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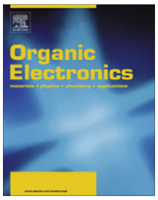

Theoretical comparative studies of charge mobilities for molecular materials: Pet versus bnpery

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ABSTRACT

Charge mobility is the most important issue for organic semiconductors. We calculate the electron and hole mobilities for prototypical polycyclic hydrocarbon molecules, perylothiophene (pet) and benzo(*g*,*h*,*i*)-perylene (bnpery) using Marcus electron transfer theory coupled with a diabatic model and a homogeneous diffusion assumption to obtain the charge mobility. The first-principles DFT calculations show that the hole mobility is about an order of magnitude higher than the electron mobility in pet. However, we find that for bnpery, the electron and hole transports are balanced, namely, very close in mobility, indicating the possible application in light-emitting field-effect transistor. The crystal packing effects on the frontier orbital coupling are found to be essential to understand such differences in transport behaviors.

1. Introduction

The charge transport mechanism in organic materials has been studied for many years [1–3]. In the application of field-effect transistors (FET) [4–6], light-emitting diodes (LED) [7–9], and photovoltaic cells (PVC) [10], organic materials possess great potentials. The charge mobility is the most important parameter in the performance of electronic devices such as organic field-effect transistor [11]. Traditionally, the organic molecules or polymers are believed to have very low carriers mobility, $\sim 10^{-5}$ cm^2/Vs. However, recently tremendous progresses have been made in increasing the mobility for organic semiconductor. In the single crystal of rubrene field-effect transistors, mobility has been found to be greater than 15 cm^2/Vs [12], and for the purified pentacene single crystal, the FET mobility has been measured to be 35 cm^2/Vs [13]. These values already compete well with the inorganic semiconductors: the typical room temperature mobilities for silicon single crystals, polycrystallines, and amorphous silicon are around a few hundreds, a few tens, and a few tenth of cm^2/Vs, respectively.

In this work, we make a comparative study on the transport properties of a class of polycycle aromatic hydrocarbons, perylothiophene (pet) [14] and benzo(*g*,*h*,*i*)-perylene (bnpery) [15] through first-principles calculation, in order to gain insights in the theoretical design of organic transport materials. The structure of pet is similar to that of bnpery. Pet has been grown in micrometer single crystal wires and has been successfully applied to fabricate transistor [16] with a room temperature mobility of 0.8 cm^2/Vs. The molecular structures are shown in Fig. 1. The crystal structures can be found in Refs. [14,15]. We will

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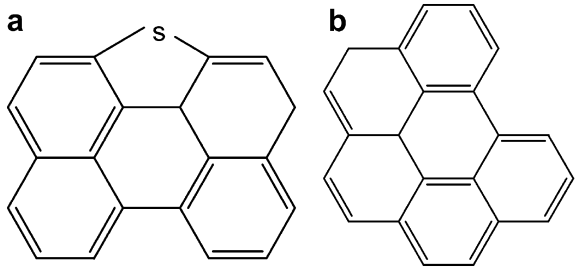

Fig. 1. Molecular structures of pet (a) and bnpery (b).

show that even though these molecules are quite similar in structure, they exhibit very different intrinsic transport properties.

2. Theoretical and computational methods

There exist two extreme models to describe the mechanism of charge transport: the coherent band model and the thermally activated hopping model. At very low temperature, the transport mechanisms in well ordered organic materials are believed to be described by a band-like model [17,18]. In this limit, the positive (hole) and negative (electron) charge carriers are fully delocalized, and the mobility can be evaluated through the effective mass approach. Even in the Holstein–Peierls model when evaluated at the first-principles level, the electron–phonon scattering induced bandwidth narrowing is not enough to give a fully localized charge picture [19]. It is found that both electron and hole transports fall in the coherent band-like regime. At room temperature, due to the thermal disorder and scattering, the transport is more appropriately described with hopping model [20–24]. In this case, the charge carriers are localized on a single molecule, jumping from one molecule to the adjacent molecule, with the hopping rate described by Marcus theory,

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

Here, k_B is the Boltzmann constant, T is the temperature, V is the transfer integral between donor and acceptor, and λ is the reorganization energy. It indicates that the rate of charge hopping depends on two microscopic parameters: the electronic coupling term V and the reorganization energy λ The reorganization energy λ is usually expressed as the sums of internal and external contributions. The internal reorganization energy is induced by relaxation in the molecular geometry, and the external reorganization energy is caused by polarization of the surrounding medium, namely, all the other molecules in the bulk materials. The external contribution to the reorganization energy is quite complicated to evaluate, which depends on the molecular permanent dipole moments as well as the polarizability. We will simply assume some values for the external contribution to discuss the influences on the mobility. The internal reorganization energy λ_i is further divided into two parts: $\lambda_\mathrm{i}^{(1)}$ and $\lambda_\mathrm{i}^{(2)}$, where $\lambda_\mathrm{i}^{(1)}$ corresponds to the geometry relaxation energy of one molecule from neutral state to charged state, and $\lambda_\mathrm{i}^{(2)}$ corresponds to the geometry relaxation energy from charged state to neutral state, see Fig. 2 [25,26].

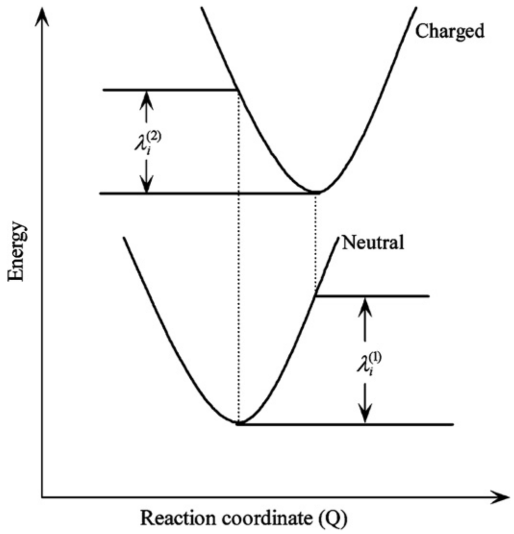

Fig. 2. Sketch of the potential energy surfaces for the neutral state and the charged state. The relaxation energies $\lambda_i^{(1)}$ and $\lambda_i^{(2)}$ are indicated.

In the evaluation of λ, the two terms were computed directly from the adiabatic potential energy surfaces [27,28],

$$\lambda = [E^{(1)}(A^+) - E^{(0)}(A^+)] + [E^{(1)}(A) - E^{(0)}(A)] \tag{2}$$

Here, $E^{(0)}(A)$, $E^{(0)}(A^+)$ are the ground-state energies of the neutral and charged states, $E^{(1)}(A)$ is the energy of the neutral molecule at the optimized charged geometry and $E^{(1)}(A^+)$ is the energy of the charged state at the geometry of the optimized neutral molecule.

Based the Einstein relation, the carrier mobility is obtained from the following Eq. (3):

$$\mu = \frac{e}{k_B T} D \tag{3}$$

where D is the diffusion constant. If we assume the charge motion is a homogeneous random walk, the diffusion constant can be evaluated as [29]:

$$D = \lim_{t\to\infty} \frac{1}{2n} \frac{\langle x(t)^2 \rangle}{t} \approx \frac{1}{2n} \sum_i d_i^2 k_i P_i = \frac{1}{2n} \frac{\sum_i d_i^2 k_i^2}{\sum_i k_i} \tag{4}$$

d is the intermolecular center-to-center distance and $n = 3$ is the spatial dimension. The hopping time between two adjacent molecules is the inverse of the rate constant $1/k$. The probability for a specific hopping route is $P_i = k_i/\Sigma_i k_i$. Namely, it is a 3-d averaged diffusion process. It is clear that the mobility is linearly proportional to the electron transfer rate. Within this mechanism, it is assumed that the localized electron can only hop between adjacent molecules, in sharp contrast to the band-like picture, where the electron is delocalized in several molecules.

The molecular structures of pet and bnpery are optimized both in the neutral and the charged states. These calculations are done at the first-principles DFT level using hybrid B3LYP functional with 6-31G* basis set [30]. All the calculations are performed in Gaussian 03 package [31].

The electronic coupling term, or the intermolecular transfer integral quantifies the electronic coupling between two interacting molecules, which is obtained through a direct approach. Namely, for the hole (electron) transport, the coupling between frontier orbitals of the two neighboring molecules is calculated from Eq. (5) [32,33].

$$V_{ij} = \langle \phi_1^0 | \hat{F}^0 | \phi_2^0 \rangle \tag{5}$$

V_{ij} is the transfer integral, ϕ_1^0 is the unperturbed frontier orbital of molecule 1, ϕ_2^0 is molecule 2 in the dimer. $\hat{F}^0$ is the Kohn–Sham–Fock operator of the dimer obtained with the unperturbed density matrix. Using the standard self-consistent-field procedure, the molecular orbitals and density matrix of the two individual molecules are calculated separately. These are used to evaluate the Kohn–Sham–Fock matrix of the dimer. This approach has been widely employed for organic molecular systems [34–36]. The calculations are carried out at the DFT level using pw91pw91 functional with 6-31G* basis set. It is shown by Huang and Kertesz, this functional gave the best description for intermolecular coupling term [37]. We have shown that this direct method for the coupling is equivalent to the site-energy corrected frontier orbital splitting method [35] and this direct method offers remarkable simplicity in computation.

3. Results and discussion

The calculated results of the relaxation energies $\lambda_i^{(1)}$ and $\lambda_i^{(2)}$ and reorganization energies λ in pet and bnpery are shown in Table 1. $\lambda_i^{(1)}$ and $\lambda_i^{(2)}$ are found to be nearly equal. It is also found that the total reorganization energy of hole for pet is slightly larger than that of bnpery. The reorganization energies for electron are nearly identical for both molecules.

Table 1
The relaxation energies $\lambda_i^{(1)}$ and $\lambda_i^{(2)}$, and the reorganization energies in pet and bnpery (in eV)

Molecular	Hole transfer			Electron transfer		
	$\lambda_i^{(1)}$	$\lambda_i^{(2)}$	λ_i	$\lambda_i^{(1)}$	$\lambda_i^{(2)}$	λ_i
Pet	0.066	0.069	0.135	0.084	0.088	0.172
Bnpery	0.063	0.062	0.125	0.082	0.082	0.164

The crystal structures for the molecules are shown in Fig. 3. The pet forms herringbone packing structure. In bnpery, two molecules form one bone in the skeleton, in place of one molecule in the herringbone structure. Starting from the crystal structure, we arbitrarily choose one molecule as the initial position for the charge to diffuse. The intermolecular transfer integrals with all the

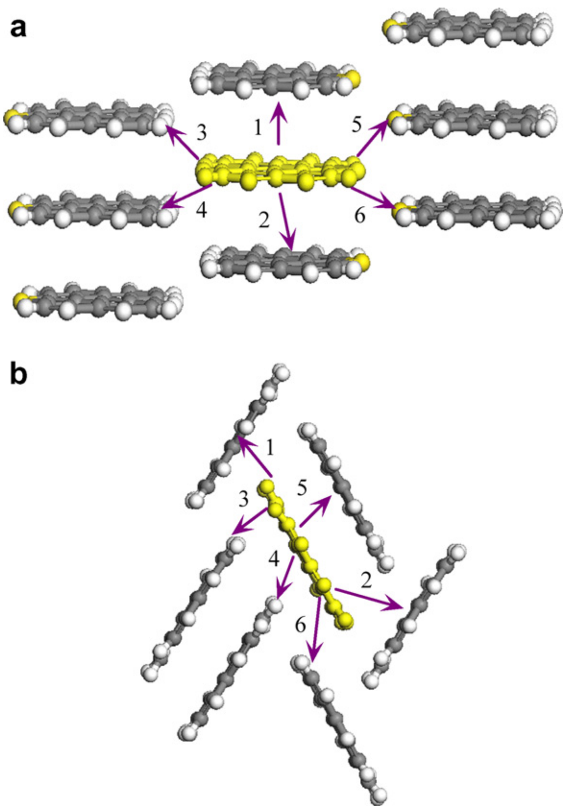

Fig. 4. Crystal structure and hopping routes in pet (a) and bnpery (b).

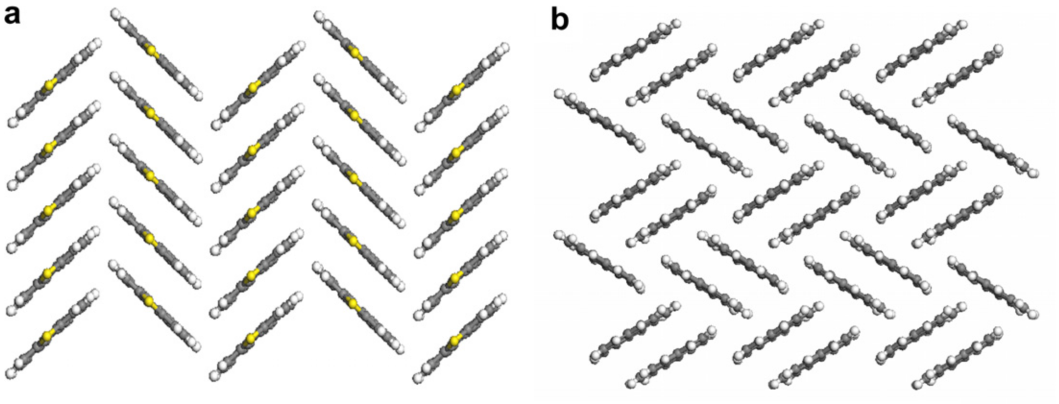

Fig. 3. (a) Herringbone structure of pet (view down the *C* axis), (b) structure of bnpery (view down the *A axis).*

Table 2
The center–center distance and the corresponding hole and electron coupling between the dimer in all the nearest neighbor pathway for pet

Pathway	Distance (Å)	Hole coupling (eV)	Electron coupling (eV)
1	4.52	0.181	6.4×10^{-2}
2	4.52	0.181	6.4×10^{-2}
3	10.21	2.8×10^{-4}	2.1×10^{-3}
4	9.18	2.0×10^{-3}	1.1×10^{-2}
5	8.76	7.8×10^{-4}	5.5×10^{-3}
6	9.89	3.4×10^{-5}	5.0×10^{-4}
Drift mobility ($T = 300$ K, in cm^2/Vs)		5.34	0.40

The calculated room temperature mobilities for electron and hole are given in the last line.

Table 3
The center–center distance and the corresponding hole and electron couplings between the dimer in all the nearest neighbor pathways for bnpery

Pathway	Distance (Å)	Hole coupling (eV)	Electron coupling (eV)
1	7.10	1.8×10^{-2}	3.4×10^{-3}
2	6.30	2.2×10^{-4}	7.5×10^{-3}
3	6.30	2.2×10^{-4}	7.5×10^{-3}
4	7.10	1.8×10^{-2}	3.4×10^{-3}
5	4.18	3.5×10^{-2}	8.1×10^{-4}
6	8.63	5.9×10^{-3}	2.6×10^{-2}
Drift mobility ($T = 300$ K, in cm^2/Vs)		0.17	0.21

The calculated room temperature mobilities for hole and electron are given in the last line.

adjacent molecules in a dimer model are evaluated. The most important six pathways (dimers) are shown in Fig. 4.

The transfer integrals for hole (for HOMO) and electron (for LUMO) are calculated, which are listed in Tables 2 and 3. The electronic coupling is determined by the relative distance and orientations of the interacting molecules. Except the case of electron coupling for bnpery, the parallel packing mode usually yields larger coupling term than the edge-corner packing, because the cofacial stacking structure is expected to provide more efficient orbital overlap.

Due to the electronic coupling for hole is much larger than for electron in pet, the calculated hole mobility is about one order of magnitude larger than that for electron. However, in bnpery, the largest transfer integral for hole is only 0.035 eV at pathway 5, and the largest transfer integral for electron is 0.026 eV at pathway 6. The hole mobility obtained is very close to and slightly less than that of electron mobility, the values being 0.17 cm^2/Vs and 0.21 cm^2/Vs, respectively. The theoretical calculation predicts that bnpery can be made as balanced transport materials. Even though the mobility is not as high as others, it can find application in light-emitting field-effect transistor.

It is intriguing to understand why bnpery behaves differently from pet. We then compare the frontier orbitals and packing modes in these two molecules, as illustrated in Fig. 5.

In pet, for the HOMO level, the wavefunction coefficients show a sign alternation for consecutive benzene along the aclinic direction, and the center-to-center offset of the two molecules of the cofacial dimer is nearly identical for benzene, and the displacement is also in the aclinic direction for pathway 1, the most efficient charge transfer route. The overall overlap is enhanced by the in-phase bonding (antibonding) of one molecular on top of the bonding (antibonding) of the other molecule for HOMO. However, for the LUMO level, the overall overlap is reduced by the cancellation of bonding (antibonding) orbital with the antibonding (bonding) interactions. Thus, the hole

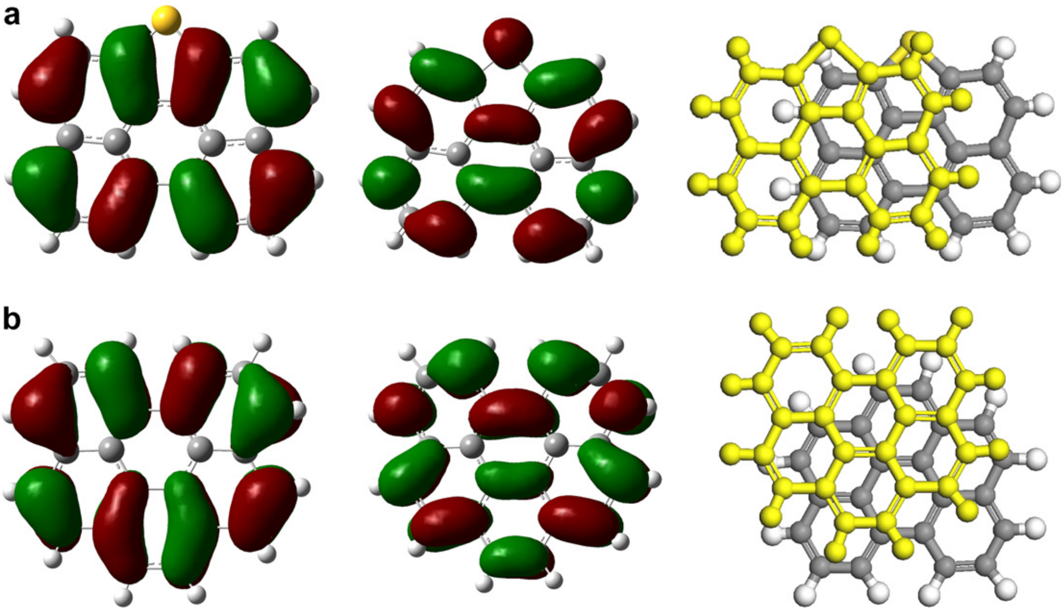

Fig. 5. HOMO, LUMO and the most important packing for (a) pet; and (b) bnpery.

transfer is more favored than the electron in pet, see Table 2. While in bnpery, the displacement between the two molecules occurs along the incline direction in pathway 5, the most efficient charge transfer route. Thus, the overall overlaps are reduced by out-phase cancellation of bonding with antibonding interaction for both HOMO and LUMO. Namely, both electron and hole possess similarly reduced charge transfer coupling terms, see Table 3. Thus, from the intermolecular interaction point of view, the hole transport character for pet and the balanced transport character for bnpery can be explained. At the same time, it also explains the reduced mobility in bnpery, namely, the cancellation of charger transfer couplings originated in packing out-phase displacement.

So far, we have completely neglected the external reorganization energy λ^e. This quantity is difficult to evaluate. Here, we simply calculate the hole mobilities for pet and bnpery as a function of λ^e, see Fig. 6. It is found that when λ^e goes from 0 to 0.2 eV, the mobility decreases about one order of magnitude. It should be borne in mind that such evaluation is too simplistic because once the polarization effect of surrounding molecules is considered, the electron coupling term should be also changed. This is out of the capability of present theoretical treatment. In addition, Marcus theory is basically a first-order perturbation in coupling term V. In fact, some of the dimer show quite strong coupling, for instance, $V = 0.181$ eV, even larger than the internal reorganization energy. We are pursuing now to develop a more rigorous approach dealing with strong coupling case.

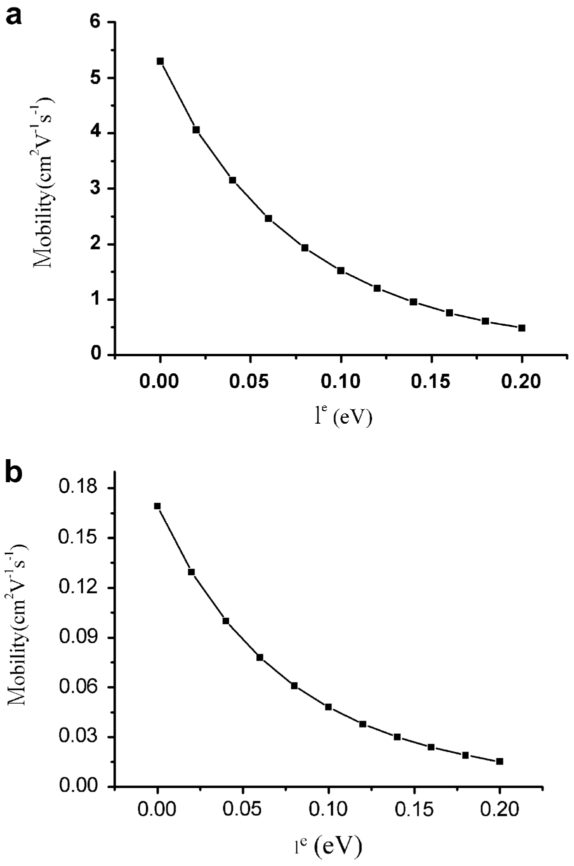

Fig. 6. Theoretical estimation of the room temperature (300 K) hole mobility as a function of external reorganization energy in the range of 0–0.2 eV.

We note that it is found that the carrier type, either electron or hole transport, in organic electronic device is determined by injection. Namely, if electron can be easily injected, then the transport will be *n*-type, and intrinsically, the materials are ambipolar in nature [38]. This view we believe is too simplistic. As we explain in the above paragraph, the intermolecular couplings for HOMO and for LUMO can be different according to the molecular structure. In solid state physics, a realistic crystal usually manifests different bandwidths for valence band and conduction band. Of course, such difference in coupling terms is not as significant as can be considered as the origin of unipolar transport, where injection plays essential role [38].

4. Conclusion

To conclude, by employing the first-principles DFT techniques and the Marcus electron transfer theory, we have comparatively investigated the transport properties for two polycyclic hydrocarbon compounds, pet and bnpery. The coupling terms are evaluated by a direct diabatic model, and the reorganization energies are calculated through adiabatic potential energy surfaces. The crystal packings are found to play essential role to determine the type of carriers in organic materials. In pet, the packing mode tends to enhance the HOMO coupling and to reduce the LUMO coupling, indicating a hole-dominant transport material. While, for bnpery, the packing mode tends to reduce both HOMO and LUMO coupling, which makes bnpery to be a promising material with great application potential in light-emitting field-effect transistor. These conclusions are drawn only based on material structures, without considering the carrier injection complexity.

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