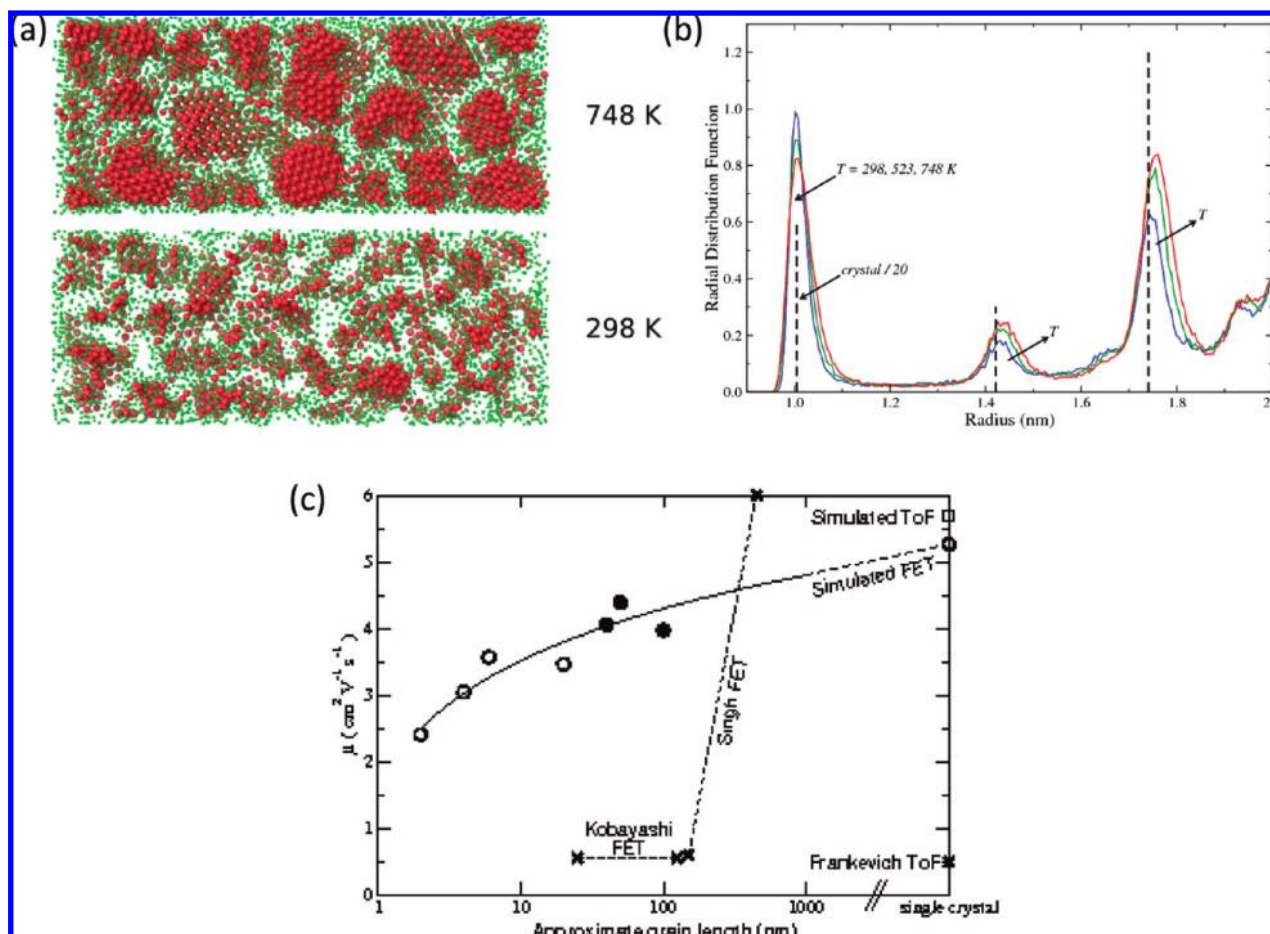


FIGURE 9. (a) Snapshots of C60 films grown on substrates held at 298 and 748 K. Crystalline regions are colored red. (b) Radial distribution function for films grown at different temperatures and for a crystal (dashed lines). (c) Saturated FET mobility as a function of grain size. Experimental saturated mobilities are shown.^{35,36}

spacing, meaning that disorder in the intermolecular separation in the noncrystalline regions is the only factor influencing transport.

C60 films were generated by simulating the physical vapor deposition process with a custom Monte Carlo code.³⁸ In agreement with experiment, higher substrate temperatures resulted in larger crystalline grains (Figure 9a). However, even the least crystalline films are consistently ordered, as shown by the radial distribution functions (RDFs) (Figure 9b). The efficiency with which C60 molecules pack arises from their high symmetry and results in the film also being well ordered electronically: even in the 298 K morphology, 99.6% of molecules have total outward hopping rates that are within 1 order of magnitude of those in the crystal.

The generated C60 films were used in simulations of field-effect transistors in which we were able to reproduce a range of experimental characteristics, including current–voltage curves, electrochemical potential profiles, and mobilities.³⁸ The saturated field-effect mobilities (Figure 9c) depend only slightly

on crystal grain size as expected from the similar RDFs. This finding is consistent with some experimental reports,³⁵ but not others,³⁶ and suggests that other factors, such as interfacial effects, could influence experimental FET mobilities.

Conclusion and Outlook

Low mobilities limit the performance of organic solar cells by enhancing the probability of charge recombination, limiting the charge separation yield, and increasing resistive losses. To maximize the potential of organic photovoltaic energy conversion, charge mobilities need to be increased, but the complexity of the transport mechanism makes it extremely difficult to predict charge mobilities from the chemical structure.

In this Account, we have shown how a combination of computational methods can be used to reproduce the electronic transport properties of a range of molecular semiconductors. In particular, we have shown that packing disorder can reduce mobility by several orders of magnitude for a disordered molecular semiconductor relative to the crystal; that

the effect of disorder on mobility is amplified by anisotropy in the orbitals involved in charge transfer; that side chains strongly influence mobility via their effect on molecular packing; and that transport in conjugated polymers is a function both of the extension of polymer chains and order in chain packing. We have shown that, in the case of two model systems, a discotic liquid crystal and disordered films of C60, mobility can be predicted quantitatively from the chemical structure.

The methods used here to simulate transport can be extended to simulate the binary structures formed in organic bulk heterojunctions and to model the process of charge transport and recombination following charge separation. Achieving a reliable capability to model, and ultimately to predict, the behavior of photovoltaic heterojunctions will require further developments. In particular, efficient coarse graining methods will be needed to model the structural behavior of macromolecular systems such as conjugated polymers; methods will be needed to incorporate the effects of dynamic conformational changes on the time scale of charge transport; and an appropriate description of the influence of local charge mobility on charge pair separation will be needed. However, the building blocks for all of these developments are available, and the result will be a powerful set of diagnostic and design tools for optimization of organic photovoltaic devices.

The authors are grateful to Drs. Denis Andrienko, Valentina Marcon, Amanda Chatten, Stavros Athanasopoulos, Christian Lennartz, Hong Li, and Wolfgang Wenzel, and to Profs. Alison Walker and Jean-Luc Bredas for fruitful discussion. Financial support from the Engineering and Physical Sciences Research Council, the U.K. Energy Research Council, and BP Solar is acknowledged.

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FOOTNOTES

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