The microscopic origins of charge transport in triphenylene systems

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We study the effects of molecular ordering on charge transport at the mesoscale level in a layer of ≈ 9,000 hexa-octyl-thio-triphenylene, HOTT, discotic mesogens with dimensions of ≈ 20 × 20 × 60 nm^3. Ordered (columnar) and disordered isotropic morphologies are obtained from a combination of atomistic and coarse grained molecular dynamics simulations. Electronic structure codes are used to find charge hopping rates at the microscopic level. Energetic disorder is included through the Thole model. Kinetic Monte Carlo simulations then predict charge mobilities. We reproduce the large increase in mobility in going from an isotropic to a columnar morphology. To understand how these mobilities depend on the morphology and hopping rates, we employ graph theory to analyse charge trajectories by representing the film as a charge transport network. This approach allows us to identify spatial correlations of molecule pairs with high transfer rates. These pairs must be linked to ensure good transport characteristics or may otherwise act as traps. Our analysis is straightforward to implement and will be a useful tool in linking materials to device performance, for example to investigate the influence of local inhomogeneities in the current density. Our mobility-field curves show an increasing mobility with field as would be expected for an organic semiconductor.

I. INTRODUCTION

Displays for smartphones, colored light sources, off grid solar cells and curved television screens are examples of applications of organic electronics. Organic semiconductors (OSCs) offer reduced production costs, versatility of synthesis processes, and compatibility with a vast range of substrates including transparent glass, metals and flexible polymeric material. However, they cannot yet compete with their inorganic counterparts in terms of charge transport performance. Charge carriers are localised to molecules or conjugated segments of molecules, in the case of polymers, and charge transport is by donor-acceptor hopping, rather than by a band mechanism. At room temperature, charge mobility is highly sensitive to molecular packing arrangements, due to the short-range of electronic orbital overlaps and their strong dependence on the relative orientation and separation of donor-acceptor pairs. A detailed knowledge of material morphologies, such as those illustrated in figure 1 for discotic OSCs, is thus essential for a proper understanding and prediction of charge mobility.

Multiscale simulations that combine models of morphology and charge transport are an important means of optimisation of materials and devices for OSC technology, particularly for the screening of candidate materials. While the charge mobilities can be measured experimentally, synthesising and characterising the films is time consuming and costly. Knowledge of local charge densities and conductive pathways can be critical to understanding heat dissipation and degradation in OSCs. These effects are not captured by the co-planar dimer model commonly used for prescreening organic molecules. Local current density variations can cause self-heating that in turn may lead to higher local conductivity and thereby creates more current flow, leading to a positive feedback loop. However, variations in charge dynamics at atomistic length scales are hard to study experimentally. Localised current flow can be studied by the cumbersome process of introducing an...
emissive interlayer into the material and measuring the light emitted\textsuperscript{18}. This procedure has a resolution of 2-3 nm and introduces errors due to interfacial interactions with the emissive layer.

A common method to describe charge mobilities is to use the Gaussian disorder model (GDM)\textsuperscript{19,20}. This approach assumes a spatially random distribution of sites where the localization length, $a$, is the relevant length scale compared to site separations\textsuperscript{21,22}. Using a lattice model to describe transport introduces an error if the lattice parameter is far from the localization length\textsuperscript{23}.

We investigate the charge transport properties of hexa-octyl-thio-triphenylene (HOTT or 8H-TT) molecules whose chemical structure and coarse-grained shape are shown in figure 1. From figure 1(a) we see that HOTT is a planar molecule, consisting of three benzene rings surrounding a central benzenic ring. The lower panels come from a preliminary atomistic simulation of HOTT used for parametrization of the coarse grained model. The semiconducting properties of discotic molecules in OSC devices have been studied both theoretically and experimentally\textsuperscript{24}. The high aspect ratio of discotic molecules allow us to examine the role of shape anisotropy and structure in charge transport processes\textsuperscript{7}.

Systems of these molecules possess a columnar phase and a disordered phase\textsuperscript{5-7,25-29}. The drastic change in structure across the phase transition means that it would be impossible to describe both phases system using the same lattice model. Experimental studies\textsuperscript{30} have shown that the mobility suddenly increases as the system goes from isotropic to columnar to crystal phases, while within a given phase it gradually decreases with temperature. Discotics possess a strongly anisotropic charge mobility in their columnar phase, much larger along the column axis than perpendicular to it\textsuperscript{9,31,32}. We compare charge transport in the columnar phase at $T=280$ K and in the disordered phase at $T=400$ K.

We have chosen to study HOTT, as a typical discotic molecule, due to the existence of previous studies that we can compare to and build upon. Lamarra et al.\textsuperscript{9} investigated 4,000 discotic molecules with a simple Miller-Abrahams description of electronic coupling that depends only on molecule separation. Studies on $\sim$1,000 discotic molecules, where charge dynamics were described by a Master Equation with charge transfer rates obtained from the Marcus expression and transfer integrals from quantum chemical calculations, showed structural anisotropy leads to anisotropic charge transport\textsuperscript{8}. Rühle et al. demonstrated a similar approach to our own\textsuperscript{23}, in a cell of 512 molecules, where they neglected metallic contacts. Because their system size is small, they found a single charge transfer channel which percolated across their entire system. These studies demonstrated the strong dependence of charge mobility upon structural ordering and the possibility of charge percolation pathways, however they did not explore the underlying causes. Herein we try to quantify the difference in transport between the two phases in terms of the microscopic processes and structure within.

We present a mesoscale model of charge transport in a film of $\sim$ 9000 molecules, modelling the equivalent of $\sim$700,000 atoms, starting from first principles. This simulation size produces a relative error in the mobility due to finite-size effects of less than 5\%\textsuperscript{34,35}. It has been shown elsewhere that a fully atomistic or a united atom molecular dynamics approach can successfully predict morphologies and transition temperatures with the accuracy of a few degrees for cyanobiphenyls\textsuperscript{36-38} and quinquephenyl\textsuperscript{39}. However, these atomistic simulations are not feasible at the mesoscale system sizes that we require here, that are of the order of tens of nanometres\textsuperscript{40}. For morphologies derived from microscopic calculations, we thus make use of coarse grained (CG) molecular dynamics (MD)\textsuperscript{41,42} parameterized with the help of small scale atomistic simulations, as will be described in the next section.

Our methods produce resolution at the microscopic level by describing the charge transport between every pair of molecules as discrete events in time so that we can identify which structural properties lead to varying local current densities. In systems this large, with so many connected pairs, graph theory\textsuperscript{43} is a useful tool to analyze the simulated charge transport trajectories. This approach is an improvement over trajectory plots in that it allows us to investigate correlations between structural and dynamic properties e.g. the electronic coupling and the observed carrier transport between molecules.

Network analysis has been used to study organic charge transport networks and kinetic Monte Carlo (KMC) methods before. Jackson et al. used dynamic network techniques to study how the charge transport network changes over time as the molecules move\textsuperscript{44}, however they did not model the resultant charge transport properties. Cottaar et al. used percolation theory on a 2D lattice to describe the effects of correlated and uncorrelated energetic disorder\textsuperscript{45}, they considered the percolative pathways in terms of the current density between lattice sites forming edges. The above study was lattice-based and although they showed the existence of favoured charge pathways they could not relate this to any structural properties of the system, and the energetic disorder was drawn from chosen distribution. Graph theoretical approaches were also applied to KMC simulations of chemical kinetics by Stamatakis & Vlachos\textsuperscript{46}, this is still a system of discrete events and the underlying algorithm is similar. Indeed, the use of graph theory to describe networks of first order events is well established in many contexts regarding kinetics. Uniquely we take advantage of the one-to-one spatial equivalence of the transport network with the morphology to quantify the microscopic contributions to macroscopic transport and describe the origins of the phenomena observed.

While other studies have combined the use of CGMD and KMC to describe transport in molecular systems they have not been able to combine the system sizes and degree of detail that we present. Furthermore we will
use the microscopic resolution of our model to describe
the nature of observed charge transport in terms of the
relationship between the difference in site energies and
transfer integrals. We explain the prevalence of rattling
motion in OSCs due to the weak effect of the applied field.
In this manner we go further than measuring the charge
mobility, to enable truly predictive modelling one must
understand the origin of the observed transport phenom-
ena.

In this paper we present a methodology that allows us
to describe charge transport in disordered OSCs with
microscopically resolved molecular packings, transport
parameters and charge dynamics. We do not have to re-
sort to tuning parameters, such as reorganization en-
ergies or coupling length scales, and our model can describe
systems with multiple molecular species, anisotropic
molecules and structural features on all length scales. Be-
low, we describe the CG MD and charge transport mod-
els in section II. We relate the microscopic properties of
the system and the resultant charge transport through
the use of a directed graph representation in section III.
In this way we identify charge transport pathways on a
microscopic scale, describe their structural features and
measure their spatial extent and separation.

II. MODELS

II.1. Coarse Grained Molecular Dynamics

Molecular dynamics can provide a realistic structure
of an OSC system for given thermodynamic parameters,
provided there is an accurate description of the effective
inter particle potential interactions. Force fields can be
developed that are suitable for a wide range of temper-
atures, pressures and densities and can reproduce multiple
phases of matter. In our CG model, we tuned the force
field for HOTT on the basis of MD simulations for a
fully atomistic model of the molecular system. CGMD has
already been shown to reproduce the phase diagram in
columnar triphenylenes. The CG potential em-
ployed for our MD simulations is based on the Gay-Berne
(GB) potential, where anisotropic particles are described
as rigid bodies of ellipsoidal shape. The potential can
be considered as a generalization of the Lennard-Jones
6-12 potential, where shape and interaction anisotropies
have been introduced.

The GB interaction potential between two particles, i and j,
depend therefore on their orientations, defined by the unit
vectors \( \hat{u}_i, \hat{u}_j \), and by their centre-centre
separating vector, \( \vec{r}_{ij} \):

\[
U(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) = 4\sigma_0 \epsilon(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) \times \left[ \frac{\sigma_0}{\vec{r}_{ij} - \sigma(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) + \sigma_0} - \frac{\sigma_0}{\vec{r}_{ij} - \sigma(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) + \sigma_0} \right]^{12}
\]

\[
\sigma(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) = \sigma_0 \left( \frac{\vec{r}_{ij}}{\vec{r}_{ij} - \sigma(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) + \sigma_0} \right)^6
\]

where \( \sigma_0 \) (\( \epsilon_0 \)) fixes the scales of length (energy),
while \( \sigma(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) \) and \( \epsilon(\hat{u}_i, \hat{u}_j, \vec{r}_{ij}) \) correspond to the
anisotropic contact distance and potential well depth,
respectively. More specifically, the contact distance is:

\[
\sigma(\hat{u}_i, \hat{u}_j, \vec{r}) = \sigma_0 \times \left\{ 1 - \chi \frac{2}{1 + \chi (\hat{u}_i \cdot \hat{u}_j)} \left[ \frac{\hat{u}_i \cdot \hat{r} + \hat{u}_j \cdot \hat{r}}{1 - \chi (\hat{u}_i \cdot \hat{u}_j)} \right] \right\}^{-1/2}
\]

where

\[
\chi = \frac{k_{GB}^2 - 1}{k_{GB}^2 + 1}
\]

is the shape anisotropy parameter, defined by the aspect
ratio, \( k_{GB} \). The well depth \( \epsilon(\hat{u}_i, \hat{u}_j, \vec{r}) \) is determined by
the product of two functions:

\[
\epsilon(\hat{u}_i, \hat{u}_j, \vec{r}) = \left[ \epsilon_1(\hat{u}_i, \hat{u}_j, \vec{r}) \right]^{\mu} \left[ \epsilon_2(\hat{u}_i, \hat{u}_j) \right]^{\nu}
\]

where

\[
\epsilon_1 = 1 - \chi' \frac{2}{1 + \chi' (\hat{u}_i \cdot \hat{r} + \hat{u}_j \cdot \hat{r})^2} \frac{\hat{u}_i \cdot \hat{r} - \hat{u}_j \cdot \hat{r}}{1 - \chi' (\hat{u}_i \cdot \hat{u}_j)}
\]

\[
\epsilon_2 = \left[ 1 - \chi'^2 (\hat{u}_i \cdot \hat{u}_j)^2 \right]^{-1/2}
\]

while the parameter

\[
\chi' = \left( \frac{k_{GB}^2}{(k_{GB})^{1/\mu_{GB}}} - 1 \right) \left( \frac{(k_{GB})^{1/\mu_{GB}} + 1}{(k_{GB})^{1/\mu_{GB}}} \right)
\]

is defined in terms of the well depth anisotropy \( k_{GB}^{1/\mu_{GB}} \),
i.e. the ratio between well depths for the side-by-side and
end-to-end interactions, respectively. The form of the GB
potential can be adjusted to a specific molecule by vary-
ing the parameters \( \mu_{GB}, \nu_{GB}, k_{GB}, k_{GB} \), with the expo-
ents \( \mu_{GB}, \nu_{GB} \) tuning the orientational dependence of
the energy. For \( k_{GB} \) and \( k_{GB}^{1/\mu_{GB}} \) values smaller than unity
the potential describes disk-like mesogens (oblate ellip-
soids), and their discotic and columnar mesophases.

The Gay-Berne parameters obtained from microscopic
level simulations in the paper are shown in Table I.

II.2. Charge Transport model

II.2.1. Kinetic Monte Carlo, KMC, simulations

We took roughly equally sized samples from the CG
morphologies, they were replicated periodically in the x
and y directions while metallic boundary conditions were
applied in the $z$ direction to model electrodes. Axes with unit vectors $\hat{e}_x, \hat{e}_y, \hat{e}_z$ were defined as shown in figure 3.

Charge motion is calculated using kinetic Monte Carlo (KMC) methods\(^\text{49}\) as it allows for interactions between the charge carriers and describes all mechanisms on a realistic timescale. Hopping rates are determined by Marcus theory where transfer integrals, representing electronic coupling, and hopping site energies are derived from electronic structure and electrostatic interactions between the charge carriers. The transfer integrals are highly sensitive to the relative orientations of the orbitals and the hopping distances involved in the transfer process\(^\text{9}\) and thus on the local packing. The parameters determining packing and charge hopping rates are determined from electronic structure calculations and there is no need for parameters to be fitted to experiment. This feature of off lattice KMC means that one can quantitatively compare charge transport properties predicted by our model across many different materials and morphologies.

We began by defining the centre of mass for each molecule as a possible charge hopping site, with a maximum occupancy of one free charge carrier. We used Marcus hopping rates\(^\text{50}\) to describe the hopping:

$$\kappa_{ij} = \frac{|J_{ij}|^2}{\hbar} \left( \frac{\pi}{\lambda k_B T} \right) \exp \left[ -\frac{(\Delta G_{ij} + \lambda)^2}{4\lambda k_B T} \right] \quad (8)$$

where the total reorganization energy, $\lambda = \lambda_{\text{inner}} + \lambda_{\text{outer}}$, were calculated for charge transport between HOTT molecules, the same value used for all molecule pairs in the system. There are two major contributions to the energy of free charges in the system: the molecular orbital energy of the host molecule, and the electrostatic energy of other free charges and any externally applied electric field across the system. We calculated the HOMO and LUMO energy levels for each molecule applied electric field across the system. We calculated the electrostatic energy of other free charges and any externally applied orbital energy of the host molecule, and the electronic coupling, and hopping site energies are derived with Gaussian\(^\text{52}\).

Following many other models of charge transport in OSCs\(^\text{12}\), the change in the Gibbs free energy $\Delta G_{ij}$ between pairs of molecules comes from electrostatic interactions between the charges in an applied bias. In a departure from standard practice, we solved the discretised Poisson’s equation with a cloud-in-cell method to allow for the long range nature of the Coulomb interactions,\(^\text{53}\)

$$\tilde{\phi} = -\nabla^2 \tilde{\rho}$$

where $\tilde{\phi}$ is the discretised electric potential and $\epsilon = \epsilon_0 \epsilon_r$ is the permittivity of free space multiplied by the material’s dielectric constant, with appropriate boundary conditions describing the applied bias. A coarse-grained charge density, $\tilde{\rho}$, is defined on a grid, projecting the charges within each voxel onto the eight voxel vertices before solving equation 9. Each hopping site’s electrostatic potential then comes from mapping $\tilde{\phi}$ onto that site. The charge density distribution and potential profile is recalculated after every KMC event.

The first reaction method (FRM) was used to select the next event to be performed in the KMC simulation\(^\text{54}\). In brief the FRM method requires us to calculate the rate ($\nu_k$) of every possible event in the system, then for each event draw a waiting time $(t_w^{(k)})$ from a Poissonian distribution parameterized by $\nu_k$. At each KMC step we perform the event with the shortest waiting time. We note that the given a set of $M$ events with rates $\nu_1, \ldots, \nu_M$ and waiting times $t_w^{(1)}, \ldots, t_w^{(M)}$, the probability that the $k^{th}$ event is performed is given by $P(t_w^{(k)} = \min(t_w^{(1)}, \ldots, t_w^{(M)}))$, which is equivalent to:

$$P(k|\nu_1, \ldots, \nu_M) = \nu_k / \sum_i \nu_i. \quad (10)$$

We ran 6 simulations with different random number seeds for each morphology. The simulations were initiated with no charge carriers present in the cell. As the simulation ran, injection of charge carriers took place at the top electrode and extraction at the bottom electrode. Injection was treated as a two step process in which the probability of a carrier being on a random hopping site adjacent to the electrode is multiplied by a Marcus hopping rate from the selected site to a site in the bulk of the device. The probability of being on an adjacent hopping site is calculated as $p = \min \left[ 1, e^{-\frac{\delta E}{k_B T}} \right]$, where $\delta E$ is the difference in carrier energy between the Fermi level of the electrode and the adjacent hopping site.

Once the dynamics reached steady state with respect to charge injection and extraction, measurements of the mean square displacement, $\langle r^2(\tau) \rangle$, were taken at intervals of $\Delta t = 5 \times 10^3$ps. If $\Delta t$ is too short, $\langle r^2(\tau) \rangle$ is dominated by charge transfer back and forth within a strongly coupled pair, in a rattling motion. Our choice of $\Delta t$ ensured that we measure charge motion that contributes to charge flow across the device. To measure the charge carrier motion we calculated the mean square distance displacement of free charge carriers as a function of time $\tau$,

$$\langle r^2(\tau) \rangle = \frac{1}{N} \sum_{i=0}^{N} \sum_{j=0}^{M} \left[ r_i(t_j + \Delta t) - r_i(t_j) \right]^2$$

where $M$ is the number of time steps. The maximum simulation time $\tau_{\text{max}}$ was set at $10^8$ps. Continuous measurements, such as the mean squared displacement, were averaged over all KMC trajectories. The mobility was measured using:

$$\mu = \frac{D}{k_B T} \quad , \quad D = \lim_{\tau \to \infty} \langle r^2(\tau) \rangle / \tau$$

where $k_B$ is the Boltzmann constant.
that the flux matrix is skew symmetric. \[ \vec{e} \]

where the right hand side is over all edges that begin at site \( i \) are over neighbouring edges, so the first (second) sum on \( i \) shows how the linked traffic \( \hat{T}_{ij} \) are shown by the arrows joining the nodes. The node labels show how the linked traffic \( \hat{T}_{ij} \) is calculated from equation 13.

II.2.2. Network Analysis

To investigate the role of a given pair of molecules in charge transport, as compared to properties of the entire system, we need to use a description that treats pairs, rather than individual molecules, as the simplest individual object. To achieve this we used tools from graph theory\(^{43}\) that explicitly consider the connections between objects as entities in their own right. We mapped the transfer integrals onto a transportation network, called a graph, that consists of nodes linked by edges, an example is illustrated in Figure 2. In this case, nodes are the HOTT molecules and edges are links between a molecule and all other molecules within the transfer cutoff \( r_c \).

To probe charge transport, we use the charge trajectories to find the elements of a traffic matrix \( T \), an order \( N \) square matrix with rows and columns each linked to molecules \( i = 1 \) to \( N \). Its diagonal elements are zero. Its off diagonal elements, \( T_{ij} \), are equal to the number of charges that hopped between site \( i \) and site \( j \) i.e. the traffic from site \( i \) to \( j \).

We also define the linked traffic, \( \hat{T}_{ij} \), of an edge as the average traffic of the set of neighbouring edges in a given direction. For an edge from \( i \) to \( j \) this set includes all edges that end at \( i \) or start from \( j \), excluding the reverse edge from \( j \) to \( i \). We can write \( \hat{T}_{ij} \):

\[
\hat{T}_{ij} = \frac{1}{2} \left[ \frac{\sum_k T_{hi} - T_{ji}}{M_i - 1} + \frac{\sum_k T_{jh} - T_{ji}}{M_j - 1} \right]
\]  

(13)

where \( M_i \) (\( M_j \)) is the number of neighbouring nodes to node \( i \) (\( j \)) and \( h \) (\( k \)) is an index over this set. The sums are over neighbouring edges, so the first (second) sum on the right hand side is over all edges that begin at site \( i \) (\( j \)) and end at site \( j \) (\( i \)). Given that the traffic \( T_{ij} \) is an extensive measurement in time, all traffic measurements are made for the same simulation time \( \tau_{max} \). There is a net flux:

\[
\vec{f}_{ij} = (T_{ij} - T_{ji}) \vec{e}_{ij} / \tau_{max}
\]  

(14)

where \( \vec{e}_{ij} \) is the unit vector linking sites \( i \) and \( j \). Note that the flux matrix is skew symmetric.

![FIG. 2. Schematic illustration of the network. Nodes are the molecules shown as ellipses. For each pair of molecules separated by less than \( r_c \) there are two edges whose directions are shown by the arrows joining the nodes. The node labels show how the linked traffic \( \hat{T}_{ij} \) is calculated from equation 13.](image)

### TABLE I. Parameters linked to MD, VOTCA and KMC calculations. The notation is defined in the text for this section

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{GB} )</td>
<td>1.0948</td>
</tr>
<tr>
<td>( \sigma_0 )</td>
<td>0.375 nm</td>
</tr>
<tr>
<td>( \epsilon_{dis} )</td>
<td>0.105 eV</td>
</tr>
</tbody>
</table>

III. RESULTS

We simulated two morphologies of HOTT molecules at two different temperatures, 9011 molecules at 280K and 8968 molecules at 400K, with the CG MD method described in section II.1. We used these two systems to investigate the effects of structural ordering on the distribution of charge transfer integrals \( J_{ij} \) as well as the long-range transport properties of the systems. Finally, we use the microscopic information embedded in the morphologies and KMC simulation to explain the trends in both short- and long-range charge transport.

The planar shape of the benzene rings allows molecules to form a \( \pi-\pi \) stacking arrangement with little steric hindrance. Figure 3 shows the morphologies of the HOTT systems generated by back-mapping the coarse-grained morphologies into atomic co-ordinates. At the lower temperature there is a clear long-range ordering of the molecules into columns. This ordering is destroyed at higher temperatures with no clear structure visible.

The peaks in figure 4 correspond to separations in a column of HOTT molecules with \( r_i \) (figure 1) parallel to the column axis, as well as regular separations between columns in the radial plane. In the disordered phase there is no ordering beyond first neighbours along \( r_i \) and a broad correlation around 2.0 nm.
the local morphology. The distribution of smaller \( J \) to a global parameter such as temperature, but rather particular coupling is more or less favoured is not due if there is any favoured set of hops (e.g. in columns), they would increase in temperature through equation 8, so if there column transfer.

Figure 5 shows the square of the transfer integrals between pairs of molecules with respect to the cartesian components of the pair separation, according to \( r^2_{ij} = \Delta x^2 + \Delta y^2 + \Delta z^2 \) (nm)

(a) Columnar phase. The dashed red line illustrates the variation of \( J^2 \) when moving along a column. (b) Disordered phase.

show that the largest transfer integrals correspond to charge transfer within the same column. Inter-column transfer occurs at \( \Delta x \approx 1.9 \) nm Given the column separation distances are much larger than \( r_c \), there are few transfer integrals between molecules beyond nearest neighbour columns. Figure 5(b) shows that the distribution of \( J^2 \) at \( T=400 \) K is isotropic, as would be expected for a disordered morphology, and decay exponentially with \( \Delta r \). The range of \( J^2 \) values is comparable to the ordered system, suggesting that the origin of large \( J^2 \) is the same at both temperatures: a pair of molecules arranged in a \( \pi \)-stacking configuration.

Looking at figures 4 and 5 we can see that although the nearest neighbour separation is similar in both the columnar and isotropic phases, the distribution of pair separations in Cartesian directions and the distribution of transfer integrals are very different. One could not use a single lattice model to recreate both of these systems: the lattice would have to be a fine cubic mesh in the isotropic phase, while it would be a coarser stacked hexagonal lattice in the ordered phase. Even with different shaped lattices one would need to describe the anisotropic coupling between molecules accurately. We stress that our model can describe all phases of a system accurately and we will show below how the same

\[
\Delta r^2 = \Delta x^2 + \Delta y^2 + \Delta z^2 \quad (15)
\]

using axes shown in Figure 3. The distribution of \( J^2 \) in the columnar phase shows spatial ordering of the transfer integrals in all three dimensions. Although the \( \Delta x \) and \( \Delta y \) distributions are similar for figures 5(a) and (b) apart from where \( J^2 \approx 1 \times 10^{-12} \), the \( \Delta z \) distribution is markedly different. In the z-direction there are islands with large values of \( J^2 \) from coupling to the nearest and second-nearest molecules in the same column. Higher order neighbours in the same column follow the same trend although \( J^2 \) are of the same magnitude as for inter-column transfer.

All possible hops are affected in the same way by an increase in temperature through equation 8, so if there is any favoured set of hops (e.g. in columns), they would be favoured at all temperatures. Thus the reason any particular coupling is more or less favoured is not due to a global parameter such as temperature, but rather the local morphology. The distribution of smaller \( J^2 \) values that correspond to inter-column hopping in the z-direction in the columnar phase is broad and continuous in both phases, falling off exponentially with \( \Delta z \), shown by the dashed line in figure 5(a). Comparing the value of \( \Delta z \) at which \( J^2 \) is large in figure 5(a) to the molecular dimensions given in figure 1, the most significant charge transfer path corresponds to hopping between molecules separated by roughly \( 2r_{||} \) - directly above or below one another.

\( J^2 \) variations in the \( x - y \)-plane shown in Figure 5(a) distinguish between intra and inter-column hopping. The clustering of \( \Delta x \) and \( \Delta y \) around \( \Delta r = 0 \) and \( \Delta r = 0.4 \) nm

FIG. 4. Pair correlation function \( g \) vs molecular separation \( r \) (nm) or HOTM molecules in columnar and disordered phases. For the former, the first peak is at 0.43 nm and represents the intra-column vertical separation, the second peak is at 0.904 nm, while the first minimum is at 0.74 nm The first peak in the disordered phase is at 0.515 nm.

Figure 5 shows the distribution of hole transfer integrals \( J^2 \) between pairs of molecules, needed for the hopping rates in equation 8, against the spatial separation, 

\[
\Delta r^2 = \Delta x^2 + \Delta y^2 + \Delta z^2 
\]
mobility parallel to the field is small compared to the intrinsic dis- 

... shows that the change in energy due to movement 

That the motion is isotropic despite an applied voltage of 

the columns contributing a third of the total movement. 

A useful measure of charge transport is the mean 

Figure 6 shows that in the columnar phase the ratio \( \langle z^2 \rangle / \langle r^2 \rangle \) is nearly 

constant at 0.9 and motion along columns is strongly 

favoured. By comparison the charge transport in the 

disordered phase is isotropic, with transport parallel to 

the columns contributing a third of the total movement. 

That the motion is isotropic despite an applied voltage of 

2.0V shows that the change in energy due to movement 

parallel to the field is small compared to the intrinsic dis-

order and transfer integrals. In the columnar phase the 

mobility \( \mu_z = 4.782 \times 10^{-6} \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) and in the 

disordered phase its value is \( \mu_z = 7.938 \times 10^{-7} \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) 

(see Supplementary Material for further details). 

The highly directional nature of the MSD in the columnar 

system suggests filamentary transport. It is known 

that one dimensional transport depends upon the sys-

tem size and eventually fails as a single defect severs the 

chain. Even if the transport chain is not severed the link 

with the lowest rate will still be the rate determining step 

with respect to long-range transport. To investigate this 

effect we modified the hopping networks to halve the sys-

tem’s effective height and changed the voltage to keep the 

field constant, this should increase the observed mobility 

as the number of weak links should reduce. The ratio 

of the halved system mobility to the original mobility, 

\( \kappa = \mu_z'/\mu_z \), is a measure of both the extent of filamen-

tary transport and the density of weak connections in 

the filaments. In the columnar system \( \kappa = 1.420 \), while 

in the amorphous system \( \kappa = 1.019 \). These measure-

ments reinforce the quantitative difference in the trans-

port mechanisms: the columnar system is reducible to 

a set of separate conducting filaments, while the amor-

phous system is truly isotropic. 

Our large system size allows us to look at spatial vari-

ations in charge transport. Figure 7(a) shows that in the 
columnar phase, the highest charge transfer rates are be-
tween sites in the same column, while transfers between 
columns are typically much weaker, consistent with fig-
ure 5. The dark blue regions within columns indicate 

continuous chains of transfers. In the disordered system 

Figure 7(b) shows there is no spatial ordering of strongly 
coupled molecule pairs. Comparing panels 7(a) and (b) 
does not explain the difference in transport properties 

between the columnar and disordered systems, nor the 

extent of rattling motion. For both phases we can see 

from figure 7(c-d) that very few pairs of molecules ex-
change free charge carriers. In the columnar phase there 
is clear spatial ordering of charge hops along columns. In 
the disordered phase, even fewer pairs of molecules ex-
change carriers and those that do are clustered in small 
groups of three or four hopping sites although measures 
of transport should be evenly spread across the film. 

Figure 7(c-d) shows the number of hops along edges as 
coloured arrows, edges where there are no hops are 
omitted. Dark blue edges that carry a noticeable level of 
traffic are clustered in small chains. The pink edges 
that carry exceptionally high traffic are isolated and have 
no obvious spatial distribution. From the applied color 

scale we can see that the maximum observed numbers of 
hops in an edge are comparable in the two morphologies 
although the number of edges that carry a noticeable 
level of traffic is smaller in the disordered system than 
the ordered system.

In graph theory the disconnected clusters in figure 7(c-

d) are called subgraphs. Using \( T_{ij} \) we identified the num-

ber of sites in each subgraph as well as their length, i.e. 
the maximum extent of the subgraph parallel to the z 
axis in Figure 8. In the ordered system the clusters are 
filamentary, their length scales linearly with the number 
of sites which are stacked in a column with a fixed pair 
separation of 6.5 nm. Inter-column connections in the 

\( x-y \) plane do not play a role in charge transport. In the 
disordered morphology the cluster size scales as \( N^{1/2} \) as 
can be seen in the figure. For a smaller simulation cell, 
the charge transport length would be directly compara-
able to the percolation length and there may only appear 
to be one or two favoured pathways. The ability to sim-
ulate a large system means we can study the density and 
growth of these pathways.

It is known that one dimensional transport will eventu-
ally fail as only a single fault will completely disrupt the 
entire transport network. In the system sizes presented 
the columnar ordering percolates the system, thus we 
cannot describe the effect of dislocations to the charge 
transport. However the study of the amorphous system 
shows that if two columnar regions are separated by a 
small amorphous region (a 1D crystal defect), transport 
will still occur, albeit slowly and isotropically. The re-

gions between columns would effectively transport charge 
an order of magnitude more slowly than the columns, 
they would be the limiting factor to the overall perfor-

cance of the device.

Figure 9 shows that the columnar phase exhibits a bi-

FIG. 6. Charge mean squared displacement \( \langle r^2 \rangle \) (solid lines) and \( \langle z^2 \rangle \) (dotted lines) versus simulation time \( \tau \) (ps) for columnar and disordered phases. Inset: A sub-sample of the 
same data on a linear scale.
FIG. 7. Simulation cells where \(0 \leq x \leq x_{\text{max}}, 0 \leq y \leq y_{\text{max}}, 0 \leq z \leq z_{\text{max}}\) and \(x_{\text{max}}, y_{\text{max}}, z_{\text{max}}\) are given in the Figure 3 caption. Panels (a-b) edges with transfer integrals \(|J_{ij}|^2 > 10^{-6}\)eV shown as arrows; panels (c-d): traffic \(T_{ij}\) between pairs (lines); panels (e-f) The extensive flux \(F_{\tau_{\text{max}}}\) integrated over \(\tau_{\text{max}}\) in columnar and disordered phases. The grids are to guide the reader’s eye.

FIG. 8. Cluster size vs cluster length along the \(z\) axis (the direction of an applied bias of 2V), for the columnar phase at simulation times of \(10^5\) (blue diamonds) and \(10^7\) ps (circles) and for the disordered phase at \(10^7\) ps (red squares) modal distribution with very few values of \(J_{ij}\) around \(10^{-6}\)eV, consistent with figure 5(a). This minimum corresponds to the first minimum in \(g(r)\) at \(r=0.74\)nm. At this molecular separation, there are very few molecule pairs that have the correct alignment for \(J_{ij}\) to exceed its cutoff value (figure 4). The columnar morphology has more edges with large \(J_{ij}\) than the disordered morphology although the maximum observed \(J_{ij}\) are comparable. These large \(J_{ij}\) occur between particles that are at closest approach, equivalent to neighbouring molecules that are parallel to the \(x\)-\(y\) plane. The large number of connected particle pairs explains the faster charge transport shown in figure 6. In the disordered system the distribution of particle separations is smoother and thus the distribution of \(J_{ij}\) is smoother too, as the strength of the coupling coupling decreases with increasing pair separation the two distributions have mirror symmetry. The dashed line in figure 9 shows that the distribution of \(J_{ij}\) over a smaller range of separations, the larger peak corresponds to the shoulder in the distribution of pair separations (see figure inset); the shoulder in \(P(J_{ij})\) also has a counterpart in the separation distribution. Averaged over a large number of configurations we would expect the distribution of \(J_{ij}\) at a fixed value of \(r_{ij}\), or a range small enough to only include nearest neighbour pairs, would become Gaussian due to the central limit theorem.

Even for the ordered morphology, the transport is poor. To get an estimate of how few edges contribute to charge transport we can compare \(N'_{\tau}\), the number of edges where \(T_{ij} > 0\), to the total number of edges
unlikely despite the change in Gibbs free energy, $\Delta G$, the columnar phase is that hops between columns are very unlikely because of the energetic disorder between nearest neighbours. $\Delta G$ changes when moving between nearest neighbours. The weakness of the asymmetry is critical to understanding why the number of edges that contribute to flux is so small. We can visualise this argument from figure 1 of the Supplemental Material (SM).

The stacking results in a relatively narrow distribution of pair separations in the two phases. For the former there is a clear bimodal distribution due to the high spatial and orientational ordering of the molecules. For the latter, the distribution is flatter. The solid line is the distribution taken over all molecule pairs up to 2.5 nm apart, the dashed line is for pairs up to 1 nm. Inset: The distribution of pair separations in the columnar and disordered phases. For the former there is a clear bimodal distribution, while the edges that host most charge hopping events occur close to $\rho_{ij} = 1.25$ nm.

$N_c$. At a bias of 2V in the columnar phase the ratio $N_{c}^*/N_c = 1.17 \times 10^{-3}$ is an indicator of the variability in transport behaviour between molecules. In the disordered system the ratio is an order of magnitude smaller, carrier hops are more localised along fewer edges. This suggests that the distribution of transfer rates is more sparse. To quantify the degree of rattling motion we calculate $\tilde{N}_{\text{hops}} = \frac{1}{2} \sum |F_{ij}|$, the number of carrier hops that contribute to a flux. The ratio of $\tilde{N}_{\text{hops}}$ to the total number of recorded hops is small, of the order $10^{-4}$ in the columnar phase and an order of magnitude smaller in the disordered phase, suggesting that most carrier hops represent rattling motion. More precise values of these quantities are included in the Supplemental Material.

The effect of the transfer integral distribution in the columnar phase is that hops between columns are very unlikely despite the change in Gibbs free energy, $\Delta G_{ij}$, being roughly equal for intra- and inter-column edges. Although the transfer integrals limit charge motion to the $z$ axis they do not dictate whether charges hop up or down columns, hence any net transport must be driven by energetic considerations. This means that a requirement for long-range transport is for the set of edges with $\Delta G_{ij} \approx -\lambda$ to be asymmetrically distributed around $\Delta z = 0$. Changes in site energies due to energetic disorder are in general much larger than the electrostatic energy changes when moving between nearest neighbours. The weakness of the asymmetry is critical to understanding why the number of edges that contribute to flux is so small. We can visualise this argument from figure 1 of the Supplemental material (SM).

Due to the low asymmetry of $\Delta G_{ij}$ with respect to $\Delta z_{ij}$, few edges contribute to the carrier flux matrix $F$. The closer $-\lambda$ is to the bottom edge of the distribution of $\Delta G_{ij}$, or the larger the optimal transfer integral separation, then the weaker the applied bias needs to be. Figure 10 shows the flow along a given edge, $T_{ij}$, plotted against the linked traffic of the edge, $T_{ij}$. There is little correlation between the traffic of an edge and the average traffic of its neighbours. However, in the ordered morphology the distribution of both traffic measures is narrower and closer to equality between the two measures. This result suggests that in the ordered system the flow along edges is more uniform and the transport environment around an edge is similar to that of the edge concerned. We can relate the strong correlation between structural ordering and electronic coupling to the dynamics of long-range charge transport: structural ordering means less variation in local structural environment (see figure 4) and corresponds to $\pi$-stacking in this system. The stacking results in a relatively narrow distribution of transfer integrals (see figure 9), affecting the dynamic behaviour, and the traffic along edges is distributed relatively narrowly around equality between $(T_{ij}) = T_{ij}$.

The edges that host most charge hopping events occur for $\Delta G_{ij} \approx -\lambda$, outside this range the rate of a hop is at least $10^6$ times smaller. Comparing two hopping events with such large differences in rates we can see that when $\nu_1 \gg \nu_2$ then using equation 10 the probability that the waiting time $t_w^{(1)} < t_w^{(2)} = \nu_1/(\nu_1 + \nu_2) \approx 1$. Recall that in the FRM we perform the event with the smallest waiting time at each iteration. Thus only hopping events with rates close to the maximum rate will occur and so only those events with $\Delta G_{ij}$ close to $-\lambda$ are relevant for transport. This limitation of charge transport to a narrow range of $\Delta G_{ij}$ explains why so few edges carry any traffic. If an OSC had a reorganization energy close to the typical difference in energy between pairs, determined by the disorder in HOMO/LUMO energies, then many more edges would be involved in transport.

If the transfer integral dominates in equation 8 then charge hopping is not spatially confined and despite differences in $\Delta G_{ij}$ many edges are equally likely to carry...
traffic. In practice, the exponential factor dominates so despite many edges having similar transfer integrals, those with $\Delta G_{ij}$ closest to $-\lambda$ carry almost all the traffic. We suggest that to identify high transfer rate edges it is more useful to consider that high transfer integrals select from the set of edges with $\Delta G_{ij} \approx -\lambda$, than favourable values of $\Delta G_{ij}$ select from the set of all edges with high $J^2$. This selective pressure explains why so few edges in the 400 K morphology carry traffic despite the isotropic nature of the transfer integrals. For predictive power one must know the distribution of $\Delta G_{ij}$, or at least $\Delta G_{ij}$ in the absence of charges, in the system as well as $\{J_{ij}\}$ to identify favoured traffic directions.

The disordered morphology which exhibits slower long-range charge transport contains molecule pairs that exchange $\sim 10^4$ holes during the simulation. Figure 7(b) and (d) shows that high traffic edges are isolated and the connected edges are not strong, either with respect to the transfer integral or the observed traffic. This lack of connectedness leads to a relatively small contribution to transport despite high coupling and traffic.

The difference in energy between two sites is composed of the inherent energetic disorder and electrostatic contributions, as the applied field is increased then it becomes relatively large compared to the disorder and $\Delta G_{ij}$ becomes correlated with $\Delta z_{ij}$. The gradient of Figure 11 is positive since the application of a field breaks the symmetry of $\Delta G_{ij}$ about $\Delta z = 0$, the population of edges with $\Delta z < 0$ move closer to $\Delta G_{ij} \approx \lambda$ while those with $\Delta z_{ij} > 0$ move farther away. A drift component parallel to the field is therefore superimposed on the the random motion of charges. Beyond an optimum bias the typical hopping rate would decrease due to the inverted region of the Marcus equation dominating when $\Delta G_{ij} \ll \lambda$. In the ordered system the most highly connected edges are already parallel to the field so the effect is amplified, while in the disordered system an increasing field will only favour those edges which are aligned correctly. No electric field dependence was observed by Kwiatkowski et al., suggesting that the origin of such a dependence is more subtle than simply the presence of energetic disorder. We suggest that the topology of the electronic transport network, defined by transfer integrals, plays a role in the electric field dependence of the mobility.

IV. CONCLUSIONS

We compared the charge transport properties of an organic semiconductor discotic system in two distinct structural phases using explicitly calculated electronic transfer integrals and orbital energies in a kinetic Monte Carlo simulation. The ordered columnar phase exhibits much higher charge carrier mobility parallel to the column axis while transport between columns is very rare. Inter-column transport is restricted by weak transfer integrals, the change in free energy both along and between columns is roughly equal due to energetic disorder.

Discrete charge transport via hopping mechanisms maps well to graph theory methods and discussion of edges and nodes. Metrics which can describe paths of arbitrary length across the system and measures of robustness help identify good charge transport criteria. If efficient charge transport is more reliant on the collective behaviour of a series of hops, on pathways rather than pairs, then graph theory is a natural expression. In the future it would be interesting to see if this approach could be used to define which sites in the system contribute to charge flux and which can be described as dynamic traps. These sites are likely to be important for light emission and recombination in optoelectronic devices.

Although the energetic term dominates the Marcus rate equation it is still important to calculate the transfer integrals explicitly. If we only consider hopping due to energetic terms we would expect to see as many hops between columns as along columns, although symmetry would lead to $\langle \Delta x \rangle = \langle \Delta y \rangle = 0$. Instead we see no hops between columns at all, due to the much weaker electronic coupling between columns as shown in figure 5. By calculating the transfer integrals between each pair of molecules we reproduced the strong coupling caused by co-planar aromatic rings. However the distribution of transfer integrals does not promote net charge transport along columns either, the distribution is symmetric with respect to $\Delta z$.

The distribution of $\Delta G_{ij}$ is weakly asymmetric with respect to $\Delta z$ - it is this asymmetry that leads to net flow of charge carriers. The asymmetry caused by the change in energy due to the applied field between molecules $i$ and $j$ is $q\Delta \phi = -q \vec{F} \cdot \vec{r}_{ij}$ where $\vec{F}$ is the local field and $\vec{r}_{ij}$ is the displacement between the molecules. The exponential decay of the transfer integrals with separation means increasing the asymmetry by increasing the nearest neighbour separations is not possible but increasing
the applied field does increase the mobility. The largest transfer integrals inside columns are linked to an intermolecular separation \(d=0.4 \text{ nm parallel to the field so with an applied bias of } 2V |\vec{q}_F(\vec{r}_{ij})| = 0.585k_B T\). Comparing the thermal energy to the driving field energy we can see why charge flux is so small and why rattling motion dominates at low applied fields.

We used the KMC trajectories to define a measure of locally correlated charge flow and thus to identify edges (directed molecular pairs as shown in figure 2) that carry high traffic, but contribute little to flow: and conversely edges that carry relatively traffic but are well connected in terms of flow. More important to particle flux is the connectedness of edges with large transfer integrals to create a pathway. We see that the disordered system has the same range of transfer integrals, compared to the ordered system yet the charge transport is slower. The lack of spatial correlations between edges with good transport properties means that it is unlikely carriers will reach good edges and if they do are unlikely to move far away. This resolved the paradox that the disordered phase contains edges that carry an order of magnitude more traffic than the columnar phase, yet performs worse far away. This resolved the paradox that the disordered system yet the charge transport is slower. The lack of spatial correlations between edges with good transport properties means that it is unlikely carriers will reach good edges and if they do are unlikely to move far away. This resolved the paradox that the disordered phase contains edges that carry an order of magnitude more traffic than the columnar phase, yet performs worse with respect to overall charge transport. To achieve efficient charge transport over device length scales it is necessary to have a continuous chain of hops, all with reasonable electronic coupling. Furthermore, the weighting of any single edge is a poor indicator of how effective that edge is in terms of long-range transport. There is little correlation between edge traffic and the average traffic of its neighbours. Assuming that the structural order of a system is compatible with high electronic coupling, as in \(\pi\)-stacked systems, we can directly correlate structural ordering to the motion of charges.

The hop with the slowest rate is the most critical hop with respect to the overall transport time along the chain, both in terms of being the slowest hop forward but also increasing the relative probability of a reverse hop back along the chain. Reducing the variance in edge weights means that the probability of one pathological molecule pair in a chain is reduced, this leads to improved charge transport across the entire chain. Isolated high-weight edges host high traffic without longer-range flow.

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