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Toward Quantitative Prediction of Charge Mobility in Organic Semiconductors: Tunneling Enabled Hopping Model

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Charge mobility is an essential figure of merit for organic semiconductors. It reaches ~30 cm² V⁻¹ s⁻¹ for solution processed printing field effect transistors (FETs),[1] close to the performance of inorganic semiconductors. There has been great progress achieved toward the theory of quantitative prediction of charge mobility by computational chemistry.[2] The intermolecular charge transfer integral V characterizes the charge delocalization, while the intramolecular charge trapping energy λ characterizes the trap effect arising from the electron–phonon interaction. The relative ratio of these two quantities dictates the transport mechanism: band-like surfing or localized charge hopping.[3] Generally speaking, when $\lambda \gg V$, the charge can be regarded as localized as described by Marcus theory, which has been successful in molecular design and has gained wide popularity with chemists and material scientists.[4] There are also some systems with close intermolecular packing which fall in the range of $\lambda \sim V$. Indeed, experiments on single crystals of polyacenes and rubrene showed that the charge transport is governed by the band model, because the λ and V values are close.[5] However, a recent experiment by Sakanoue and Sirringhaus (SS) on a solution processed 6,13-bis(triisopropylsilyl ethynyl)-pentacene (TIPS-P) FET device showed a "band-like" transport behavior ($\frac{d\mu}{dT} < 0$) but the optical spectroscopy indicated a localized charge signature.[6] Namely, the charge modulation spectroscopy (CMS) showed a sub-band absorption around 1.3 eV, which coincides well with the absorption band for the electrochemically doped (single cation) TIPS-P molecule. For temperatures ranging from 43 to 300 K, the charge induced absorption

occurs at the same position, only the bandwidth becomes larger at high temperature, *i.e.*, the localization length (one molecule) is independent of temperature. Further measurement showed that the Hall mobility is different from FET mobility, indicating the transport is indeed hopping-like:[7] in a band model, one can define group velocity as the first order derivative of band energy with respect to the momentum, due to which the Lorentz force causes the Hall effect; while in a hopping model, the velocity is not well-defined, the Hall mobility was shown to be about 1/3 of the drift (FET) mobility.[8]

This is a quite paradoxical observation, namely, the FET measurement indicated "band-like" while the optical measurement indicated localization. In this work, we present a tunneling enabled localized charge transport model by considering full quantum charge transfer theory and dynamic disorder effects coupled with kinetic Monte Carlo simulation. It is a model with Holstein polaron plus Su–Schrieffer–Heeger contribution, thus more realistic. We first show that the localized charge can present a "band-like" transport behavior through a quantum tunneling effect and we show that the dynamic disorder effect tends to enhance the charge mobility, instead of limiting transport.

SS presented an explanation based on two types of charge localization mechanisms: at low temperature, the charge is trapped by impurities and at either higher temperature or larger bias voltage, the de-trapped charge is localized by thermal fluctuation as proposed by Troisi et al.[9] We point out here that if localization were dependent on temperature, the localization length along with the optical feature (charge induced absorption) would shift with temperature. This is not the case in the experiment. Instead, the experimental observation showed that the charge induced absorption peak in the FET device is always at the same position as in the singly charged molecule. Previous quantum chemistry calculations for TIPS-P showed that the side-chain substitution reduces V from 100 meV in pentacene to about 20 meV, and at the same time, increases λ from 100 meV in pentacene to 220 meV.[10a] Thus, with $\lambda \gg V$, we do expect a localized charge description. The "band-like" transport by local charge fits well with a mechanism proposed earlier by us considering quantum nuclear tunneling effects.[11] Under such a picture, the dynamic disorder (non-local electron–phonon coupling) can be incorporated by a classical molecular dynamics simulation coupled with a kinetic Monte Carlo simulation.[12] For a large class of organic semiconductors with $\lambda \gg V$, our method can be used to predict charge mobility. We will show that such an approach can not only explain the "exotic"

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behavior for TIPS-P, but also give quantitative charge mobility values. We then apply such an approach to electron transport systems: naphthalene and perylene diimide derivatives as well as perfluoroalkyl modified oligothiophene.

In the Holstein small polaron limit, the charge becomes fully localized on a single molecule and the hopping rate to the neighbor molecule is often described by the semiclassical Marcus theory $k_{CT} = \frac{|V|^2}{\hbar} \left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp(-\frac{\lambda}{4k_B T})$. The diffusion constant can be simply expressed as $D = a^2 k_{CT}$ (a is the intermolecular spacing) and the mobility is expressed by the Einstein relationship $\mu = eD/k_B T$.[13] Such a dimer model has been extended to three-dimensional networks by adding rate-biased weights.[3a] Yang et al. proposed a random walk simulation method to account for the spatial inhomogeneity,[14] in parallel to a percolation model developed for a porous medium, which is valid for general three-dimensional molecular packing structures. Chang and Chao suggested an interesting rule that "non-bonding" character at frontier orbitals can largely reduce charge reorganization energy based on extensive quantum chemistry calculations.[15] Brédas and collaborators have proposed practical material design strategies aimed at enhancing V or reducing λ.[16]

We noted that the commonly employed Marcus formula was derived in the high temperature approximation ($k_B T \gg \omega$) and with the short-time approximation (strong electron–phonon coupling), where ω is the typical frequency of the environment. In the original Marcus theory, the charge transfer process in $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$, the charge reorganization involved only solvent motion, which is of low frequency character. For organic semiconductors, the localized charge strongly interacts with the high frequency intramolecular vibration, typically, $k_B T \ll \omega$. Thus, the high temperature approximation fails. Previously, there have been attempts to account for the quantum effect through the Marcus–Levich–Jortner formula with one effective quantum mode, namely, by defining either a linear or square Huang–Rhys factor weighted frequency: $\bar{\omega} = \sum_i S_i \omega_i / \sum_i S_i$[17] or $\bar{\omega}^2 = \sum_i S_i \omega_i^3 / \sum_i S_i \omega_i$,[18] where S_i is the Huang-Rhys factor for mode i. The definition of an effective mode is not clear. Since a full quantum all-mode charge transfer rate formula is available,[11] there is no need to make approximation or define an effective mode. We thus seek a more rigorous approach:

$$k_{i \to f} = \frac{|V|^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp \left\{ -\sum_j S_j \left[(2\bar{n}_j + 1) - \bar{n}_j e^{-i\omega_j t} - (\bar{n}_j + 1) e^{i\omega_j t} \right] \right\} \quad (1)$$

Here, $\bar{n}_j = 1/(e^{\hbar \omega_j / k_B T} - 1)$ is the occupation number for the j-th phonon mode with frequency ω_j, and S_j measures the coupling strength between the carrier on-site energy and the j-th intramolecular vibration mode. In the limits of strong coupling ($\sum_j S_j \gg 1$) so that short time approximation can be applied ($e^{i\omega t} \approx 1 + i\omega t + (i\omega t)^2/2$) and in high temperature ($\hbar \omega_j / k_B T < 1$, $\bar{n}_j \approx k_B T / \hbar \omega_j$), Equation (1) goes back to the Marcus formula with $\lambda = \sum_j \lambda_j = \sum_j S_j \hbar \omega_j$, where λ_i is the charge

reorganization energy through the i-th intramolecular vibration mode, which can be calculated through a displaced harmonic oscillator model. The convergence of numerical integration of Equation (1) can be achieved by choosing the vibrational mode with the largest Huang-Rhys factor with short time approximation. Intermolecular coupling V between molecules m and n is calculated with the site-energy overlap correction method:[19]

$$V_{mn} = \frac{V_{mn}^0 - \frac{1}{2}(e_m + e_n) O_{mn}}{1 - O_{mn}^2} \quad (2)$$

Here, $e_m = <\Phi_m|H|\Phi_m>$, $V_{mn}^0 = <\Phi_m|H|\Phi_n>$, and $O_{mn} = <\Phi_m|O|\Phi_n>$, where $\Phi_{m(n)}$ is the frontier molecular orbital of an isolated molecule $m(n)$ in the dimer representation. Namely, for hole (electron) transport, the HOMO (LUMO) should be plugged in. H and O are the dimer Hamiltonian and the overlap matrices, respectively.

In the above description, the electronic coupling V is kept fixed, and the vibration involved in the charge transfer process is only from intramolecular contribution. The non-local electron–phonon coupling effects arising from the intermolecular vibration in this work is included by molecular dynamics (MD) simulation followed by a kinetic Monte Carlo simulation performed for a molecular crystal at a fixed lattice constant with a supercell of $5 \times 5 \times 3$, a replica of the original unit cell. The COMPASS force field[20] is applied, which can reproduce the crystal structure at room temperature. Constant temperature is achieved after equilibration for 60 ps using a Berendsen thermostat in the NVT ensemble at different temperatures at a time step of 1 fs. The simulation time is 120 ps, and 2000 frames were extracted by taking a snapshot every 60 fs along the trajectory. For each snapshot, density functional theory (DFT) calculations are performed to obtain the intermolecular transfer integral V. A discrete Fourier transformation is then performed for the fluctuation of V: $\Delta V_{mn}(t) = V_{mn}(t) - <V_{mn}>$, in the form of:

$$V_{mn}(t) = \langle V_{mn} \rangle + \sum_{k=0}^{N/2} Re V_k \cdot \cos(\omega_k t + \varphi_0)$$

$$+ \sum_{k=0}^{N/2} Im V_k \cdot \sin(\omega_k t + \varphi_0) \quad (3)$$

where N is the total number of MD snapshots, $Re V$ and $Im V$ are the amplitudes, based on which the contributions of intermolecular vibration modes to the transfer integral fluctuation can be obtained. The phase factor ϕ_0 is chosen randomly because there is hardly any correlation between transfer integrals fluctuation for different pairs. At each step of the kinetic Monte Carlo simulation, the phase factor for each Fourier component is randomly set as $r\omega kt$, where r is a random number uniformly distributed in [0, 1], ωk is the Fourier frequency, and t is the total simulation time. The probability of hopping from site m to the nearest neighbor site n is determined as $P_{mn} = k_{mn} / \sum_{n'(\neq n)} k_{mn'}$ and the simulation time is incremented by $1/\sum_n k_{mn}$.[21] The diffusion constant is obtained as $D = <l^2>/(2dt)$ averaging over 5000 trajectories, where d is the spatial dimension.
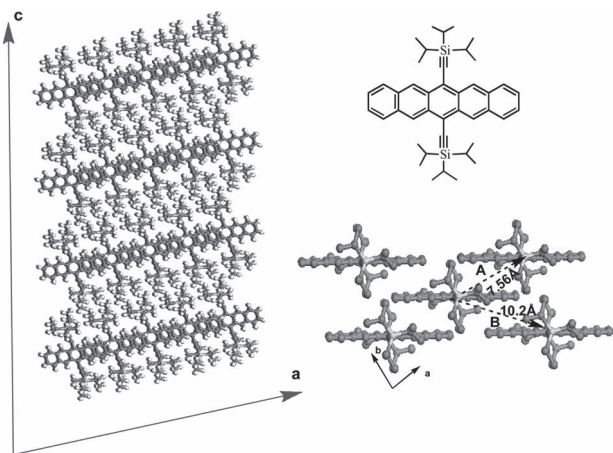
Scheme 1. (Left) A 5 × 5 × 3 supercell structure of a TIPS-pentacene crystal of thin film phase. (Right top) molecular structure and (right bottom) an *ab* plane structure extracted from the supercell. Two pairs of molecules are indicated as dimer A and B.
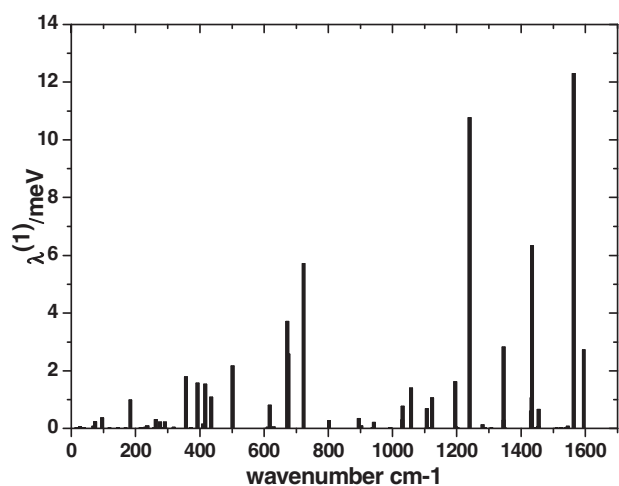

Figure 1. Contribution of the normal modes to the charge reorganization energy $\lambda^{(1)}$, which is the relaxation energy for singly positively charged molecule from the equilibrium structure of the neutral molecule.
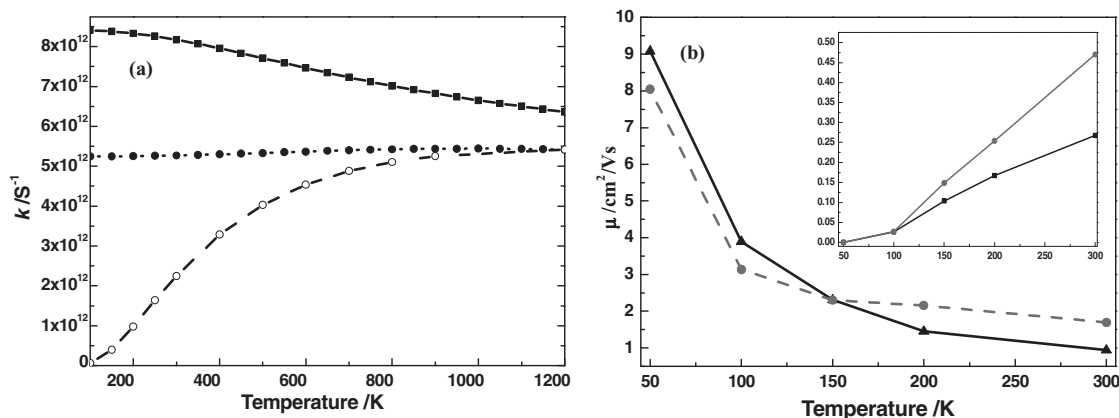
Molecular structure and crystal packing for TIPS-P[10b] are shown in **Scheme 1**.

The quantities that appear in Equation (1) can be directly calculated by DFT. Namely, the intermolecular integral *V* is calculated for all the neighboring molecular pairs. The vibration frequencies for neutrals and cations are calculated based on their optimized molecular geometry by DFT for neutral molecules and unrestricted DFT for singly charged molecules, respectively, with a BhandHLYP functional and a 6-31G(d) basis set. The corresponding Huang–Rhys factors are obtained through normal mode analysis under the displaced harmonic oscillator approximation. The relaxation energy for each mode (electron–phonon coupling) is depicted in **Figure 1**,

The charge reorganization energy obtained by summing over all the normal mode relaxation energy is 217 meV, very close to 222 meV calculated from full geometry optimization, indicating the harmonic oscillator approximation is successful. We compare the quantum rate with the classical one in **Figure 2**a. The semiclassical Marcus charge transfer (CT) rate increases with *T* while the quantum rate is insensitive and slightly decreases with *T* at higher temperature. We also present a result from the quantum CT rate but with short time approximation, which deviates from the full quantum rate even at high temperature. This is because the assumption of short time approximation $\sum_j S_j >> 1$ is not fully satisfied, since our numerical calculation gives $\sum_j S_j = 1.97$. It is found that the semiclassical Marcus rate approaches the quantum rate around *T* ~1000 K, indicating that the high temperature approximation is not valid for organic semiconductors at room temperature.

We then look at the non-local intermolecular vibration contribution. A DFT calculation is performed to obtain the intermolecular transfer integral *V* at each MD snapshot at different temperature. For dimer A, the distribution of *V* is depicted in Figure S1, Supporting information. It is seen that at 300 K, the deviation of *V* is much larger than the *V* at equilibrium, indicating that the thermal fluctuation or dynamic disorder is severe for TIPS-P. Following the dynamic Monte Carlo simulation outlined earlier, we obtained the final results as depicted in Figure 2b, where for the sake of comparison, results obtained from fixed averaged *V*s are also presented, both for full quantum and the semiclassical cases.

Figure 2. a) Hole transfer rates (*k*) for dimer A: filled squares for full quantum rate, filled circles for quantum rate with short time approximation, and open circles for semiclassical Marcus theory. b) Hole mobility: dashed line for dynamic disorder and solid line for dynamically averaged static *V*s. The classical Marcus rate result is shown in the inset.

We conclude here that i) the quantum nuclear tunneling effect does give a $\frac{d\mu}{dT} < 0$ band-like behavior for localized charge in TIPS-P, in sharp contrast to Marcus theory (compare the inset in Figure 2b); ii) the dynamic disorder tends to reduce the mobility at lower temperature but to enhance the mobility at room temperature. This is precisely the phonon-assisted current mechanism; and iii) the room temperature hole mobility is calculated to be 1.7 cm² V⁻¹ s⁻¹, very close to 1.5 cm² V⁻¹ s⁻¹ of the SS experiment.[8] Such good agreement, both qualitative and quantitative, indicates the power of prediction for molecular design.

To further explain the experimentally observed temperature-dependent charge modulation spectroscopy in TIPS-P, we employ a vibration correlation function formalism[22] coupled with time-dependent DFT/CAM-B3LYP/6-31G(d) to investigate the temperature dependence of the optical absorption spectra both for singly charged and neutral TIPS-P (details see Supporting Information). Upon charging, there occurs a molecular geometry relaxation, which results in a molecular orbital level shift, presenting several sub-gap absorption bands due to the appearance of a singly occupied molecular orbital (SOMO), or polaron level. Both the calculated peak position and the temperature-broadened width are in good agreement with the experiment, see Figure S2, Supporting Information, which confirms the local nature for the transport carrier. The line-width increases naturally with temperature due to the increasing phonon population of the intramolecular vibration. We note that such a broadening was attributed to be an average over various domains of charge localization induced by dynamic disorder.[6] Our result does not support such a claim.

Last, we extend our approach to more solution processed n-type organic semiconductors, which have attracted extensive attention recently. The naphthalene and perylene diimide (NDI, PDI) derivatives as well as perfluoroalkyl modified oligothiophene (Figure S3, Supporting Information) have demonstrated high electron mobility ranging from 0.1 to 6 cm² V⁻¹ s⁻¹.[23] It should be noted that the experimental charge mobility depends on several external factors, including device fabrication condition, material processes, and disorder and impurities present in the organic film. Theoretical calculations can not only figure out the underlying transport processes and mechanism, but also can give an intrinsic value, which can serve as some standard. We theoretically study here the charge transport of eight n-type organic semiconductors with the quantum method discussed above (more details are presented in the Supporting Information). For comparison, the mobility obtained from Marcus theory is also taken into consideration with available experimental data in Table S1, Supporting Information, and **Figure 3**. It is seen that i) our quantum CT method correlates well with the experimental results; and ii) Marcus theory always underestimates the mobility and the even the trend does not correlate the experiment.

To summarize, we present a quantum tunneling enabled localized charge transport model which can reliably predict the charge mobility in organic semiconductors. We first explain the exotic behavior found in TIPS-P where optical spectra indicated charge is localized on one single molecule but the transport measurement showed "band-like" temperature dependence.
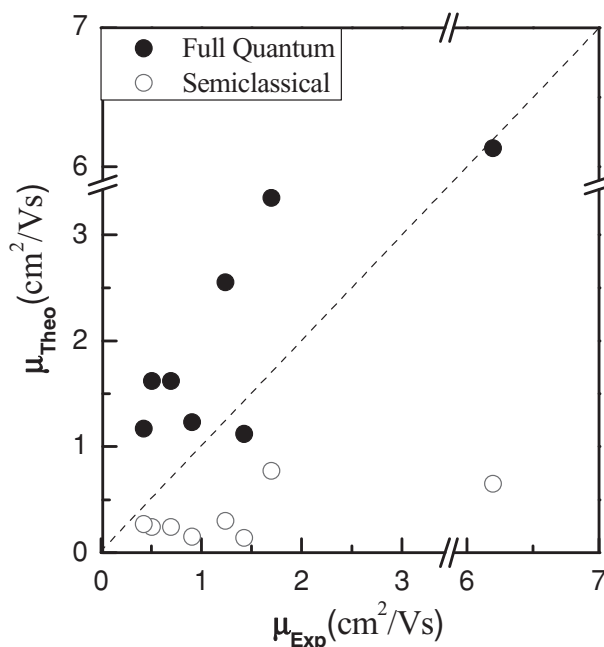

Figure 3. Correlation between the experimental and the calculated electron mobility for molecules **1–8** (for structures see the Supporting Information) with full quantum and the semiclassical Marcus methods.

It is explained by the quantum nuclear tunneling effect of the localized charge coupled with high frequency intramolecular vibration. The charge induced absorption is thus naturally of singly charged cation character. At room temperature, the dynamic disorder does not limit transport, but enhances mobility by a phonon-assisted current mechanism. This picture is consistent with the experimental facts: i) for the whole temperature range, localized charge was manifested by CMS, with a peak position independent of temperature; and ii) at high bias voltage when the trap levels are filled, the mobility is "bandlike" $\frac{d\mu}{dT} < 0$. Previous explanations relied on combined mechanisms: trap induced localization at low temperature and dynamic disorder induced localization at high temperature. We point out that different localization mechanisms should present different and temperature-dependent localization length, which is absent in the experiment. The optical absorption peak position is very sensitive to the number of molecules with one charge on it. Namely, the charge induced absorption peak position would constantly shift with temperature and bias if localization were caused by dynamic disorder. This is certainly not the case in the experiment. We conclude that for a large class of organic semiconductors with $V \ll \lambda$, charge mobility can be predicted from our tunneling enabled local charge hopping model. We then applied this method to eight n-type compounds including naphthalene and perylene diimide derivatives and perfluoroalkyl-modified oligothiophenes. Excellent agreement with experiment is found. It is also indicated that the commonly employed semiclassical Marcus theory not only underestimates the charge mobility value but also does not correlate the general trend for these eight compounds.