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Theoretical modelling of carrier transports in molecular semiconductors: molecular design of triphenylamine dimer systems

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Abstract

Charge transport in molecular systems and biosystems can be different from that in inorganic, rigid semiconductors. The electron–nuclear motion couplings play an important role in the former case. We have developed a theoretical scheme to employ the Marcus electron transfer theory coupled with a direct diabatic dimer model and the Brownian diffusion assumption to predict the carrier mobility for molecular materials. For triphenylamine, a typical molecular transport material, the design strategies regarding the formation a cyclic or a linear dimer are evaluated from theoretical calculations for the carrier mobility. We made a comparison between the mobility and the electrical polarizability. It is found that in the case of triphenylamine dimer, these two quantities have different trends. The fact that the macrocycle possesses higher mobility but lower polarizability than the linear chain is due to the difference in the reorganization energy. The theoretical predicted temperature dependences are analysed within the hopping mechanism. The calculated room-temperature mobilities are in reasonable agreement with experimental values.

1. Introduction

Molecular electronics (ME) is under intensive investigation for applications in nanotechnology. ME mainly consists of two areas: electronic devices at the molecular scale, and device applications with molecular materials. There has been increasing interest in the latter case, namely, conjugated organic semiconducting materials in electronic device applications [1–9], due to the properties of low cost, versatility of chemical synthesis, ease of processing, and flexibility.

The most important parameter to characterize the performance of a semiconducting field-effect transistor (FET) is the room-temperature carrier mobility. For inorganic semiconductor single crystals, the room-temperature mobility can reach as high as 10^3 – 10^6 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Traditionally, organic materials usually possess a very low mobility of 10^{-6} – 10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Recent progresses have demonstrated that a mobility of around a few tenths of a $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ can be realized in organic FET devices [10], and even larger values of about a few tens of $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ have been reported and predicted [2–4, 11].

The molecular structure, relative orientations and solid-state packing have a strong influence on the charge transport

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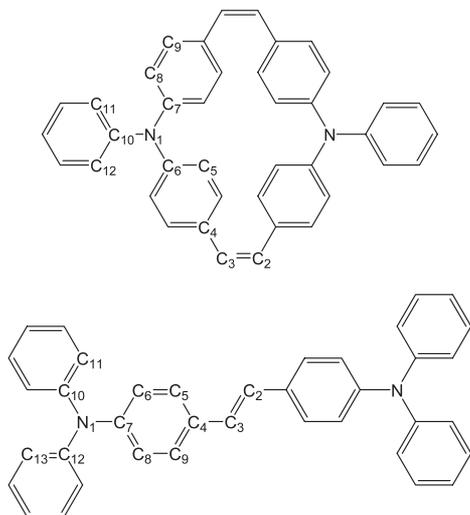


Figure 1. Chemical structures of compound **1** (upper panel) and compound **2** (lower panel).

behaviour [12–14]. Triphenylamine (TPA) derivatives have been widely employed as hole transport materials in molecular electronics applications [15, 16]. However, their performances have been found to be unsatisfactory due to their amorphous nature in the solid state [17–20]. In order to improve the mobility of TPA, a design strategy of making dimers of TPA, either in the form of a macrocycle (compound **1**) or of a linear chain (compound **2**) has been demonstrated with success [21]; see the molecular structures in figure 1. A double bond linkage was chosen for more extended π -conjugation [22–24]. Our theoretical calculation has been found to be in good agreement with the experiments results [21], and gave a deeper insight into how the molecular structure changes the transport properties. In [21], the present authors have presented the computational scheme as well as the calculated hole mobilities combined with experimental results. In this theoretical work, which can be regarded as a theoretical paper to complement [21], we will focus on the following issues which have not previously been discussed in detail: (i) descriptions of the theory behind the computation; (ii) methodological comparison with other approaches; and (iii) a discussion of the transport mechanism and the temperature dependence, in addition to prediction of the mobility. Furthermore, we have made a comparison between the molecular polarizability and the mobility. Intrinsically, at the molecular level, the electrical conduction is related to the polarizability, except for the influence of the contact with electrodes. Namely, from the Kubo linear response theory, both the conductivity and polarizability are proportional to the current–current correlation function [25]. However, at the material level, these two quantities can behave differently. The polarizability is mostly related to the local response of a molecule to the external electric field, while the mobility is a global response. It has been long established that, for a nonlinear optical response, a linear molecule chain is more favourable than a ring or a ball [26, 27]. It is thus interesting to have a look at the situations for transport behaviour.

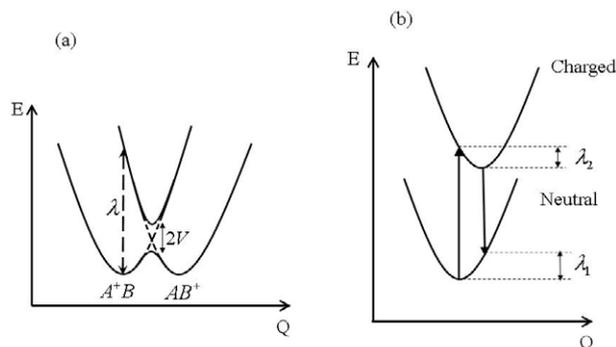


Figure 2. (a) Schematic representation of a charge exchange reaction pathway for a hole transferred from molecule A to molecule B through a transition state by weak (nonadiabatic) coupling. Q is a single effective reaction coordinate (or normal mode) representing an ensemble of modifications in molecular geometry. (b) When the intermolecular relaxation is neglected, (a) can be regarded as a sum of two separate processes with the two energetic terms λ_1 and λ_2 defining the internal reorganization energy for a neutral molecule and its cation.

2. Theoretical background and methodology

Generally speaking, there are two types of carrier motion in materials: (i) the coherent band model, as in the case of rigid inorganic semiconductors, and (ii) the incoherent hopping model. In the band model, the carrier moves as a highly delocalized plane wave in an energy band with a relatively long mean free path ($\sim \mu\text{m}$). The hopping integral is large compared with dynamic disorder, for instance, the reorganization energies resulting from charge transfer from one molecule to another. The band model is usually suitable for inorganic semiconductors where the interaction between different sites is through strong valence bonds. At high temperature, the dynamic structure disorder may invalidate the band transport model, suggesting that hopping may be the dominant mechanism at room temperature. The basic characteristic of this model is that the lattice phonons, both intramolecular and intermolecular vibrations, are strongly coupled with the charge motion.

Here, we model the charge transport as a Brownian motion process, as described by a particle diffusion process, see [21, 28], coupled with the Marcus theory for the electron transfer rate for a self-exchange reaction process [29–31]:

$$W = \frac{V^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left(-\frac{\lambda}{4k_B T} \right). \quad (1)$$

There are two major parameters that determine the self-exchange electron-transfer (ET) rate: the intermolecular transfer integral (V) and the reorganization energy (λ); see figure 2(a). The reactant (the initial state) is a molecular dimer $|M_1^+ M_2\rangle$ and the product (final state) is $|M_1 M_2^+\rangle$, with M^+ denoting the cationic molecule M . The reaction coordinate Q in figure 2(a) is an ensemble of geometric deformations of the dimer system, namely, the modification of the bond lengths, bond angles, etc, during the reaction: $M_1^+ \rightarrow M_1$, and $M_2 \rightarrow M_2^+$. Here, we neglect the influence of intermolecular interaction on the molecular deformation. Thus, the total

reorganization energy λ can be expressed as a sum of two relaxation energy terms [32, 33]: (i) the difference between the energies of the neutral molecule in its equilibrium geometry and in the relaxed geometry characteristic of the ion; and (ii) the difference between the energies of the radical ion in its equilibrium geometry and in the neutral geometry, as sketched in figure 2(b). We calculate the reorganization energies at the density functional theory (DFT) level using the B3LYP functional and 6-31g(d) basis set [12]. According to the Marcus theory, the reaction barrier is $\lambda/4$ because of the nature of the displaced harmonic oscillator shown in figure 2(a). It should be pointed out that, in this work, the polarization effects from the surrounding molecules, as well as the charge reorientation, have been neglected. This value is difficult to evaluate theoretically and is one of the challenges for theoretical chemistry [34–36]. However, for the non-polar molecules investigated here, this effect should be minor.

The next step is to calculate the electronic coupling term. Here we use the single-crystal structures of compounds **1** and **2** to generate all the possible nearest-neighbour intermolecular hopping pathways; see [21]. The electronic coupling can be obtained either by Koopmans' theorem, which has been widely employed [37], or by directly evaluating the coupling element for the frontier orbitals [38, 39]. In the former case, the charge transfer integral corresponds to half of the splitting of the HOMO or LUMO levels for holes or electrons. Brédas and co-workers have extensively investigated the parameters governing the transport on many conjugated systems by frontier orbital splitting [40]. Valeev *et al* cautioned recently that when the dimer is not cofacially stacked, the site-energy correction due to the crystal environment should be taken into account [41].

In this work, we adopt a direct approach to investigate the charge transport properties [38, 39]. Troisi and Orlandi have applied this approach to calculate charge transfer coupling in DNA and obtained quite satisfactory results in comparison with experiments. This formalism has also been employed in a parameterized way to investigate the spin-dependent exciton formation rates in polymer electroluminescence [42]. The electronic coupling for hole transfer in this scheme can be written as

$$V = \left\langle \phi_{\text{HOMO}}^{0,\text{site1}} \left| F \right| \phi_{\text{HOMO}}^{0,\text{site2}} \right\rangle. \quad (2)$$

$\phi_{\text{HOMO}}^{0,\text{site1}}$ and $\phi_{\text{HOMO}}^{0,\text{site2}}$ represent the HOMOs of two non-interacting molecules from DFT. F is the Kohn–Sham–Fock matrix for the dimer; its density matrix is constructed from non-interacting molecular orbitals. In practice, the Fock matrix is evaluated as

$$F = SC\varepsilon C^{-1} \quad (3)$$

where S is the overlap matrix for the dimer taken from the crystal structure, and the Kohn–Sham orbital C and eigenvalue ε are obtained by diagonalizing the zeroth-order Fock matrix without any self-consistent field iteration [38]. The GGA functional is chosen to be pw91pw91/6-31g(d). It has been shown that this choice of functional gives the best description for the bandwidth of organic solid [43]. Intuitively, one would think of a Hartree–Fock orbital because by definition it is a real electronic orbital and the Kohn–Sham orbital is fictitious. However, it has been known that the Hartree–Fock bandwidth for a polymer is always about 20%–30% larger than the result

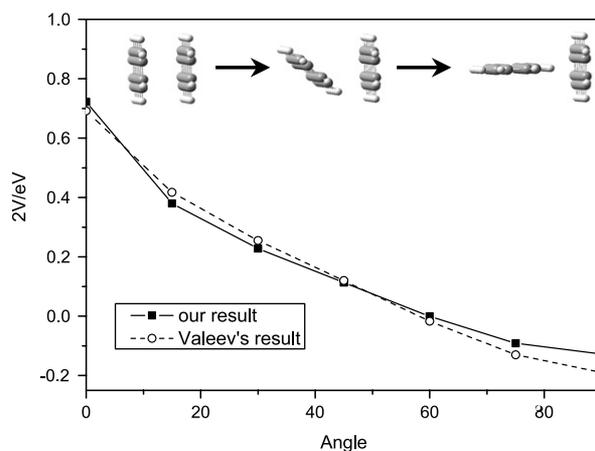


Figure 3. Electronic coupling between a pair of pentacenes separated by a distance R and a tilt angle γ , as parameterized by $R(\gamma) = 3.5 + 1.5 \sin(\gamma)$. Namely, the centre-to-centre distance is 3.5 \AA ($\gamma = 0$) for the face-to-face arrangement, and 5 \AA for the perpendicular face-to-edge arrangement. The solid line is obtained from our direct method, and the dashed line is from the site-energy corrected energy splitting method of Valeev *et al* [41].

from (photoemission) experiments [44]. And from previous studies, the electronic coupling from the DFT orbital is usually about 20% less than that of the Hartree–Fock orbital [38, 39]. Thus, we can believe that the Kohn–Sham orbitals from DFT can give a better description for the orbital coupling, which is proportional to the bandwidth.

Note that this diabatic direct approach is not only simpler than the energy splitting approach: for a complex system, it is difficult to find the pair of split orbitals originating from the individual frontier orbital; but also it avoids the problem of site-energy difference arising from the symmetry in the crystal. In fact, the splitting method can sometimes lead to wrong answers if the two molecules of the dimer are inequivalent in the crystal. In fact, this fact has been largely ignored before. Even in a dimer formed by same molecule, the site energies can be different for the two molecules because they polarize each other differently if they are inequivalent in the crystal. Namely, the energy level splitting can be expressed as $\sqrt{(2V)^2 + (e_1 - e_2)^2}$ only when the molecule stacks symmetrically (cofacially for instance), the site energies are equal, $e_1 = e_2$, and the energy splitting corresponds to twice the electronic coupling, $2V$. Our diabatic approach directly evaluated the V term, regardless of whether the site energies are equal or not.

To illustrate the robustness of the direct approach adopted here, we take the example of pentacene dimer, which has been widely investigated as an organic semiconductor; see figure 3. It is clearly shown that for the full range of tilt angles between two molecules in the dimer, the direct method gives essentially the same results as the site-energy corrected splitting approach of Valeev *et al* [41]. We note that many previous work have fully neglected this correction and could eventually lead to wrong molecular design strategies.

The diffusion coefficient can be approximately evaluated as [21, 28, 45]

$$D = \lim_{t \rightarrow \infty} \frac{1}{2d} \frac{\langle x(t)^2 \rangle}{t} \approx \frac{1}{2d} \sum_i r_i^2 W_i P_i. \quad (4)$$

i represents a specific hopping pathway with r_i being the hole hopping distance (intermolecular centre-to-centre distance). $d = 3$ is the spatial dimension. Here, we assume that the hole hopping occurs only between nearest-neighbour molecules. P is the relative probability for the i th pathway, $P_i = W_i / \sum_i W_i$. The basic assumption is that the hole transport is a slow process during which the solvent and solute molecules have enough time to reach equilibrium. This is pertinent for a soft organic system. The drift mobility of hole hopping, μ , is then evaluated from the Einstein relation $\mu = eD/kT$. All the quantum chemistry calculations are performed with the Gaussian03 package [46].

3. Results and discussion

The B3LYP/6-31g(d) optimized molecular geometry for compounds **1** and **2** are presented in table 1, where the neutral and cation systems are also compared. For compound **1**, the geometrical structure of the radical cation differs slightly from the neutral one. The torsion angles of the phenyl groups change within a narrow range from 3.8° to 5.6°. In the case of compound **2**, a wide range of 8.7°–15.6° is observed. The closed ring structure of compound **1** restricts the rotation of the phenyl groups. This fact indicates the intrinsic difference of the relaxation processes occurring in these two systems: in compound **1**, the small differences between the neutral and cation geometries lead to a low reorganization energy of 0.173 eV: for the neutral molecule the energy difference between its equilibrium geometry and in the optimized cation geometry is 0.088 eV, and for the radical cation the energy difference between its equilibrium geometry and the neutral geometry is 0.085 eV, the total reorganization energy being $0.088 + 0.085 = 0.173$ eV. But for compound **2**, where a large geometry relaxation occurs in the biphenyl core, the reorganization energy reaches a value of 0.317 eV: 0.171 eV from the neutral molecule plus 0.146 eV from the cation.

The average room-temperature hole drift mobilities are calculated to be $2.7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **1**, and $1.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **2**. These values compare very well with the experimental results of $0.5\text{--}1.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **1** and $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **2** [21], respectively, except that the theoretical value for **2** is about one order of magnitude larger than the experimental value. In fact, our experimental partners explained that since compound **2** was found to have much lower mobility than compound **1**, the subsequent processing and optimization of materials have been carried out carefully. We have good reason to believe that if these were done for **2**, the agreement of theory and experiment would be much better. We note that the electron couplings for the two systems do not differ much; for instance, the largest matrix elements of V are 8.65×10^{-3} eV and 6.26×10^{-3} eV, respectively for **1** and **2**. However, the calculated mobilities differ by one order of magnitude. As we mentioned before, the charge transfer reaction barrier is $\lambda/4$. Thus it is reorganization energy which really makes the difference.

We then examine the temperature dependence. In general, at low temperatures, a band-like behaviour is expected in which the mobility decreases with temperature. As the temperature increases, the hopping mechanism starts to dominate for organic materials in which the mobility increases

Table 1. B3LYP-optimized geometrical parameters for the neutral and cation structures of compounds **1** and **2**. Bond lengths, bond angles and dihedral angles values (only the symmetry-unique values) are listed in this table.

	Neutral	Cation	Δ
Compound 1			
C ₂ C ₃	1.35 Å	1.36 Å	0.01 Å
C ₃ C ₄	1.48 Å	1.46 Å	−0.02 Å
N ₁ C ₆ , N ₁ C ₇	1.42 Å	1.41 Å	−0.01 Å
C ₇ C ₈	1.40 Å	1.41 Å	0.01 Å
C ₈ C ₉	1.40 Å	1.39 Å	−0.01 Å
C ₁₀ C ₁₁ , C ₁₀ C ₁₂	1.41 Å	1.40 Å	−0.01 Å
C ₁₀ N ₁ C ₇ , C ₁₀ N ₁ C ₆	121.3°	121.1°	−0.2°
C ₆ N ₁ C ₇	117.4°	117.9°	0.5°
C ₁₁ C ₁₀ N ₁ C ₇	35.1°	40.7°	5.6°
C ₅ C ₆ N ₁ C ₇	44.0°	40.2°	−3.8°
C ₈ C ₇ N ₁ C ₁₀	46.1°	41.3°	−4.8°
Compound 2			
C ₂ C ₃	1.35 Å	1.37 Å	0.02 Å
C ₃ C ₄	1.46 Å	1.43 Å	−0.03 Å
C ₄ C ₅ , C ₄ C ₉	1.41 Å	1.42 Å	0.01 Å
C ₅ C ₆ , C ₈ C ₉	1.39 Å	1.38 Å	−0.01 Å
C ₆ C ₇	1.41 Å	1.42 Å	0.01 Å
C ₇ C ₈	1.40 Å	1.42 Å	0.02 Å
N ₁ C ₇	1.42 Å	1.38 Å	−0.04 Å
N ₁ C ₁₀ , N ₁ C ₁₂	1.42 Å	1.43 Å	0.01 Å
C ₄ N ₁ C ₃	120.1°	121.3°	0.2°
C ₄ N ₁ C ₂	119.7°	117.5°	−2.2°
C ₂ N ₁ C ₃	120.2°	121.2°	1.0°
C ₁₁ C ₁₀ N ₁ C ₇	42.2°	51.2°	10.0°
C ₁₃ C ₁₂ N ₁ C ₁₀	42.5°	51.2°	8.7°
C ₆ C ₇ N ₁ C ₁₀	39.6°	24.0°	−15.6°

with temperature. And at very high temperature, at which the thermal energy becomes large enough to dissociate the polaron, the residual charge is scattered by thermal phonons, and as a result the mobility decreases again with temperature [47]. Assuming that the reorganization energy and transfer integrals are temperature independent, the theoretical temperature dependence of the mobility is depicted in figure 4. Hopping models predict the mobility to have a temperature dependence of $T^{-3/2} \exp(-\lambda/4k_B T)$. The exponential law dominates at low temperatures and the power law $T^{-3/2}$ dominates at high temperatures after the barrier is fully overcome and the charge behaves like band motion. The maximum is directly related to the barrier height $\lambda/4$. It should be noted that the present model can only be applied at high temperature and small electron coupling. At low temperature, the quantum tunnelling effect of nuclear motion should be considered. And if the coupling is strong, then it is impossible to define a barrier, and the charge transport should be described by the nonequilibrium Green's function approach. More general transport theory is under development in our group.

Intrinsic molecular conductance is closely related to the molecular electric polarization. Namely, a more polarizable molecule tends to transport charge more easily. This is obviously seen from the close similarity in expressions of the two quantities [25]: both are derived from dipole–dipole (or velocity–velocity) correlation functions. To compare the transport behaviour with the electric polarization, we have calculated the static molecular first- and third-order

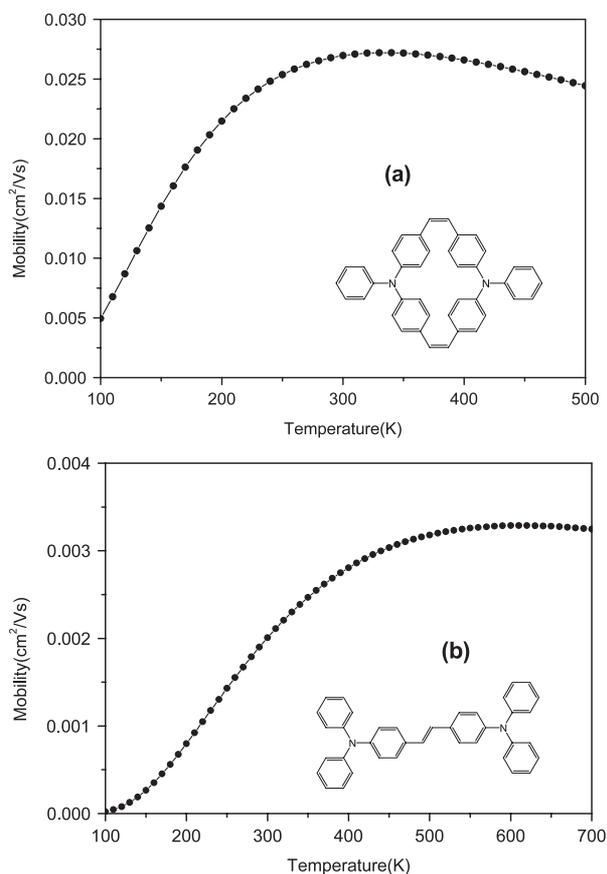


Figure 4. The predicted temperature dependence of the drift mobility for a macrocycle (a) and a linear chain (b). Both are typical examples of thermally activated electric conduction.

Table 2. The calculated first- and third-order polarizability values of compounds **1** and **2**, indicating that the linear chain (compound **2**) is more polarizable than the macrocycle (compound **1**).

Compound	1	2
α ($\times 10^{-24}$ esu, or \AA^3)	125.75	131.66
γ ($\times 10^{-36}$ esu)	147.95	548.00

polarizabilities using a finite-field method. The finite electric-field value is chosen to be as small as 0.004 au. The results are presented in table 2. In contrast to the intuitive perception, we point out that the more conductive molecule (compound **1**) is less polarizable. This is fully understandable: for a single molecule, it should be expected that more polarizable means more conductive, but for molecular materials, the diffusion process is dominant, and then the conduction is dependent on the barriers that originate from the lattice relaxation as well as the intermolecular interaction.

4. Conclusion

To summarize, we have used the Marcus electron transfer theory and first principles by assuming a hopping mechanism to investigate the drift mobility of triphenylamine-based molecular transport materials. The first-principles diabatic direct coupling method is applied to calculate the charge transfer couplings; this method is found to be in full

agreement with the site-energy corrected frontier orbital splitting method. The theoretical room-temperature mobility is in good agreement with experimental values. The theoretical temperature dependence of the mobility under the hopping mechanism is shown, which is subject to be verified by experiment. It is also pointed out that the a polarizable molecule could be less conductive due to the charge reorganization effect in molecular materials.

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