

A map of high mobility molecular semiconductors

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The charge mobility of molecular semiconductors is limited by the large fluctuation of intermolecular transfer integrals, often referred to as off-diagonal dynamic disorder, which causes transient localisation of the carriers' eigenstates. Using a recently developed theoretical framework, we show here that the electronic structure of the molecular crystals determines its sensitivity to intermolecular fluctuations. We build a map of the transient localization lengths of all high-mobility molecular semiconductors to identify what patterns of nearest neighbour transfer integrals in the 2D high-mobility plane protect the semiconductor from the effect of dynamic disorder and yield larger mobility. Such map helps rationalising the transport properties of the whole family of molecular semiconductors and is also used to demonstrate why common textbook approaches fail in describing this important class of materials. These results can be used to rapidly screen many compounds and design new ones

with optimal transport characteristics.

In the comparison of the charge transport properties of families of materials it is very desirable to identify few key parameters that can be used to rationalize the observed differences in charge mobility. For example, effective masses and mean free paths can be used for wide band semiconductors, hopping rates between nearest neighbour sites would characterize molecular solids where molecular orbital overlaps are very weak, and relatively simple phenomenological theories are available to describe transport in highly disordered materials. Such a simple reduction is not yet established for the class of high mobility molecular semiconductors, i.e. those displaying mobilities exceeding $\sim 1 \text{ cm}^2/\text{Vs}$ and the most interesting from the technological point of view. As noted many times in the past ¹⁻⁴ band transport models are unsatisfactory for these materials because of a too short mean free path and, similarly, hopping theories yield unphysically high hopping rates ⁵ alongside incorrect temperature dependences, even when they reproduce the absolute mobility.

A number of authors have contributed over the years to develop a transport model that seems suitable for this class of materials and that has now reached a high level of predictive power ^{4,6}. A starting point is the observation that the transfer integrals between nearest neighbouring molecules undergo large fluctuations ⁷: due to the softness of the intermolecular interaction and the sensitivity of the transfer integrals to small nuclear displacements⁸⁻¹⁰, the amplitude of these fluctuations is comparable to the average value of the transfer integrals. Developing on this idea, the carrier dynamics has been studied in models that capture the essential physics, both numerically and

analytically^{7,11–18}, or performing non-adiabatic molecular dynamics simulations in models with atomistic detail^{19,20}. All these studies revealed a common microscopic origin for the unconventional charge transport of organic semiconductors: the dynamic disorder broadens the density of states (DOS) and causes a localisation of the instantaneous eigenstates. This phenomenon, whose origin is genuinely quantum-mechanical, is especially strong at the band edges where charge carriers reside¹², and is intuitively associated with a suppressed mobility. As disorder fluctuates in time, however, one cannot speak of localisation in the traditional sense²¹. Based on extensive numerical evidence^{6,7,11–14,16} it was proposed^{13,14} that the effect of dynamic disorder is to cause a *transient localisation* over a length L_τ within a fluctuation time given by the inverse of the typical inter-molecular oscillation frequency, $\tau \sim 1/\omega_0$. The fact that this initial localisation time must be overcome before charge diffusion can actually take place is responsible for the long known breakdown of semiclassical transport, causing the mobility to fall below the Mott-Ioffe-Regel limit (apparent mean free paths shorter than the inter-molecular distance)³.

The effects of transient localisation were given a mathematical basis using a relaxation time argument^{13,14}, resulting in the following analytical formula for the charge mobility:

$$\mu = \frac{e}{k_B T} \frac{L_\tau^2}{2\tau}, \quad (1)$$

with e the electron charge, k_B the Boltzmann constant and T the temperature. The theory embodied in Eq. (1), which has been shown to agree quantitatively with the most accurate numerical studies presently available^{4,15}, goes beyond the semi-classical band transport approaches (as it contains quantum localization corrections) and it is alternative to traditional hopping theories (which assume that the wavefunction coherence is lost at each hop, an assumption that does not hold in

high mobility materials). This allows us to reliably and efficiently compute the mobility of actual semiconducting materials, treating all possible molecular structures of interest on the same footing and with an affordable numerical effort.

As the transient localisation length L_τ is what ultimately determines how a given material performs, regardless of the detail of the model it would be particularly useful to be able to assess this quantity — and, at once, make quantitative predictions for the charge mobility — without going each time through a complex quantum dynamics simulation. To this aim we proceed to study systematically an *ensemble* of models, encompassing in practice all the different physical situations that can be encountered in organic semiconductors. We start by observing that, with the exception of fullerene derivatives, virtually all molecular semiconductors pack into crystal structures where it is easy to identify a high mobility plane (where the pi-stacking interaction is found), while the mobility perpendicular to this plane is one-two orders of magnitudes smaller²². Because of the weak interactions between molecules, considering a tight binding model with one orbital per molecular site already provides a very accurate description of the electronic structure. We shall therefore consider a 2D lattice with unit vectors \vec{a} and \vec{b} as depicted in Fig. 1a where each molecule is surrounded by 6 neighbours and the nearest neighbour transfer integrals take three different average values J_a , J_b , J_c in the three directions. If we allow for some of the transfer integrals to be null or a pair of parameters to be identical, such lattice can represent practically all of the high-mobility molecular semiconductors discovered so far including the polyacenes (e.g. pentacene, rubrene), substituted pentacenes²³, thienoacenes²⁴, phthalocyanines²⁵, and perylenediimide derivatives²⁶.

Based on the present theoretical framework, we can now investigate how different systems respond to the dynamic disorder that is intrinsic to organic semiconductors. We are interested in computing the localisation characteristics of a large set of J_a , J_b , J_c . In practice, we choose $J_a^2 + J_b^2 + J_c^2 = J^2 = \text{const.}$, defining a one-to-one correspondence between points on a spherical surface and a molecular semiconductor with a given set of transfer integrals. This mapping of an entire set of materials into a spherical surface is very appealing because one can visualise specific properties for all materials into one single graph, as will become clear below. As far as molecular disorder is concerned, we consider the fluctuations of the transfer integrals to be uncorrelated among molecular pairs, a situation that is realised in organic semiconductors owing to the presence of many low frequency phonons which are thermally populated²⁷ (see SI for details). To make a meaningful comparison between different structures while keeping the number of free parameters to a minimum, we fix the fluctuation to a fraction of the average coupling that is the same in all bond directions, i.e. $\Delta J_a/J_a = \Delta J_b/J_b = \Delta J_c/J_c \equiv \Delta J/J$, but this assumption can be released straightforwardly. The values of both J and $\Delta J/J$ will be varied within the range that is computed for realistic materials (see table I in the SI). The value of the fluctuation time τ instead does not vary much between materials and its effect on the mobility is rather weak (details in SI). We shall therefore take a constant $\hbar/\tau = 5$ meV throughout this work, corresponding to a period of molecular oscillation ~ 1 ps.

For each given structure, we first evaluate the localisation properties of the states of energy E ($\ell_\tau^2(E)$, shown in Fig. 1b), and then average this quantity over the thermally populated states in order to obtain the transient localisation length that enters in Eq. (1) (see SI for details). We

explicitly consider holes (top edge of the band), but the extension to electrons is straightforward by exchanging any sign of the J 's. Fig. 1c reports the resulting map of L_τ^2 at room temperature for all possible values of J_a , J_b , J_c on the sphere, for a typical $J = 0.1\text{eV}$ and disorder strength $\Delta J/J = 0.5$. The first observation is that the range of localisation is extremely broad, spanning almost two orders of magnitude between few and $\pi L_\tau^2 \sim 10^2$ molecules, i.e. different electronic structures respond very differently to similar amounts of disorder. Consequently, because it is directly proportional to L_τ^2 , the mobility also varies by more than one order of magnitude for the different systems across the ensemble. The symmetry of the map reflects the symmetry of the electronic Hamiltonian which remains identical if any two transfer integrals are interchanged or the sign of two transfer integrals is changed at the same time (24 symmetry elements). This imposes that three points are symmetry-independent critical points: $(1, 0, 0)$, (α, α, α) and $(-\alpha, \alpha, \alpha)$ with $\alpha = 1/\sqrt{3}$. The point $(1, 0, 0)$ has the strongest localisation (lowest mobility), as expected because it corresponds to a one-dimensional system. Point (α, α, α) represents a system that is *isotropic* in the conducting plane, and the global maximum of the L_τ^2 map. $(-\alpha, \alpha, \alpha)$ is a local maximum with a much smaller L_τ^2 , despite being also isotropic, as explained further below.

To best appreciate the quantitative variations of L_τ^2 , we now study this quantity along the $J_b = J_c$ cut illustrated in Fig. 1c (dashed line). This cut includes both the point of maximum symmetry (α, α, α) corresponding to $\theta_0 = \arccos(1/\sqrt{3}) \simeq 0.955$, and the one-dimensional structures at $\theta = 0, \pi$. Note that, following the symmetry properties discussed in the preceding paragraph, a cut with $J_b = -J_c$ (or, considering electrons instead of holes) is equivalent to exchanging θ with $\pi - \theta$. Fig. 1d reports L_τ^2 vs. the azimuthal angle θ for three different values of $J = 0.05, 0.1$

and 0.15 eV, illustrating a key finding of this work that validates the generality of our spherical map: the mobility in the transient localisation regime depends only marginally on the *absolute* magnitude of the transfer integrals J . This can directly be contrasted with the results of band theory, $\mu \propto 1/m^* \propto J$, and hopping theory, $\mu \propto J^2$, which both predict this parameter to be determinant for charge transport. In view of this result, the broadly accepted strategy of increasing the molecular overlaps to improve the material performances does not appear to be a very efficient one: as Fig. 1d suggests, experimental efforts should rather focus on optimising the *relative* values of the J s in the different bond directions.

The linear cut in Fig. 1d confirms that the transient localisation is strongest for the one-dimensional structures at $\theta = 0, \pi$, where L_τ becomes comparable with the lattice spacing a , while localisation effects are considerably weaker for more isotropic band structures²¹, leading to larger localisation lengths and proportionally larger mobilities. An immediate consequence is that the highest performing materials should be sought among the ones close to the critical point at $\theta = \theta_0$, where the materials are less susceptible to the effect of dynamic disorder. This corresponds to molecular systems where the transfer integrals with the non-equivalent nearest neighbours are as close as possible in absolute value and their product has a *positive* sign (a negative product would correspond instead to the much lower maximum at $\pi - \theta_0$).

To assess the validity of the present map, in Fig. 3 we compare our theoretical results with the experimental mobility of several compounds for which a mobility decreasing with temperature has been demonstrated, to which the theory applies. The map works very well despite sizeable

variations in transfer integrals between the considered compounds. For example, the calculated transfer integral in the direction of largest mobility in TMTES-Pn is $J_a = 258$ meV and only 76.8 meV in C10-DNBDT, from which one could naively expect the mobility of the former to be larger than that of the latter, which is opposite to the experimental situation. The remarkable agreement shown in Fig. 1d provides experimental confirmation that the absolute value of J is not a key parameter in determining the mobility, as expected from transient localisation theory. According to the map, the very high mobility observed for C₁₀-DNTT and C₁₀-DNBDT can be explained by their vicinity to the "hot-spot" with similar hopping integrals in magnitude and sign. The low mobility of TMTES-pentacene is due to its quasi one-dimensional pattern of transfer integrals which, expectedly, is not beneficial for transport. Much more surprising and excellently captured by our model is the relatively small mobility measured for pentacene, a long standing mystery of organic electronics. The hopping integrals are large and fairly isotropic for this material but their product is negative, i.e. pentacene is on the "wrong" side of the semiconductor map, where the mobility is bound to be 4-5 times lower according our model. Finally, the very low mobility measured in TIPS-pentacene can be easily explained from the anomalously large thermal disorder present in this material (see Table I in SI and Fig. 4 below) which leads to a very suppressed L_τ^2 when compared to the universal curve.

Having developed an ensemble of systems and having a broadly applicable theory at our disposal, we can look at further important aspects of the charge transport mechanism systematically. For example, the temperature dependence of the mobility is often used to discriminate between different transport models. The exponent of the observed power-law dependence, $\mu \sim T^{-p}$, can be

monitored along the parameter θ to study its dependence on the electronic structure. We find, as illustrated in Fig. 3a, that for the considered type and level of disorder the exponent p varies in the range $0.7 < p < 1.3$, with the largest value found for a band structure similar to that of rubrene.

We can use our results to benchmark the predictions of standard textbook approaches, which ignore the crucial quantum effects that are instead retained here. Within Marcus theory, as well as any other non-adiabatic hopping theory, the mobility depends strongly on the absolute value of the transfer integrals ($\mu \propto J^2$), but very little (< 5%) on their relative values in different directions, which is incompatible with the experimental results reported in Fig. 2. Moreover, because they rely on inter-molecular transfer *probabilities* rather than on quantum mechanical amplitudes, hopping theories cannot capture the dramatic difference between molecular structures where the sign of one transfer integral is exchanged (i.e. θ and $\pi - \theta$ on the map), and would therefore provide totally wrong predictions in materials such as pentacene (cf. Fig. 1d). This is shown in Fig. 3b, where we have reported the θ -dependence of the hopping mobility considering a fixed reorganization energy across the ensemble and properly including the effect of inter-molecular fluctuations on the transfer rates (see SI). The mobility computed from semiclassical band-theory, to lowest order in the molecular fluctuations (see SI), is also reported in Fig 3b. Here some trends of Eq. 1d are qualitatively reproduced, in particular the existence of an absolute maximum at the isotropic point $\theta = \theta_0$. However, the band-theory mobility is generally largely overestimated, because it does not account for the initial localisation processes that are a key aspect of the transport mechanism in organic semiconductors⁴, and the predicted dependence on J is again incompatible with the experimental observations. Finally, band transport is unable to reproduce the systematic variations

of the power-law exponent of the temperature dependence, especially where localisation effects are the strongest ($\theta \simeq 0, \pi$, see Fig. 3a).

The anisotropy of the mobility is another experimentally relevant parameter that has been used to distinguish between competing transport models. We show in Fig. 3c that even though the mobility itself is both qualitatively and quantitatively different from the predictions of band transport theory, the ratio μ_y/μ_x closely follows the anisotropy of the effective mass, at least within our choice of an isotropic relative disorder $\Delta J/J$ (this is true everywhere except at $\theta = 2\theta_0$, where the effective mass m_x^* diverges). Therefore, measuring a sizeable transport anisotropy which coincides with the predictions of band theory is by no means a guarantee of semiclassical band-like behaviour.

While the mobility with its anisotropy and temperature dependence are very sensitive to the electronic structure we have found that other parameters have a fairly uniform effect across our ensemble. If we include the presence of randomness in the on-site energies to reproduce the effect of a moderate (static) extrinsic disorder we find a mobility reduced below the intrinsic values calculated in the clean limit (Fig. 4) but the suppression factor is rather weakly dependent on the material band structure (in the $\sim 0.55 - 0.7$ range in the case considered here of a Gaussianly distributed site-disorder of spread $\Delta = 0.7J$). For larger levels of disorder, the intrinsic transport is eventually washed out and Eq. (1) breaks down, and alternative approaches based on incoherent hopping should be used instead.^{28,29} It was proposed theoretically^{4,14} on the basis of Eq. (1), and used as an experimental guide^{30,31} that improved materials can be designed if the dynamical off-

diagonal disorder is overall reduced. We have verified (also in Fig. 4) that a reduction of dynamical disorder of 20% causes an increase of the mobility of a factor of about $1.5 - 2$ for all values of θ . The fact that the reduction of on-site (extrinsic) disorder or off-diagonal (intrinsic) disorder have the same effect regardless of the electronic structure is a valuable insight for the design of new materials. In practice one should attempt to reduce both of these while, independently, trying to identify materials that are close to the optimal points with $\theta=\theta_0$. We predict that a factor up to ~ 10 in mobility is controlled solely by the sensitivity to the dynamic disorder, which is described by our semiconductor map. We also note that the idea that good materials should display a weak coupling between charge carrier and intramolecular vibrations to produce a weaker band renormalization³² is not challenged by this approach: local electron-vibration coupling, which is not sufficiently strong to induce polaronic localisation, renormalises J and ΔJ isotropically and in equal measure, because intramolecular modes are much faster (in the 100-220 meV range and with ~ 2 order of magnitude smaller amplitude) and therefore uncorrelated with low frequency modes. Finally, existing computational tools for organics³³ can be easily adapted to evaluate the mobility with material specific parameter sets, including anisotropic or correlated fluctuations, i.e. relaxing some of the simplifications introduced here to build a universal map. An illustration of the excellent accuracy that can be reached when transient localisation theory is supplemented by an *ab initio* determination of the relevant microscopic parameters is given in Fig. S3 of the SI file.

In essence, our systematic study unveils the characteristics rendering holes in a molecular semiconductor more *insensitive* to disorder and therefore displaying a higher mobility. This finding, supported by the available experimental data, leads to a new design principle, distinct and

complementary to those already known: in addition to reducing both intrinsic and extrinsic disorder, the top molecular semiconductors should have intermolecular transfer integrals with all their six neighbours similar in magnitude and identical in sign, regardless of their overall absolute values. In principle, one could use this model to make hypotheses on the chemical structure of new molecular semiconductors from scratch, relying on the ever improving field of crystal structure prediction ³⁴. However, one can more immediately and efficiently analyse databases of known molecular crystals in search of compounds with the desirable electronic characteristics: it would take few minutes per compound to establish its position on the map with the help of electronic structure calculations, noting that the vast majority of known compounds have not been purified and grown in large crystals to the point of displaying intrinsic mobility. This protocol will enable a more systematic and rational process of material selection for organic electronics.

Methods

To calculate the transient localisation length for each choice of J_a , J_b , J_c on the ensemble of tight-binding models defined in Fig. 1a, we use transient localisation theory in the relaxation time approximation (RTA) as described in Refs. ^{4,13,14} (more details can be found in the SI). The numerical simulations of the carrier dynamics are performed using the efficient technique introduced in Ref. ³⁵ on clusters consisting of 320000 molecules, which is sufficient for convergence at the considered levels of disorder and temperature. For the comparison with textbook approaches in Fig. 3, the hopping mobility is evaluated assuming hopping rates proportional to the square of the hopping integral, including an enhancement due to intermolecular fluctuations. For the band transport theory calculations we consider the same ensemble of tight-binding models and evaluate the mobility to lowest-order in the fluctuations of the transfer integral ¹² as described in the SI.

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Figure 1 Electronic structure and transient localisation map. **a**, crystal structure of a generic molecular crystal with lattice spacing a and three different nearest-neighbour transfer integrals, J_a , J_b , J_c . **b**, DOS and energy resolved transient localization length calculated for an isotropic electronic structure with $J = 0.1\text{eV}$, $J_a = J_b = J_c = J/\sqrt{3}$, thermal fluctuation $\Delta J/J = 0.5$ and fluctuation time $\tau = \hbar/5 \text{ meV}$ (lengths are in units of a). **c**, map of the thermally averaged L_τ^2 on the spherical surface defined by $J_a^2 + J_b^2 + J_c^2 = J^2$. All data are calculated for $k_B T = 25\text{meV}$ and averaged over the two directions x and y . **d**, L_τ^2 along the cut $J_b = J_c$ shown in Fig. 1c, as a function of the azimuthal angle $\theta = \arccos(J_a/J)$, for three different values of J .

Figure 2 Experimental validation. The interval of values of L_τ^2 found in Fig. 1d (shaded area) is compared here with the experimentally measured mobility in different compounds (right axis). The experimental values have been divided by the area $\sim ab/2$ per molecule in the highly conducting plane to eliminate the trivial dependence on geometric lattice parameters contained in Eq. (1). Source of experimental data and full chemical names given in the SI.

Figure 3 Charge transport characteristics on the ensemble of organic semiconductors. **a**, Power-law exponent of the mobility $\mu \propto T^{-p}$. The inset shows the actual temperature dependence calculated on the three points highlighted in light gray (one-dimensional lattice), dark gray (transfer integral pattern of rubrene) and black (isotropic transfer integrals). We have taken $\Delta J/J \propto \sqrt{T}$ from the equipartition principle and fixed

the fluctuation to the reference value $\Delta J/J = 0.5$ at $T/J = 0.25$ with $J = 0.1$ eV. The dashed line is the result from semiclassical band transport theory. **b**, Mobility from non-adiabatic hopping (dotted, in arbitrary units) and Boltzmann semiclassical transport theory (dashed, calculated taking a representative value $a = 7.2\text{\AA}$), compared with the results of Fig. 1d at $J = 0.1$ eV; the mobility was obtained using Eq. (1) and taking a characteristic fluctuation time $\tau = 0.13$ ps (see SI). **c**, Anisotropy of transport, μ_y/μ_x compared with the band mass anisotropy m_x^*/m_y^* (dashed line). The x direction is parallel to the a unit vector.

Figure 4 Effect of thermal and extrinsic disorder. Transient localisation calculated by varying the amount of disorder in the samples, and mobility from Eq. (1) assuming $a = 7.2\text{\AA}$. Blue, circles: reducing the intrinsic thermal fluctuations of the transfer integrals from $\Delta J/J = 0.5$ to $\Delta J/J = 0.4$. Gray, diamonds: adding a Gaussian extrinsic disorder of spread $\Delta = 0.7J$.