Electronic Structure and Microscopic Charge-Transport Properties of a New-Type Diketopyrrolopyrrole-Based Material

Jin-Dou Huang, a Wen-Liang Li, b Shu-Hao Wen,* c and Bin Dong* a

Recently, diketopyrrolopyrrole (DPP)-based materials have attracted much interest due to their promising performance as a subunit in organic field effect transistors. Using density functional theory and charge-transport models, we investigated the electronic structure and microscopic charge transport properties of the cyanated bithiophene-functionalized DPP molecule (compound 1). First, we analyzed in detail the partition of the total relaxation (polaron) energy into the contributions from each vibrational mode and the influence of bond-parameter variations on the local electron–vibration coupling of compound 1, which well explains the effects of different functional groups on internal reorganization energy \( (\lambda) \). Then, we investigated the structural and electronic properties of compound 1 in its isolated molecular state and in the solid state form, and further simulated the angular resolution anisotropic mobility for both electron- and hole-transport using two different simulation methods: (i) the mobility orientation function proposed in our previous studies (method 1); and (ii) the master equation approach (method 2). The calculated electron-transfer mobility \( (0.00003–0.784 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \) from method 1 and \( 0.02–2.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) from method 2 matched reasonably with the experimentally reported value \( (0.07–0.55 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \). To the best of our knowledge, this is the first time that the transport parameters of compound 1 were calculated in the context of band model and hopping models, and both calculation results suggest that the intrinsic hole mobility is higher than the corresponding intrinsic electron mobility. Our calculation results here will be instructive to further explore the potential of other higher DPP-containing quinoidal small molecules. © 2015 Wiley Periodicals, Inc.

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Introduction

Organic semiconductors are playing more and more important roles in the field of electronic and optoelectronic materials for their low manufacturing costs, large-area coverage, and flexibility. For the past decades, most attentions have been paid to the development of hole transporting, or p-type, semiconductors and a great deal of progress has been made in improving their conductive performance and developing simple fabrication techniques.1,11 Oligothiophenes and acene derivatives, as prototypical p-channel semiconductors, show high hole-mobility and good air-stability. They have been preliminarily applied in fabrication of electronic devices such as field effect transistors (FETs) and light emitting diodes.11,12 Recently, oligothienoacenes and their derivatives, which combine chemical stability of the thiophene ring and rigid planarity of linear acenes, have been designed and synthesized, and their electronic and conducting properties were widely investigated in both experimental and theoretical aspects.13 In our group, the charge-transport properties of the close oligothiophene analogues, oligofuran, and oligopyrrole, are systematically investigated using quantum chemistry calculations combined with the Marcus–Hush electron transfer theory.14 The calculation results showed that oligofuran and oligopyrrole possess intrinsic hole mobilities as high as or even higher than those of oligothiophenes. Compared with p-channel materials, the development of high-performance ambient-stable n-channel materials has largely lagged behind that of p-channel materials due to the fact that (i) the transport in n-channel conductors is degraded easily by air, which acts as an electron trap together with the dielectric surface trapping sites, and (ii) their low electronic affinity hinders efficient injection of electrons into the empty lowest unoccupied molecular orbital (LUMO) of the semiconductor molecules. In the last few years, numerous attempts were made to overcome these difficulties, and some new n-channel semiconductors have been realized via functionalization of acene,
oligothiophene, perylene bisimide, and diketopyrrolopyrrole (DPP)-based n-structures with electron-withdrawing substituents such as −CN, −F, perfluoroalkyl, dicyanomethylene, carbonyl, and imide groups.[5] Among these candidate parent compounds, the electron-accepting DPP moiety has been receiving considerable attention as promising materials for organic electronic applications because of its favorable optical property and thermal/ambient stability. Moreover, structural modification of the DPP unit is easy in terms of attaching alkyl chains to the lactam N atoms to induce easy solution processability and to allow the connection of various donor–acceptor building blocks to the 2- and 5-positions of the DPP moiety. For example, Palai et al. investigated the optical, electrochemical, and charge-transport properties of bithiophene-functionalized DPP small molecules, and their results suggested that the non-functionalized DPP core with only solubilizing alkyl chain could be applied to low-cost organic electronics as an organic semiconductor.[6] Sonar et al. synthesized a new class of solution processable DPP-based derivatives functionalized with electron withdrawing end capping groups (trifluoromethylphenyl and trifluorophenyl), and the investigation of their photophysical, electrochemical, and photovoltaic properties suggested that DPP moiety could be used as a promising building block to synthetize solution processable n-type organic semiconductors for organic solar cell.[7] Very recently, Qiao et al. reported a novel series of bithiophene-functionalized DPP small molecules with electron-withdrawing dicyanomethylene at the terminal thiophene unit and these compounds showed typical n-channel behavior with dominant electron transport. The representative of them, compound 1 (C_{36}H_{38}N_{6}O_{2}S_{2}, as shown in Fig. 2c), exhibited maximum electron mobility on vapor-processed films up to 0.55 cm² V⁻¹ s⁻¹ under ambient conditions, and has been successfully applied as active semiconducting layers for high-performance and ambient-stable n-channel organic FETs.[5,6] In the theoretical studies, however, there are very few reports on the structure–function relationship and theoretical simulation of charge-transfer mobility in DPP-based derivatives up to now. A theoretical investigation on the relationship between the nature of the different functional groups and device performance is very instrumental in guiding the molecular design and development of novel organic semiconducting materials, which is also the topic of this work.

Herein, we took the compound 1 as an example to analyze the partition of the total relaxation (polaron) energy into the contributions from each vibrational mode and the influence of bond-parameter variations in compound 1 on the local electron–vibration coupling, which well evaluates the effects of different functional groups on internal reorganization energy (λ). Furthermore, we investigated the structural and electronic properties of compound 1 in its isolated molecular state and in the solid state form, and further simulated the angular resolution anisotropic mobility for both electron- and hole-transport using the newly developed methods.[8] To the best of our knowledge, this is the first time that the microscopic charge transport parameters in DPP-based material compound 1 were calculated in the context of both band model and hopping models, and the anisotropic mobility in this potentially important family of DPP-based semiconductors was predicted in theory. Our work also provides the first in-depth molecular picture of the structure-transport property relationships. It will be instructive to further explore the potential of other higher DPP-containing quinoidal small molecules.

Computational Methods

Organization energy, ionization potential, and electronic affinity

The reorganization energy λ associated with charge transport process in organic solid materials can be evaluated in two ways.[9] The first is the adiabatic potential-energy surface method, in which the λ can be expressed as follows:

$$\lambda = \lambda_1 + \lambda_2 = (E^+_1 - E^-_1) + (E^- - E)$$

(1)

Here, $E_1$ and $E_0$ represent the energies of the neutral and cation/anion species in their lowest energy geometries, respectively; $E^+_1$ and $E^-_1$ are the energies of the neutral and cation/anion species with the geometries of the cation/anion and neutral species, respectively. The other method is the normal-mode (NM) analysis method, which provides the partition of the total relaxation energy into the contributions from each vibrational mode:

$$\lambda = \sum \lambda_i = \Sigma (\omega_i \Delta Q_i^2) / 2,$$

(2)

where ΔQ_i represents the displacement along normal mode Q_i between the equilibrium geometries of the neutral and charged molecules; $\omega_i$ is the corresponding frequency. The NM analysis and $\lambda_i$ were obtained through the DUSHIN program.[10] In addition, it is worthwhile to mention that Sato et al. proposed a new method of the calculation for vibronic coupling constants and vibronic coupling density which could also be used to analyze the electron–vibration interaction on the basis of the electronic and vibrational structures.[11]

From the adiabatic potential-energy surfaces of neutral/charged species, the vertical ionization potential (VIP), adiabatic ionization potential (AIP), vertical electronic affinity (VEA), and adiabatic electron affinity (AEA) can be calculated as:

- **VIP** = $E^+_1 - E$
- **AIP** = $E^-_1 - E$
- **VEA** = $E - E^-_1$
- **AEA** = $E - E^+_1$

(3)

Full geometry optimizations of the monomer molecules and the reorganization energy calculations are performed using the B3LYP functional in conjunction with the 6-311G** basis set. These calculations are performed with the Gaussian 03 package.[12]

Electronic coupling

The intermolecular electronic coupling $V_{ij}$ which describes the overlap of electronic wave functions between the donor and acceptor states, can be written as:[13]
where $S_{ij}$, $J_{ij}$, and $e_{ij}$, respectively represent the spatial overlap, charge transfer integrals, and site energies. These physical quantities can be calculated as follows:

$$e_{ij} = \langle \Psi_i | H | \Psi_j \rangle, \quad (5)$$

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle, \quad (6)$$

$$J_{ij} = \langle \Psi_i | H | \Psi_j \rangle. \quad (7)$$

Here, $H$ is the system Kohn–Sham Hamiltonian of the dimer system, and $\Psi_{ij}$ means the monomer highest occupied molecular orbital (HOMOS; for hole transport) or LUMOs (for electron transport) with L{"o}wdin’s symmetric transformation which can be used as the orthogonal basis set for calculation.

The calculations of all electronic couplings in different molecular dimers are performed with the PW91/TZ2P of density functional theory (DFT) implemented in the Amsterdam density functional program. Here, the physical meaning of the electronic coupling can be looked as the off-diagonal Hamiltonian matrix element between the final and initial diabatic states in the charge transfer processes. The direct coupling (DC) method for electronic coupling defines one electron batic states in the charge transfer processes. The direct coupling method assumes that the charge-localized monomer orbitals dimer states in terms of localized monomer orbitals, and this method assumes that the charge-localized monomer orbitals are the diabatic states. Recent tests showed that the DC method calculated electronic coupling values can be very close to those derived from even expensive coupled cluster singles and doubles (CCSD)-based schemes in most of the systems except the small coupling systems. Considering the advantage of low computational cost for DC method and the big systems we investigated here, we adopt the DC method for the electronic coupling calculation in this work.

**Anisotropic mobility**

At room temperature, it is generally accepted that the transport in organic materials takes place via charge carrier hopping between adjacent molecules. Based on hopping mechanism, our previous works[4a,8b,17] presented a model to simulate the anisotropic mobility of organic semiconducting materials by projecting the different intermolecular electronic coupling pathways to the conducting channel:

$$\mu_\theta = \frac{e}{2k_B T} \sum_i W_i r_i^2 P_i \cos^2 \gamma_i \cos^2 (\theta_i - \Phi). \quad (8)$$

where $r_i$, $\gamma_i$, and $\theta_i$ mean the packing parameters of the organic molecules in the organic crystals. $\theta_i$ and $\Phi$ are the orientation angles of the different intermolecular electronic coupling pathways, and conducting channel direction relative to the reference axis, separately; $r_i$ is the intermolecular hopping distance (see Fig. 4). $P_i = W_i / \Sigma_i W_i$ is the hopping probability of the ith hopping pathway; $\gamma_i$ is the angles of the hopping pathways relative to the transport plane of the organic molecular stacking layer. For two-dimensional (2D) transport within the basal stacked organic layers, the charger-carrier transport between layers is less efficient and the hopping pathways in the transport stacking layer are mainly considered. In this case, the $\gamma_i$ is 0°. $W_i$ is the charge hopping rate between adjacent organic molecules based on Marcus–Hush theory in the high-temperature limit:

$$W = \frac{V^2}{\hbar} \left( \frac{\pi}{k_BT} \right)^{1/2} \exp \left( - \frac{\lambda}{4k_BT} \right). \quad (9)$$

$\lambda$ is the reorganization energy and $V$ is the intermolecular effective electronic coupling.

**Band structure and density of states**

The DFT calculations for electronic structures of compound 1 in its solid state form were performed using the projector augmented wave pseudopotentials as implemented in the Vienna $ab$ initio simulation package code.[18] The energy cutoff is set to 400 eV for the plane wave basis, and the exchange-correlation functional is treated by Perdew–Burke–Ernzerhof form generalized gradient approximation.[19] The convergence threshold for self-consistent field energy is set at $10^{-4}$ eV. For the structural relaxations, the cell parameters is constrained to the experimental values for avoiding unphysical expansions of the unit cell, and all the atomic positions are fully optimized until the force on each atom is converged to 0.01 eV/Å. The Brillouin zone is sampled by $4 \times 4 \times 4$ Monkhorst–Pack k-point grids[20] for geometry optimizations, and then sampled by the finer $6 \times 6 \times 6$ grids for the self-consistent energy calculations and the density-of-states (DOS) plots.

**Results and Discussion**

**Reorganization energy and geometric structure**

As one of the key parameters influencing the intrinsic charge-transport rates, the reorganization energy mainly arises from the changes in equilibrium geometry of the donor and acceptor sites consecutive to the gain or loss of electronic charge and the reorganization of the surrounding medium during charge-transfer process. These two contributions are referred to as the inner and external reorganization energy, respectively. In organic crystals, external reorganization energy is usually neglected because of the low dielectric constants of molecular solids, and fortuitous cancelation of errors that includes neglect of tunneling contributions to the rate constants.[8a,21] Here, we mainly calculated the inner reorganization energy which reflects the geometric changes in the molecules on ionization and vice versa, and further analyzed the contributions of different vibration modes to the reorganization energy as well as the influence of the various bond length variations on the reorganization energy.

The reorganization energies evaluated from the adiabatic potential energy surface of neutral/charged molecule (the four-point approach) and from the NM analysis are collected in Table 1. The energies obtained by the two methods were nearly identical, which indicates that the harmonic oscillator of the lattice vibration is a good approximation. For sake of
A comprehensive analysis of the contributions of different vibration modes, we display the frequency dependence of mode-specific reorganization energy in Figure 1. Decomposition of the inner reorganization energy into individual contributions from the relevant vibrational modes, as shown in Figures 1a and 1b, indicates that both low-frequency and high-frequency modes contribute much to the electron-transfer reorganization energy: 38% of the total relaxation energy originates from vibrational modes at about 1350 cm$^{-1}$ or higher, and 33% of the relaxation energy comes from low-frequency modes below 650 cm$^{-1}$. In contrast, the contributions to the hole-transfer reorganization energy mainly come from high-frequency modes above 1350 cm$^{-1}$ (see Figs. 1c and 1d). The calculation results indicate that 74% of the total relaxation involves vibrational modes above 1350 cm$^{-1}$ or higher, and less than 6% comes from models below 650 cm$^{-1}$.

Further analysis reveals that the frequency below 650 cm$^{-1}$ is mainly related to the bending vibration of molecular backbone, while most higher frequency (>650 cm$^{-1}$) corresponds stretching vibration of chemical bonds in the molecule, especially C=C=C=C bonds. Thus, we can conclude that the bending vibration induced by variation of bond angles contributes more to the electron-transfer reorganization energy than the hole-transfer reorganization energy. Moreover, the ~2320 cm$^{-1}$ mode characterized by C-CN stretching vibration (see Supporting Information Fig. S1a) also has a slight contribution to electron-transfer reorganization energy (~5 meV), but contributes very little to the hole-transfer reorganization energy, which indicates the introduction of CN groups only slightly increase the reorganization energy related to electron-transfer.

On electron-transfer process, the reorganization $\lambda_N$ (140 meV) and $\lambda_A$ (143 meV) are almost the same; however, the mode-specific contributions are quite different. The larger contributions to the $\lambda_N$ mainly come from the vibration modes at 605 cm$^{-1}$ (11.6 meV), 1002 cm$^{-1}$ (12.5 meV), 1222 cm$^{-1}$ (8.6 meV), 1518 cm$^{-1}$ (28.5 meV), and 1754 cm$^{-1}$ (7.3 meV) in a neutral state. The largest one presents at 1518 cm$^{-1}$, which corresponds to the stretching vibration of CC bonds in the conjugate molecular backbone (see Supporting Information Fig. S1b). In $\lambda_A$, four modes with frequencies 613 cm$^{-1}$ (12.6 meV), 1448 cm$^{-1}$ (11.6 meV), 1478 cm$^{-1}$ (20.8 meV), and 1725 cm$^{-1}$ (12.1 meV) in an anion state have significant contributions. The largest one presents at 1478 cm$^{-1}$, which also corresponds the stretching vibration of CC bonds (see Supporting Information Fig. S1c). In this vibration mode, the displacement vectors show obviously different characters with the vibration mode at 1518 cm$^{-1}$ in neutral state, suggesting these frequencies, respectively, corresponds to two different vibration modes.

On hole-transfer process, the larger contributions to the $\lambda_N$ come from the vibration modes at 1518 cm$^{-1}$ (31.4 meV), 1570 cm$^{-1}$ (8.1 meV), and 1588 cm$^{-1}$ (7.7 meV) in a neutral state. The largest one also presents at 1518 cm$^{-1}$, as same as the case on electron-transfer process, and it contributes by

| Table 1. DFT-B3LYP/6-311G** calculated reorganization energies by adiabatic potential surface of the neutral and charged species and by normal mode analysis; $\lambda_N$, $\lambda_A$, and $\lambda_C$ is reorganization energy for neutral, anionic, and cationic molecules, respectively; $\lambda_{tot}$ is total reorganization energy. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\lambda_N$ (eV) | $\lambda_A$ (eV) | $\lambda_{tot}$ (eV) | $\lambda_N$ (eV) | $\lambda_C$ (eV) | $\lambda_{tot}$ (eV) |
| Adiabatic potential | 0.136 | 0.146 | 0.282 | 0.072 | 0.072 | 0.144 |
| Normal mode | 0.140 | 0.143 | 0.283 | 0.075 | 0.070 | 0.145 |
nearly half to the reorganization energy $\lambda_C$. The larger contributions to the $\lambda_C$ mainly come from the vibration modes at 1459 cm$^{-1}$ (15.2 meV) and 1553 cm$^{-1}$ (11.9 meV) in the cation state, and these vibration modes are different from the vibration modes corresponding to 1518, 1570, and 1588 cm$^{-1}$ in neutral state. Moreover, the vibration modes at 1459 cm$^{-1}$, which contributes most to $\lambda_C$, contributes by less than 25% to the reorganization energy $\lambda_C$.

Through above analysis, we can know that the reorganization energy related to charge-transfer mainly originated from bond length relaxations, despite the bond angle changes that correspond bending vibrations also make a percentage of contribution, especially to the electron-transfer organization energy. The following discussion mainly focuses on the influence of various bond-length variations on the organization energy of compound 1.

The changes of CX (X = C, O, N, and S) bond length on oxidation and reduction of an isolated 1 molecule are depicted in Figures 2a and 2b, and the numbering of CX bonds is shown in Figure 2c. It is easy to see that the CC bond relaxations on electron-transfer (reduction) process are more pronounced than those on hole-transfer (oxidation) process except CC bond 7 (see Fig. 2a), which indicates the changes of CC bond lengths contribute more to $\lambda_o$ than to $\lambda_h$.

For the chemical bonds between carbon atom and heteroatom, the geometric relaxations exhibit various characteristics. As shown in Figure 2b, the bond-length variation of C=N bonds (1' and 2') between the neutral and reduced forms is about 0.003 Å, significantly larger than the ones between the neutral and oxide forms (<0.001 Å), which reflects that the different extents of C=N bond relaxation impact on removing and adding an electron to a molecule. It should be noted that the relaxation extent of C=N bonds is much smaller than those of most of C=C bonds, and hence C=N bond compression/stretching only adds a much smaller contribution to $\lambda_o$ and $\lambda_h$ compared with the C=C relaxation, as is also suggested by the previous frequency analysis results. Therefore, the addition of nonconjugated C=N group, as a strong electron-withdrawing group, to known p-type molecular cores could improve electron affinity (EA) of parent molecules and has very small influence on their reorganization energies, which may be a promising way to convert p-type semiconductors into ambipolar or n-type semiconductors.

For the C=O bond (5'), the bond-length variations on oxidation and reduction are 0.007 and 0.009 Å, respectively, suggesting that the bond relaxations of bond 5' have a slight contribution to both $\lambda_o$ and $\lambda_h$. It is consistent with our previous investigation that partial chemical oxidation of the organic
molecule could push the reorganization energies to be larger than the ones of their parent compounds, especially for electron-transfer reorganization energies. For C–N bonds 3’ and 4’ in heterorings, the geometric relaxation occurs predominantly on hole-transfer process; in contrast, the relatively weak geometric changes on electron-transfer process contribute less to $\Delta_{r}$. An interesting characteristic is that bonds 3’ and 4’ show similar bond-length variation ($\approx$0.019 and $\approx$0.017 Å, respectively) during hole-transfer process, but during electron-transfer process bond 3’ ($\approx$0.001 Å) shows much smaller bond-length variation than bond 4’ ($\approx$0.015 Å), which may be related to the strong electron withdrawing group C of. From the Mulliken charge variation shown in Supporting Information Figure S2, it is clear that the difference of charge distribution on the C17 (or C59) atom before and after adding an electron to the molecule (0.03 e$^{-}$) is larger than the difference of charge distribution on the C57 (or C15) atom (0.003 e$^{-}$) due to the large electronegativity of O atom, and the larger bond 4’ length variation is in response to the larger electronic change.

The C=S bonds (6’ and 7’) undergo geometric changes to a greater extent in the cationic state than in the anionic state, which is similar with C=N bonds in heterorings. On electron-transfer process, conversely, the bond-length variations of bond 6’ (about 0.0034 Å) and 7’ (about 0.0031 Å) are very similar with each other; however, on hole-transfer process, the bond-length variation of bond 6’ is about 0.020 Å, significantly larger than that of bond 7’ (0.004 Å), which is in sharp contrast to the geometric relaxations on oxidation and reduction of C=N bonds. These observations mainly related to the local bonding character in the frontier molecular orbitals as will be discussed in Molecular Electronic Structure section. Through comparison of the contributions of C=S/C=C–N bonds and C=C bonds in the heterorings to the reorganization energy values, we speculate that the partial substitution of C=C–N bonds with C=S/C=C–N bonds in conjugated system may be beneficial to improve electron-transfer properties.

Molecular electronic structure

Table 2 collected the HOMO energy, the LUMO energy, HOMO–LUMO gap (HLG), ionization potential (IP), and EA. For comparison, the experimental values previously reported by Qiao et al. are also shown in Table 2. The calculated HOMO energy, LUMO energy, and HLG is $-6.45$, $-4.61$, and 1.85 eV, respectively, which are close to the corresponding experimental values: $-6.24$, $-4.51$, and 1.73 eV. The calculated AEA and VEA value is about 3.67 and 3.52 eV, respectively, which meets the requirements of n-type organic semiconductors: (i) EA must be high enough to allow efficient injection of electrons into the empty LUMO of the semiconductor molecules ($>$3.0 or 2.8 eV), and at the same time, (ii) EA should not be too high so as not to decrease its stability in ambient conditions ($<$4.0 eV). The appropriate EA value ensures its low injection barriers and ambient-stability in application as active semiconducting layers of n-channel OFETs. Furthermore, our calculation results also show that the AIP and VIP values of molecule 1 is separately 7.41 and 7.48 eV, which is much larger than those of pentacene (6.13 and 6.17 eV) and sexithiophene (5.74 and 5.90 eV). Although the increased IPs make the molecule 1 more stable and antioxidative but such high value might also create a high injection barrier for p-channel OFETs when using it to fabricate devices. Previous calculated results indicated that the criteria of IP values and EA values for designing air-stable ambipolar OFET materials are 5.905–7.026 eV and 2.797–3.479 eV, respectively. Therefore, compound 1, whose IP value located outside the criterion for IP values of the air-stable p-channel OFET materials, can only be used as air-stable n-channel OFET materials.

Figure 3 shows the wave functions for the frontier molecular orbitals of neutral molecule 1 and the corresponding cation and anion. Here, the frontier orbitals are drawn in rather contracted form (Isosvalue $\approx$ 0.025 a.u.), and the orbital distribution with small wave function amplitude is not shown. An obvious spatial similarity between the HOMO distribution of molecule 1 and the LUMO distribution of the corresponding cation can be seen through comparing Figures 3a and 3b. It indicates that the hole-transfer process is closely related to the electron extraction from the HOMO. Likewise, the spatial similarity between the LUMO distribution of molecule 1 and the HOMO distribution of the corresponding anion indicates that electron-transfer process correlates with the electron addition to the LUMO. The detailed analysis of the calculated orbital energies also shows that the HOMO (or LUMO) energy level is well separated by more than 1 eV from the HOMO–1 (or LUMO + 1) level. According to recent investigations by Li et al., the dimer HOMO (or LUMO) level has significant contributions only from the HOMOs (or LUMOs) of the two monomers, that is, the molecular orbitals involved in charge-transfer process is mostly HOMOs (or LUMOs).

From Figures 3a and 3c, we can see that the HOMO distributed on the chemical bond is mainly along the long molecular axis direction while the LUMO is mostly along the short molecular axis. These characters are contrary to the frontier molecular orbital distributions of oligothiophenes and oligofurans. Another interesting character is that most frontier molecular orbitals, especially HOMO, localize on the single atom rather than chemical bond, and exhibit obvious nonbonding character. These distribution characters not only have an important effect on the electronic coupling between neighbor molecules.
monomers (discussed in Crystal Electronic Structure section), but also correlate with the local structural adjustment for electron/hole transfer. In previous investigations, Chang and Chao proposed that bonding and antibonding characters in the frontier orbital usually cause change in bond order, and thus lead to the large bond length adjustment; in contrast, nonbonding only involves one atom, and not cause change in bond order, therefore, nonbonding induces relatively small bond length adjustment on electron/hole transfer. As shown in Figure 3a, the HOMO localized on CC bonds exhibits a certain proportional nonbonding character except the ones between thiophene ring and DPP core. The nonbonding character well explains the observation (see Fig. 2) that CC bonds 1–6 shrink or expand in a relative small range compared with CC bond 7 during hole-transfer process. Compared with HOMO, the percentage of nonbonding character in LUMO is obviously decreased. As shown in Figure 3c, it can be seen that only CC bonds between CN group and its neighbor C show strong nonbonding character, the other CC bonds have an obvious bonding or antibonding character, which rationalizes the observations: (i) CC bonds 1 and 2 show relatively small bond length variation compared with the other CC bonds, and (ii) most CC bonds undergo geometric changes to a greater extent in the anionic state than in the cationic state.

Moreover, the frontier molecular orbitals localized on the heteroatom X or C–X bonds also show various characters. As shown in Figures 3a and 3c, both HOMO and LUMO localized on the N atoms in CN groups have strong nonbonding character, which induced negligible bond length alteration (see bond 1′ and 2′ in Fig. 2b). For the C–N bonds 3′ and 4′, the HOMOs show strong antibonding character and bonding character (see Fig. 3a), respectively, and thus both C–N bonds in heterorings undergo geometric changes to a great extent on hole-transfer process; in contrast, the LUMOs show obvious nonbonding character, as shown in Figure 3c, which leads to relatively small C–N bond relaxation.

For the C=O bond 5′, the spatial distribution of the frontier molecular orbitals shows that the percentage of nonbonding character is smaller in LUMO than in HOMO, which rationalizes the observation that the bond length alteration of bond 5′ is slightly larger on electron-transfer process than on hole-transfer process. It is also worth noticing that the HOMO localized on the C−S bonds in the thiophene ring show obvious asymmetry. The HOMO localized on the bond 6′ shows strong antibonding character, while the HOMO related to the bond 7′ mainly localized on the S atom, and shows strong nonbonding character, which well explains the fact that the bond 6′ changes more significantly relative to bond 7′. The LUMO localized on the bond 6′ and 7′ is symmetry and shows strong nonbonding character, and thus bond 6′ and 7′ undergo relatively small geometry structure relaxations and relaxation extents of 6′ and 7′ are similar.

Crystal electronic structure

Figure 4 illustrates the X-ray crystal structure of compound 1 obtained by Qiao et al. For sake of convenient viewing, the molecule 1 is replaced by green ball which is placed on the geometric centers of molecule 1. There is only one molecule per unit cell, and thus the smallest stacking distance between the neighboring molecules along a, b, and c axis is separately.
8.365, 10.028, and 14.090 Å, which equals to the corresponding cell parameters a, b, and c, respectively. According to Bre-das’s calculation result that the electronic couplings decay exponentially with the intermolecular distance,[26] the large stacking distance along c axis is unfavorable for the charge transfer. The direct calculations of electronic couplings also show that the electronic coupling in L1 is only 0.9 meV for hole-transfer and 0.02 meV for electron-transfer, respectively, which suggests that the layered molecular packing structure of compound 1 gives rise to a 2D transport within the basal stacked organic layers (a–b plane).

The molecular arrangement in the a–b plane is also shown in Figure 4. Under the nearest-neighbor approximation, six types of charge hopping pathways or dimers are found: P1, P2, P3, P4, P5, and P6. By symmetry, P1 is the same as P4, P2 is the same as P5, and P3 is the same as P6. Therefore, only the electronic couplings in P1, P2, and P3 are needed to be calculated, and the calculation results are collected in Table 3. Comparison of the electronic couplings in different hopping pathways (or dimers) shows that the electronic couplings in P2 are much larger than those in P1 and P3 on both hole-transfer and electron-transfer process. The electron-transport electronic coupling (Vh) in P2 is about 59.0 meV, while the electron-transport electronic couplings in P1 and P3 are 3.4 and 0.3 meV, respectively; the hole-transport electronic coupling (Ve) in P2 is about 58.4 meV, in contrast, the hole-transport electronic couplings in P1 and P3 are 8.6 and 0.2 meV, respectively. These observations are mainly related to the shapes of the frontier molecular orbitals of the isolated molecule and the relative displacements of adjacent molecules along the molecular axes.

The packing structures of P1, P2, and P3 are shown in Figure 5. In P1 and P3 dimers, the intermolecular distances are 8.365 and 10.028 Å, respectively, both of which are smaller than that in P2 (10.644 Å), however, the relative displacements of the two adjacent molecules along the short molecular axis in P1 and P3 are obviously larger than that in P2 dimer. As shown in Figures 5a and 5b, there exists a relative displacement of more than one molecular width between two parallel molecules in P1 and P3 dimers, and thus the relatively small intermolecular spatial overlapping between adjacent molecules leads to weak intermolecular electronic couplings. In P2, the displacement between adjacent molecules along short molecular axis is negligible (see Fig. 5c), which means that P2 dimer are more close to perfectly cofacial configuration. In such a configuration, the global overlap is considerably increased by bonding or antibonding interactions between the π-atomic orbitals. Nevertheless, it should be also noted that there still exists a displacement of about 10.1 Å along long molecular axis direction (equivalent to 3/5 molecular length, as shown in Fig. 5d) in P2 dimer, which is not beneficial to achieving optimal electronic coupling. The crystal packing structure of compound 1 can be further optimized to tend toward ideal face-to-face π-stacked crystal-packing structure and achieve higher carrier mobility through functionalizing the molecular structure or optimizing the experimental condition.

The electronic band structure of the molecule 1 crystal is shown in Figure 6 along various orientations in reciprocal space. The strong dispersion responsible for the large bandwidth of conduction and valence bands is along the a-axis (P1 direction), b-axis (P3 direction), and P2 direction (in the ΓA, ΓB, and Γ5 section of the Brillouin Zone); in comparison, a flat

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<tr>
<th>Dimers</th>
<th>Vh (meV)</th>
<th>Ve (meV)</th>
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<tbody>
<tr>
<td>P1</td>
<td>8.6</td>
<td>3.4</td>
</tr>
<tr>
<td>P2</td>
<td>58.4</td>
<td>59.0</td>
</tr>
<tr>
<td>P3</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>L1</td>
<td>0.9</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 3. Calculated electronic coupling terms Vh (for hole-transfer) and Ve (for electron-transfer) for all pathways of compound 1.
band is observed along the c-axis which is perpendicular to the molecular layers. These characters also indicate that the hole/electron mobility is 2D in the a–b plane, and charge-transfer between molecular layers contributes little to hole/electron mobility. Based on band structure of the molecule 1 crystal, the effective electron \((m^*_{e})\) and hole masses \((m^*_{h})\) of charge carriers for the most dispersive bands were evaluated by fitting.
Table 4. Hole and electron effective masses $m_i$ at $\Gamma$ in the crystal of compound 1.

<table>
<thead>
<tr>
<th></th>
<th>$d^2E(k)/dk^2$</th>
<th>$m_i/m_0$</th>
<th>Parallel to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole at $\Gamma$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-0.008$</td>
<td>$-54.6$</td>
<td>$A$</td>
</tr>
<tr>
<td></td>
<td>$0.097$</td>
<td>$0.89$</td>
<td>$B$</td>
</tr>
<tr>
<td></td>
<td>$0.023$</td>
<td>$19.0$</td>
<td>$C$</td>
</tr>
<tr>
<td></td>
<td>$-1.40$</td>
<td>$0.31$</td>
<td>$Ab$</td>
</tr>
<tr>
<td></td>
<td>$0.105$</td>
<td>$4.2$</td>
<td>$A$</td>
</tr>
<tr>
<td></td>
<td>$0.373$</td>
<td>$1.17$</td>
<td>$B$</td>
</tr>
<tr>
<td></td>
<td>$0.046$</td>
<td>$9.5$</td>
<td>$C$</td>
</tr>
<tr>
<td></td>
<td>$1.10$</td>
<td>$0.39$</td>
<td>$Ab$</td>
</tr>
<tr>
<td>Electron at $\Gamma$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ m_i = \hbar^2 \left( \frac{d^2E(k)}{dk^2} \right)^{-1} \]

Holes in compound 1 are light with the smallest hole effective mass equal to $0.31m_0$, and the smallest electron effective mass at the band edge is $0.39m_e$, slightly heavier than the smallest hole effective mass. Both hole and electron effective mass minimum values are along $P_2$ direction. These characters are consistent with the direct calculations of electronic couplings.

Moreover, we also calculated the DOS for the molecular crystal of compound 1. From the partial DOS shown in Supporting Information Figure S3, we can see that both the valence band top states and the conduction band bottom states are mainly contributed by the C 2p orbitals. Besides, p states of heteroatoms are also located at the edges of the valence band and conduction band. For example, the top of valence band consists of C 2p and N 2p states followed by O 2p states and S 3p states; and the bottom of conduction band consists of C 2p states, N 2p states and O 2p states, nearly no S 3p state. Combined with the aforementioned HOMO and LUMO distributions, these observations are easy to understand. As shown in Figure 3a, the HOMO distributes around the most C atoms and all heteroatoms in the parent molecule, suggesting the p orbitals of both C atoms and heteroatoms in the parent π-conjugated backbone contribute to the HOMO or the valence band maximum. The contribution of these different atoms to the valence band maximum depends on the proportion of various atoms to some extent. The relative ordering of the atomic numbers involved in forming valence band edge is as follows: C (12) > N (6) > O, S (2), hence C 2p orbitals contribute most to valence band edge, the next is N 2p orbitals, and the contributions of O 2p orbitals and S 3p orbitals to valence band edge is the smallest. Different from HOMO, LUMO mainly distributes around the C atoms and O atoms in the parent π-conjugated backbone, as well as N atoms in CN groups, therefore, the conduction band edge mainly consists by the C 2p states, O 2p states, and N 2p states, in contrast, S 3p orbitals contribute very little to the conduction band edge.

Anisotropic mobility

The anisotropic hole and electron mobilities in the single crystal of molecule 1 are estimated by the Marcus–Hush electron transfer theory combined with mobility orientation function eq. (8) (method 1), and the simulation results are shown in Figures 7a and 7b. It can be seen that the angle dependence of hole and electron mobility in single crystal shows remarkable anisotropic behavior. Interestingly, the predicted mobility anisotropy curves for hole-transfer and electron-transfer show very similar distribution characteristic: both the maximum hole mobility value and the maximum electron mobility value appear near $\Phi = 62^\circ/242^\circ$ and the corresponding lowest hole and electron mobilities appear near $\Phi = 152^\circ/332^\circ$, which suggests that the optimum values of electron- and hole-transfer mobility appear near $P_2$ direction due to the relatively larger electronic coupling in $P_2$ dimer.

Additionally, the master equation approach (method 2), which has been described in detail elsewhere,[8a] was also used to describe the anisotropic charge-transport property of the molecular crystal 1. For comparison, the results of the simulations are also shown in Figures 7a and 7b. We can see that the predicted mobility anisotropy curve obtained by master equation approach show a similar distribution characteristic.
Table 5. Theoretical hole-diffusion mobilities ($\mu_h$) and electron-diffusion mobilities ($\mu_e$) at room temperature ($T = 300$ K)

<table>
<thead>
<tr>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>$3.00 \times 10^{-3}$</td>
</tr>
<tr>
<td>$0.96-4.02$</td>
<td>$10^{-5}-0.78$</td>
</tr>
</tbody>
</table>

[a] Reference 5e.

with the results by orientation-function method: the maximum hole and electron mobility values appear in the same transport direction. Also, we can see that the optimum charge-carrier transport direction is along $\Phi = 75^\circ/225^\circ$, slightly larger than the results calculated by mobility orientation-function, which reflects the slight discrepancy of two methods in the description of anisotropic mobility.

The ranges of hole and electron mobilities estimated in the same layer (namely $ab$-plane) are summarized in Table 5 and compared with the corresponding experimental data. It can be seen that the range of the electron mobility simulated by method 1 ($3.00 \times 10^{-3}$–$0.784$ cm$^2$ V$^{-1}$ s$^{-1}$) and method 2 ($0.02$–$2.26$ cm$^2$ V$^{-1}$ s$^{-1}$) agree reasonably with the experimental values ($0.07$–$0.55$ cm$^2$ V$^{-1}$ s$^{-1}$), which proves the validity of our simulation methods. It is also noticeable that the maximum hole mobility value ($4.022$ cm$^2$ V$^{-1}$ s$^{-1}$) for method 1 and $11.73$ cm$^2$ V$^{-1}$ s$^{-1}$ for method 2) is nearly five times larger than the maximum electron mobility ($0.784$ cm$^2$ V$^{-1}$ s$^{-1}$ for method 1 and $2.26$ cm$^2$ V$^{-1}$ s$^{-1}$ for method 2). The higher hole mobility mainly originates from the relatively small $\lambda_h$ value (0.144 eV) compared with $\lambda_e$ value (0.282 eV). Taking no account of injection barrier of the hole, we can conclude that the molecular crystal of compound 1 has the potential to be developed as a high-performance p-type or ambipolar organic semiconducting materials.

Conclusion

In this article, we theoretically investigated the electronic structure and microscopic charge transport properties of compound 1, a representative of DPP-based materials. The calculation results show that the HOMO localized on $\pi$-conjugate molecular backbone exhibits more proportion of nonbonding character compared with LUMO, and thus most CC bond relaxations on electron-transfer process are more pronounced than those on hole-transfer process, which well explains the observation that compound 1 shows much higher electron-transfer reorganization energy (0.282 eV) than the corresponding hole-transfer reorganization (0.144 eV). Decomposition of the reorganization energy into individual contributions from the relevant vibrational modes indicates: (i) the contributions to the charge-transfer reorganization energy mainly come from the stretching vibration of molecular backbone; and (ii) the bending vibration induced by variation of bond angles contributes more to the electron-transfer reorganization energy than the hole-transfer reorganization energy. Furthermore, charge transport is discussed in the framework of both band and hopping models, and the first in-depth molecular picture of the charge transport parameters are provided. The transport parameters calculated here in the context of both theoretical models suggest that the intrinsic hole mobility in the compound 1 is higher than the corresponding intrinsic electron mobility. These theoretical investigations of compound 1 are helpful to understand the structure–function relationship and intermolecular charge transport behaviors, and also provide guidance for the molecular design and development of other novel DPP-containing quinoidal small molecules.

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Keywords: organic semiconductor · normal-mode analysis · band structure · hopping mechanism · anisotropic mobility

![Additional Supporting Information may be found in the online version of this article.](image-url)

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