Theoretical Exploration of Carrier Dynamics in Amorphous Pyrene–Fluorene Derivative Organic Semiconductors

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ABSTRACT: In this report, a series of amorphous organic optoelectronic pyrene–fluorene derivative materials (BP1, BP2, PFP1, PFP2, OP1, OP2) were systematically investigated through a theoretical method. Their molecular structures are different due to the difference of substitution groups at C9 of the fluorene core, which include electron-rich pyrene group (PFP1 and PFP2), relatively neutral phenyl group (BP1 and BP2), and electron-withdrawing oxadiazole group (OP1 and OP2). In the beginning, through the physical model analysis, this report proposes that the concept of p-type or n-type is not flawless because there is no real doping process in these molecular organic semiconductors. To prove such a concept, the Marcus theory and first-principles were employed to calculate the intrinsic transfer mobility of these materials. Not as the common method used for the single crystal, in this report, a series of disorderly designed lattice cells were constructed to represent the disordered distribution of the amorphous pyrenyl–fluorene derivatives. Then, the reorganization energy of materials was calculated by the adiabatic potential energy surface method. The transfer integral of dimers was calculated in possible hopping pathways near the central molecule. Research results show that the six pyrene–fluorene materials all possess intrinsic bipolar transfer characteristics. In addition, it is also showed that the electron-rich group is not necessary to improve hole transfer, and that the electron-withdrawing group is also not necessary to improve electron transfer.

1. INTRODUCTION

Due to the application in the fields of organic light-emitting diodes (OLEDs),1,2 organic field-effect transistors (OFETs),3,4 organic photovoltaic cells (OPVs),5,8 π-conjugated organic semiconductors (OSCs) recently have received extensive attention in industrial and scientific community. Compared with traditional inorganic semiconductors, OSCs show some superior qualities, which include low-device-fabrication cost especially for spin-coating, a variety of materials for different applications due to easy molecular engineering and mechanical flexibility. Obviously, from the performance principle of organic photoelectronics, the charge-transfer process plays a vital role in all optoelectronic devices. Besides the charge-transfer investigation on the common commercial OSCs, the newly synthesized materials should be focused on since their amount is greatly larger than the commercial materials. During then, after years of research on pyrene–fluorene derivatives,5–8 our group discovered the π−π hyperconjugation effect, which means the electron cloud of two isolated conjugation systems (nonconjugated pyrene group and pyrene–fluorene group) could be delocalized and transferred to each other. Then, the further exploration of the inner charge transfer in such materials is necessary for their further application.

So in this work, from the viewpoint of energy level structure, charge (electron and hole) transfer of a series of amorphous pyrene–fluorene derivatives (BP1, BP2, PFP1, PFP2, OP1, OP2) is theoretically investigated. The chemical structures of the studied materials are shown in Figure 1. From the molecular structure, if the pyrene–fluorene is considered to be the main conjugation, there are three different aromatic group substitutions on the C9 of the central fluorene core. Then, the phenyl group could be considered to be a relatively neutral group (in BP1 and BP2) because that the pyrenyl group could be electron-rich group and the oxadiazole group could be electron-withdrawing group compared with the phenyl group. In common sense in OSCs, the BP1 and BP2 are the p-type materials for hole transporting. The incorporation of electron-rich group will lead to more “p-type” and, thus, larger hole transport (PFP1 and PFP2). To systematically compare, oxadiazole group has also been incorporated as the electron-withdrawing group (OP1 and OP2), which should be the n-type and electron transfer according to the general concept.

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Among these compounds, BP1, BP2, PFP1, and PFP2 have been synthesized in our previous work,\textsuperscript{10} OP1 and OP2 with oxadiazole substitution are just theoretically designed up to now.

In the traditional inorganic semiconductors such as classical single-crystal silicon, they can function as p-type or n-type. A p-type semiconductor is formed by doping a trivalent element (such as boron) into a pure silicon crystal to replace the position of the silicon atom in the crystal lattice. Correspondingly, an n-type semiconductor is formed by doping a pentavalent element (such as phosphorus) into a pure silicon crystal to replace the position of the silicon atom in the crystal lattice. In an n-type semiconductor, electrons are majority carrier, and holes are minority carriers. As to the p-type semiconductor, its hole concentration is much larger than that of the electron. Moreover, the current definition of organic semiconductors is also extended by these traditional concepts just as the above description.\textsuperscript{11}

When a simple physical model is used to describe the carrier transport in OSC (OPV in this scheme), the charge transfer is mainly divided into three steps, as shown in Figure 2, where two molecules (PFP1 and OP1) are presented for a clear description. First, the electron is excited from the hole–electron pair in the highest occupied molecular orbital (HOMO) of the molecule to its lowest unoccupied molecular orbital (LUMO). After the transition, the electron–hole pair is separated. Second, the electron is transferred in the LUMO and the remaining hole is transferred in the HOMO in the same molecule. Third, the electron is transferred in the LUMO to the LUMO of another molecule. The hole in the HOMO is also transported to the other HOMO of the next molecule. The general intermolecular charge transfer in room temperature and amorphous organic materials can be described through the hopping model. During the whole process, the electron concentration should be the same to the hole concentration since they are the original electron–hole pair. There is no theoretical difference between the charge transport in HOMO and LUMO since the difference is only the energy level. The only difference might occur in the intermolecular hopping process. Does the great thermal lattice fluctuation in

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**Figure 1.** Chemical structures of the monomers of the studied amorphous materials.

**Figure 2.** Process of charge transfer in PFP1 and OP1.
amorphous OSCs have the same or different influence on the electron and hole transport? If it is the same or similar, then all of the undoped molecules in this report should be intrinsic bipolar transport in contrast to the traditional p- or n-type.

Common charge-transfer studies on OLEDs, OPVs, and OFETs always have the effect of the external electric field, such as the incorporation of two or three electrodes, cathode modification, and so on.\textsuperscript{12,13} It should be noted that the external electrical field will seriously influence the transport characteristics, especially in the three-electrode OFETs. Besides the organic semiconducting molecules, there are additional electrodes, insulating materials, and the corresponding interfaces to affect the transfer in OSCs. To make sure that the research target is organic molecules themselves and to avoid these external influencing factors, it is necessary to explore carrier transport in amorphous pyrene–fluorene derivatives from purely theoretical research. The results of the research show that they are all intrinsic bipolar OSCs, which will lead to an idea change in their application in the organic photoelectronics.

2. THEORETICAL METHOD

The molecules researched in this report are all amorphous, so the charge-transfer process can be explained by the hopping model, during which the semiempirical Marcus–Hush theory is the most representative one. It can be used to explain the carrier transport rate between adjacent molecules, following the formula $M^+ + M \rightarrow M + M^+$, where $M$ represents a neutral molecule and $M^+$ represents an adjacent ionized molecule.\textsuperscript{14} There are already lots of researches about the charge-transfer properties of OSC crystals in recent years.\textsuperscript{15–19} However, although most OSCs are amorphous, the lack of research on newly designed and synthesized amorphous OSCs in the hopping model is still the reality in the field of organic photoelectronics up to now.

Under this model, the disordered distribution of the material can be expressed in terms of a three-dimensional space. Then, a series of representative cell lattices are constructed to represent the disordered distribution of materials. These cell lattices are disorderly designed to be large enough, and then one single molecule is selected as the central molecule in the lattice. Such a molecule and the adjacent molecule form lots of two-molecules (dimers, so-called amorphous cell), which could represent the minimum periodic unit of the real molecule pattern. Next, for each cell lattice, the charge-transfer rate was investigated between the dimers. The sum of these data gives the electron or hole mobility of the cell lattice, which is considered as the simulated intrinsic mobility of these materials.\textsuperscript{20} This method avoids the assumption of isotropy since the disordered distribution generally exists in most of OSCs.

First, the geometry of all molecules (in Figure 1) was optimized at the B3LYP/6-31G(d) level. Then, the construction of the amorphous cell and forcite modules of Accelrys’ Materials Studio 8.0 programs were used to generate amorphous cell representations of BP1, BP2, PFP1, PFP2, OP1, and OP2. None of these amorphous organic materials studied here has the experimental density values. We use Rigby’s developed program\textsuperscript{21} to relatively accurately determine the material density. The molecular monomer structure shown in Figure 1 was first optimized using molecular mechanics and the COMPASS force field.\textsuperscript{22} Cubic amorphous cells (10) were prepared for each molecule. Each cell is filled with enough optimized monomer molecules to reach about 1600 atoms per cell. The initially selected cubic lattice parameter is a density close to 1 g/cm$^3$, and the cells are energy-minimized after generation. Then, each cell was experienced four consecutive molecular dynamics processes, and all dynamic runs had a time step of 1 fs. First, running at a constant volume and temperature (NVT) run of 10 000 steps; second, with the Andersen thermostat for NVT operation 40 000 steps; then, constant pressure and temperature (NPT) is 10 000 steps; the last NPT process is 100 000 steps; the NPT process utilized both Andersen thermostats and Berendsen barostat and an additional pressure of 0.0001 GPa. A complete atomic coordinate system is written in every thousand steps of the production run, which is used to calculate the average density and its standard deviation. The calculated densities of BP1, BP2, PFP1, PFP2, OP1, and OP2 are 1.041, 1.079, 1.025, 1.102, 1.052, and 1.089 g/cm$^3$, respectively.

These density values are subsequently used to produce more than 50 different amorphous lattices for each molecule, each with approximately 20 molecules, with a side length of $a$ = 25.3056, 26.4904, 26.7794, 25.9933, 25.9812, and 26.1645 Å for BP1, BP2, PFP1, PFP2, OP1, and OP2, respectively. The previous calculation steps are then repeated, and the energy is minimized.

At room temperature, the hopping model is used to describe the charge transfer of OSCs.\textsuperscript{14,25,24} According to the theory of the hopping model, the mobility of amorphous organic solids depends critically on two parameters:\textsuperscript{25} reorganization energy $\lambda$ and charge-transfer integral $V$. The essence of the transfer integral $V$ is the overlapping of the electron cloud of two molecules, which is highly impacted by the relative spatial location of the solids.\textsuperscript{26} The charge-transfer rate $W$ can be described by the Marcus equation

$$ W = \frac{2\pi}{h} V_{DA}^2 \left( \frac{1}{4\pi k_B T} \right)^{1/2} \exp \left[ -\frac{(\lambda + \Delta G^0)^2}{4\lambda k_B T} \right] $$

where $V$ is the electron coupling matrix element between adjacent molecules, that is, the transfer integral, reflecting the intensity of the electron interaction ($V_{DA}$ means the transfer integral between donor and acceptor. In this report, it means the two adjacent molecules, and denoted with $V_j$; $T$ is the temperature; $k_B$ and $h$ are the Boltzmann constant and the Planck constant, respectively; Among them, $V$ and $\lambda$ are two decisive factors affecting the speed of charge transfer.

Reorganization energy is usually divided into internal reorganization energy and external reorganization energy. The internal reorganization energy is essentially the relaxation energy of the charged molecular state to the neutral configuration, which is related to the change of the molecule structure. The external reorganization energy, which is often ignored when calculating the reorganization energy of the reaction, is affected by the polarization of the solvent molecule. Compared with the internal reorganization energy, external reorganization taken environmental polarization effects into account and the values are usually small, so only the internal reorganization energy is considered only since charge transfer takes place in the solid.\textsuperscript{27} The monomer structures are optimized by the adiabatic potential energy surface method, which can be expressed by the following formula

$$ \lambda = E^{\#}_a - E^{\#}_i + E^{\#} - E $$
where $E$ is the neutral state energy in the neutral configuration; $E^+$ is the neutral state energy in the ion configuration; $E^-$ is the ion state energy in the ion configuration; $E^\text{fi}$ is the ion state energy in the neutral configuration. All configuration calculations are performed at the B3LYP/6-31G(d) level with the Gaussian 09 program.

Charge-transfer integral indicates the degree of electron cloud overlap of the frontier orbits of two adjacent molecules. The isolated orbital method is a relatively accurate method for evaluating the transfer integral. The core of the method is that in the case of single-electron approximation, the migration of charges between molecules mainly occurs between the frontier orbitals of adjacent molecules. The electron-transfer integral between two orbitals can be approximated by direct coupling. The electrons run in the LUMO orbital of adjacent molecules, and the holes are the migration among HOMO orbitals. \( \Psi_a, \Psi_b \) refer to the frontier orbital of molecules \( a \) and \( b \), respectively; \( H_{ab} \) is the one-electron Hamiltonian operator of dimers, which can be calculated by this method of the isolated orbit. The frontier orbital coupling strength of adjacent molecules is directly calculated. When considering the nonorthogonality of isolated molecular orbitals, that is, the spatial overlap integral of isolated orbits \( \langle \Psi_a \mid \Psi_b \rangle = S_{ab} \neq 0 \), it is necessary to do symmetric orthogonalization for isolated orbits, the Löwdin transformation, which gives the so-called effective electron-transfer integral

$$ V = \frac{J_{ab} - S_{ab}(H_{aa} + H_{bb})/2}{1 - S_{ab}^2} $$

The effective electron-transfer integral \( V \) obtained by orthogonally changing the basis function is the electronic coupling in the Marcus–Hush semiempirical charge-transfer rate formula. The HOMO eigenvalue of the molecule \( a \) is used as the site energy of the isolated orbit where

$$ J_{ab} = \langle \Psi_a^{\text{HOMO}} | h_{ab} | \Psi_b^{\text{HOMO}} \rangle $$
$$ S_{ab} = \langle \Psi_a^{\text{HOMO}} | \Psi_b^{\text{HOMO}} \rangle $$
$$ H_{aa} = \langle \Psi_a^{\text{HOMO}} | h_{ab} | \Psi_a^{\text{HOMO}} \rangle $$
$$ H_{bb} = \langle \Psi_b^{\text{HOMO}} | h_{ab} | \Psi_b^{\text{HOMO}} \rangle $$

On this basis, the Einstein equation was applied to evaluate the carrier mobility of the material, which can be expressed as the following equation

$$ \mu = \frac{\varepsilon D}{K_B T} $$

where \( \varepsilon \) is the unit charge and \( K_B \) is the Boltzmann constant, \( T \) represents the thermodynamic temperature, and \( D \) is the diffusion coefficient between the dimers, which is the sum of the diffusion coefficients of all transition pathways within 12 Å away from the central molecule.\(^{28}\) The formula is as follows

$$ D = \frac{1}{2n} \sum_{a \neq b} r_{ab}^3 W_{ab} P_{ab} $$

where \( n = 3 \) represents the spatial dimension. \( r_{ab} \) represents the length of the dimers, whose charge is transferred from the molecule \( a \) to molecule \( b \); \( W_{ab} \) represents the rate of charge hopping; and \( P_{ab} \) is the probability of charge transfer from the molecule \( a \) to molecule \( b \).

3. RESULTS AND DISCUSSION

3.1. Frontier Molecular Orbital. All geometric structures are optimized with the density functional theory (DFT) method at the B3LYP/6-31G(d) level. The results of the molecular optimization studied are shown in Figure 3. The HOMO and LUMO energy distributions of BP1, BP2, PFP1, PFP2, OP1, and OP2 have been listed in Table 1 and Figure 3. There are also experimental values for comparison.

![Image](Image 327x441 to 429x488)

**Figure 3.** Illustration of the frontier molecular orbitals for all molecules at the B3LYP/6-31G(d) level using the QM/MM method.

|          | HOMO  | LUMO  | expt.\(^{10,29}\) |
|----------|-------|-------|-----------------|
| BP1      | -5.12 | -1.54 | -5.83/−2.68     |
| BP2      | -5.06 | -1.64 | -5.72/−2.72     |
| PFP1     | -5.09 | -1.52 | -5.39/−2.27     |
| PFP2     | -5.06 | -1.64 | -5.36/−2.37     |
| OP1      | -5.17 | -1.60 |                 |
| OP2      | -5.14 | -1.73 |                 |

In organic semiconductors, the splitting of the highest occupied orbital HOMO or the lowest unoccupied orbital level LUMO leads to the transfer integration of the dimers of two adjacent molecules, thereby describing electron or hole transport. It can be seen from Figure 3, both the HOMO and LUMO orbitals have the \( \pi \)-orbital conjugation feature and are mainly distributed on the pyrene–fluorene main conjugated core.

PFP1 and PFP2 have higher HOMO values than BP1, BP2 and OP1, OP2. The only difference is the C9 substitution of the fluorene core. BP1 and BP2 are substituted by phenyl, and PFP1 and PFP2 are replaced by the nonconjugated pyrene, which is an electron-rich group; and OP1 and OP2 are substituted by an electron-withdrawing group oxadiazole.

3.2. Reorganization Energy. Here, the adiabatic potential energy surface method was used to evaluate the intramolecular electron and hole reorganization energy at the B3LYP/6-31G(d) level; the simulated reorganization energy results are

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shown in Table 2. According to eq 1, the carrier transition rate is inversely related to the reorganization energy. As shown in Table 2, the calculated $\lambda_h$ (the reorganization energy of the hole) ranges from 0.1338 to 0.2733 eV for these compounds, which are slightly larger than that of pentacene (0.129 eV). The calculated $\lambda_e$ (the reorganization energy of the electron) ranges from 0.0136 to 0.1541 eV for these compounds. The hole reorganization energies of PFP1 and PFP2 are very close. Similarly, BP1 and BP2, OP1 and OP2 are also very close, which indicates that the increase of $\pi$-conjugation has little effect on the reorganization energy of the holes. The hole reorganization energy and electron reorganization energy of the three materials PFP1, PFP2, and BP2 are close to each other, suggesting that they probably are bipolar charge-transport materials. The reorganization energy of PFP1 is smaller than that of BP1 and OP1, and PFP2 is also smaller than BP2 and OP2. This indicates that the substituents at the C9 position have a great influence on the reorganization energy.

### 3.3. Transfer Integral

The charge-transfer integral of amorphous materials is an important factor in determining its charge-transport performance. The spatial orientation of the dimers and the order of molecular packing have a great influence on it. The main carrier-transfer pathways in the studied molecules are listed in Figures 4, 5, and 6. Due to the disorder of amorphous molecules, the transfer integrals among dimers composed of adjacent molecules within 12 Å of the selected central molecule were mainly calculated. The distance to the central molecule and the detailed stacking ways are listed in Table 3. The basis set is B3LYP/6-31G(d), and the eigenvalue of the HOMO orbit instead of the site energy is employed. The results can also be seen in Table 3.

It can be seen from Table 3 that in all of the selected pathways of the studied molecules, the dimers with large $\pi$-conjugation have larger transfer integrals. In the intermolecular transfer pathways of the OP2, the distance of pathway 1 is the closest and the transfer integral is the largest. Among them, the value of the hole is 45.42 meV, the electron’s is 13.76 meV. The pathway 3 is the farthest, and the transfer integral is the smallest, where is 1.57 meV for the hole and 4.02 meV for the electron. Traditionally, the transfer pathway with large $\pi$-$\pi$ stacking arrangement has a corresponding larger transfer integral. Since the three-dimensional lattice was constructed to simulate the actual situation of the amorphous material, the direct arrangement of each dimer has a partial $\pi$-$\pi$ stack, edge to edge or side to side. Therefore, it is found that the center distance of the dimer is also an important factor influencing the transfer integral. Generally, the closer dimer distance results in the larger transfer integral. Compared with OP1, the order of molecular stacking in OP2 changed with the degree of conjugation of the fluorene core, and the transfer integral of the closest dimer increased. Compared with PFP1, the introduction of electron-withdrawing oxadiazole substituents in OP1 leads to a decrease in the transport integral of the main transport pathways. By increasing the degree of conjugation of PFP1, the transfer integral of the main dimers of PFP2 is unexpectedly reduced, although it is larger than that of OP2, which should be ascribed to the molecular packing disorder.

For the same degree of conjugation of the fluorene core, the order of the transfer integral is OP1 > BP1 > PFP1, OP2 > BP2 > PFP2. Since oxadiazole group is smaller than the pyrenel group, which will lead to a more tightly stack and

### Table 2. Intramolecular Hole and Electron Reorganization Energies of All Compounds were Calculated by the Adiabatic Potential Energy Surface Approach

| Compound | $\lambda_h$ (eV) | $\lambda_e$ (eV) |
|----------|-----------------|-----------------|
| PFP1     | 0.1388          | 0.1008          |
| PFP2     | 0.1338          | 0.0886          |
| BP1      | 0.2565          | 0.1541          |
| BP2      | 0.1725          | 0.1263          |
| OP1      | 0.2733          | 0.1396          |
| OP2      | 0.1757          | 0.0136          |
smaller dimmer distance. Then, OP1 and OP2 have larger orbital overlap and, thus, larger charge-transfer integral.

3.4. Carrier Mobility. According to the Marcus equation and the Einstein relationship, reorganization energy and transfer integral are two decisive factors affecting the mobility of carriers. Increasing the transfer integral could be the main way to improve its mobility. Generally, the smaller reorganization energy and the larger transfer integral result in greater carrier mobility.31 By calculating the charge-transfer rate constant $W$ of the main transport pathways, the diffusion coefficient $D$, the charge mobility values at normal temperature ($T = 300$ K) are listed in Table 4 and Figure 7. The average value of the hole mobility showed OP1 > BP1 > OP2 > PFP1 > PFP2 > BP2. The average value of the electron mobility showed OP1 > BP2 > BP1 > PFP1 > OP2 > PFP2. Their electron mobility is close to the hole mobility, and the values differ in one order of magnitude. Therefore, it is believed that these materials belong to bipolar transport organic semi-

| Molecule | Pathway | Dimer CM distance(Å) | $V_{\text{Hole}}$(meV) | $V_{\text{Electron}}$(meV) |
|----------|---------|----------------------|----------------------|----------------------|
| OP1      | 1       | 7.166                | -3.57                | -4.08                |
|          | 2       | 9.276                | -6.63                | 16.38                |
|          | 3       | 9.312                | 1.9×10⁻¹             | -2.8×10⁻¹             |
|          | 4       | 10.519               | -1.03                | 1.72                 |
|          | 5       | 8.827                | -5×10⁻¹              | 2.94                 |
|          | 6       | 9.966                | -52.28               | 23.01                |
| OP2      | 1       | 5.764                | -45.42               | -13.76               |
|          | 2       | 10.293               | -13.2                | -10.38               |
|          | 3       | 7.682                | 1.57                 | -4.02                |
| PFP1     | 1       | 7.026                | -24.7                | 2.8                  |
|          | 2       | 10.005               | 8.2×10⁻¹             | 9.7                  |
|          | 3       | 9.81                 | 12.4                 | 5.1                  |
|          | 4       | 11.542               | -4.4                 | 6.7                  |
|          | 5       | 10.613               | 1.2                  | -1.59                |
|          | 6       | 10.635               | 4.7                  | 1.84                 |
| PFP2     | 1       | 9.718                | 6.9×10⁻¹             | 1.81                 |
|          | 2       | 11.839               | -5.3×10⁻¹            | -6.6×10⁻¹            |
|          | 3       | 11.799               | 2.3×10⁻¹             | 9.8×10⁻¹             |
|          | 4       | 8.943                | -3.6×10⁻¹            | -1.92                |
|          | 5       | 12.125               | -4.01×10⁻¹           | 1.91                 |
| BP1      | 1       | 10.259               | -2.31                | 2.7×10⁻¹             |
|          | 2       | 7.189                | -2.4×10⁻¹            | -1.18                |
|          | 3       | 11.488               | -1.9×10⁻¹            | 1.9×10⁻¹             |
|          | 4       | 7.435                | 47.83                | -13.22               |
|          | 5       | 11.298               | 2.54                 | 4.3×10⁻¹             |
|          | 6       | 10.107               | 8.8×10⁻²             | 1.2×10⁻¹             |
| BP2      | 1       | 11.1                 | -3.41                | 15.73                |
|          | 2       | 10.619               | -4.01                | -10.74               |
|          | 3       | 9.056                | -2.23                | -2.83                |
|          | 4       | 11.446               | -1×10⁻²              | -3.4×10⁻¹             |

$R = 2$-ethylhexy; $V_{\text{Hole}}$ means the transfer integral of the hole and $V_{\text{Electron}}$ means the transfer integral of the electron.
Table 4. Calculated Reorganization Energy and Corresponding Hole and Electron Mobilities ($\mu$) for Several Amorphous Materials

| materials | $\lambda$ (eV) | $\mu$ (cm$^2$/V s) | $\lambda$ (eV) | $\mu$ (cm$^2$/V s) |
|-----------|---------------|-------------------|---------------|-------------------|
| BP1       | 0.154         | 0.639–1.189       | 0.257         | 4.58 $\times$ 10$^{-2}$–0.101 |
| BP2       | 0.126         | 1.03 $\times$ 10$^{-2}$–1.16 $\times$ 10$^{-2}$ | 0.173         | 1.12 $\times$ 10$^{-2}$–0.425 |
| PFP1      | 0.101         | 9.98 $\times$ 10$^{-4}$–0.346 | 0.139         | 2.95 $\times$ 10$^{-3}$–9.31 $\times$ 10$^{-2}$ |
| PFP2      | 0.089         | 1.75 $\times$ 10$^{-4}$–0.031 | 0.134         | 2.21 $\times$ 10$^{-3}$–3.56 $\times$ 10$^{-3}$ |
| OP1       | 0.140         | 0.018–1.995       | 0.273         | 0.205–0.239       |
| OP2       | 0.014         | 0.071–0.316       | 0.176         | 0.054–0.042       |

In the previous research, there are few reports on the experimental bipolar transfer on OSCs in the diode. One wonderful report is about the bipolar transport of diarylsubstituted terfluorene in the diode determined by the TOF method, in which, the bipolar transport was ascribed to the 3-dimension structure of the diaryl groups substitution at C9 of fluorene. The research in this report shows that the 3-dimension structure is not necessary to the bipolar transport, even if which will lead to different packing disorders. The more experimental bipolar reports are in OFETs. In OFETs, there is an additional gate electrode and the corresponding insulating layer, which will significantly influence the inner carrier transport in OSCs. As to the most excellent work of the bipolar organic field-effect transistor, the n-type effect was achieved through the additional electrode modification. And such interface engineering will also significantly influence the inner transport, which should not be considered as the intrinsic carrier transfer since the influence of external fields is complicated.

There are also some calculation reports on the bipolar transport in single-crystal OSCs. Since most of OSCs are amorphous, some works also research the amorphous materials. However, the used methods for investigating the amorphous OSCs are the methods for single crystal, which should not be suitable since the packing pattern and transfer pathways in the amorphous and single crystal are greatly different. The four materials (BP1, BP2, PFP1, and PFP2) have been synthesized, and their primary optoelectronic properties have been investigated in our previous work. All of the research materials in this report have been explored through the real amorphous methods. So the intrinsic bipolar transfer characteristics achieved in this report could be considered to be the subsequent work in our group and could be real characteristics of amorphous OSCs.

4. CONCLUSIONS

In traditional opinion, the incorporation of electron-rich group will lead to the so-called p-type OSCs and hole transporting. The electron-withdrawing group will lead to the n-type OSCs and electron transport. The p-type or n-type concept is originated from the doping in inorganic semiconductors. From the qualitative physical model analysis according to the six pyrene–fluorene derivatives (BP1, BP2, PFP1, PFP2, OP1, and OP2), at the beginning, this report states that the concept of p-type or n-type is not complete because there is no doping in these OSCs except that in some other doped devices. Then, the relevant charge-transfer pathways are confirmed between adjacent molecules of these materials by simulating the true spatial distribution of the six materials. In further, the reorganization energy, the charge-transfer integrals, and the mobility of these materials are calculated. The results show that pyrene–fluorene derivative OSCs possess intrinsic bipolar transfer characteristics. The electron-rich group substitution does not necessarily lead to that the hole mobility is larger than the electron mobility. And the electron-withdrawing group incorporation also does not necessarily mean that the electron mobility is smaller than that of electrons.
mobility should larger than the hole mobility. The results also show that the mobility values are significantly influenced by the intramolecular conjugation and intermolecular packing (thus, the transfer integrals). The different values in electron and hole mobilities in one same pyrene–fluorene material also show that the transfer mechanisms of the hole and electron are different. In real experimental research, the trap originated from the chemical impurity and the interface effect is not avoidable. So, in a reasonable deduction, the trapping mechanisms for electron and hole carrier should also be different. At last, the organic semiconductors possess many interesting properties, and the more different and similar molecular structure should be synthesized and investigated through experimental and theoretical methods to propose the theoretical system of OSC itself.

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**Notes**

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**REFERENCES**

(1) Wu, T.-L.; Huang, M.-J.; Lin, C.-C.; Huang, P.-Y.; Chou, T.-Y.; Chen-Cheng, R.-W.; Lin, H.-W.; Liu, R.-S.; Cheng, C.-H. Diboron compound-based organic light-emitting diodes with high efficiency and reduced efficiency roll-off. Nat. Photonics 2018, 12, 235–240.

(2) Huang, J.; Su, J.-H.; Tian, H. The development of anthracene derivatives for organic light-emitting diodes. J. Mater. Chem. 2012, 22, 10977–10989.

(3) Ashraf, R. S.; Meager, I.; Nikolka, M.; Kirkus, M.; Planells, M.; Schroder, B. C.; Holliday, S.; Hurhangee, M.; Nielsen, C. B.; Sirringhaus, H.; McCulloch, I. Chalcogenophene coomorer comparison in small band gap dikenopyrrolopyrrole-based conjugated polymers for high-performing field-effect transistors and organic solar cells. J. Am. Chem. Soc. 2015, 137, 1314–1321.

(4) Horowitz, G. Organic field-effect transistors. Adv. Mater. 1998, 10, 365–377.

(5) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated polymer-based organic solar cells. Rev. Chem. 2007, 107, 1324–1338.

(6) Tang, C.; Liu, F.; Xia, Y.-J.; Lin, J.; Xie, L.-H.; Zhong, G.-Y.; Fan, Q.-L.; Huang, W. Fluorene-substituted pyrene—Novel pyrene derivatives as emitters in nondoped blue OLEDs. Org. Electron. 2006, 7, 155–162.

(7) Liu, F.; Tang, C.; Chen, Q.-Q.; Shi, F.-F.; Wu, H.-B.; Xie, L.-H.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. Supramolecular π–π Stacking Pyrene-Functioned Fluorenes: Toward Efficient Solution-Processable Small Molecule Blue and White Organic Light Emitting Diodes. J. Phys. Chem. C 2009, 113, 4641–4647.

(8) Liu, F.; Tang, C.; Chen, Q.-Q.; Li, S.-Z.; Wu, H.-B.; Xie, L.-H.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. Pyrene functional diarylfluorones as efficient solution processable light emitting molecular glass. Org. Electron. 2009, 10, 256–265.

(9) Tang, C.; Xu, H.; Liu, F.; Xia, Y.-J.; Huang, W. Isolated large Π systems in pyrene–fluorene derivatives for intramolecular through-space interaction in organic semiconductors. Org. Electron. 2013, 14, 782–789.

(10) Qiu, S.-Y.; Xu, H.; Li, L.; Xu, H.-T.; Meng, L.-K.; Pang, H.-S.; Tang, C.; Pang, Z.-Q.; Xiao, J.; Wang, X.; et al. Influence of π–π Hyperconjugation Effect on Thermal, Morphological, and Photo-electronic Properties of Non-Conjugated Pyrene Derivatives. J. Phys. Chem. C 2017, 121, 9230–9241.

(11) Dimitrakopoulos, C. D.; Malenfant, P. R. Organic thin film transistors for large area electronics. Adv. Mater. 2002, 14, 99–117.

(12) Meijer, E.; De Leeuw, D.; Setayesh, S.; Van Veenendaal, E.; Huisman, B.-H.; Blom, P.; Hummelen, J.; Scherf, U.; Klapwijk, T. Solution-processed ambipolar organic field-effect transistors and inverters. Nat. Mater. 2003, 2, 678–682.

(13) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. General observation of n-type field-effect behaviour in organic semiconductors. Nature 2005, 434, 194–199.

(14) Marcus, R. A. Electron transfer reactions in chemistry. Theory and experiment. Rev. Mod. Phys. 1993, 65, 599–610.

(15) Rossi, M.; Sohlerk, K. Predictions of hole mobility in molecular organic crystals: incorporating thermal effects. J. Phys. Chem. C 2009, 113, 6821–6831.

(16) Robertson, J. M.; Sinclair, V.; Trotter, J. The crystal and molecular structure of tetracene. Acta Crystallogr. 1961, 14, 697–704.

(17) Duan, Y.-A.; Li, H.-B.; Geng, Y.; Wu, Y.; Wang, G.-Y.; Su, Z.-M. Theoretical studies on the hole transport property of tetrathienoarene derivatives: The influence of the position of sulfur atom, substituent and π-conjugated core. Org. Electron. 2014, 15, 602–613.

(18) Yin, J.; Chaitanya, K.; Ju, X.-H. Theoretical investigations of charge carrier transport in organic semiconductors and the naphthalene bismide N-substituted with alkoxyphenyl groups. Can. J. Chem. 2015, 93, 740–748.

(19) Copoceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J.-L. Charge transport in organic semiconductors. Chem. Rev. 2007, 107, 926–952.

(20) Lee, C.; Waterland, R.; Sohlerk, K. Prediction of Charge Mobility in Amorphous Organic Materials through the Application of Hopping Theory. J. Chem. Theory Comput. 2011, 7, 2556–2567.

(21) Rigby, D. Fluid density predictions using the COMPASS force field. Fluid Phase Equilibr. 2004, 217, 77–87.

(22) Sun, H.; Ren, P.; Fried, J. The COMPASS force field: parameterization and validation for phosphazenes. Comput. Theor. Polym. Sci. 1998, 8, 229–246.

(23) Derrida, B. Velocity and diffusion constant of a periodic one-dimensional hopping model. J. Stat. Phys. 1983, 31, 433–450.

(24) Silbey, R.; Munn, R. General theory of electronic transport in molecular crystals. i. local linear electron–phonon coupling. J. Chem. Phys. 1980, 72, 2763–2773.

(25) Deng, W.-Q.; Goddard, W. A. Predictions of hole mobilities in oligoaacene organic semiconductors from quantum mechanical calculations. J. Phys. Chem. B 2004, 108, 8614–8621.

(26) Tse, S. C.; Cheung, C. H.; So, S. K. Chapter 3: Charge Transport and Injection in Amorphous Organic Electronic Materials. In Organic Electronics: Materials, Processing, Devices and Applications; CRC Press: Boca Raton, 2007.

(27) Bromley, S. T.; Blas, F.; Mas-Torrent, M. Dependence of charge transfer reorganization energy on carrier localisation in organic molecular crystals. Phys. Chem. Chem. Phys. 2008, 10, 121–127.

(28) Lee, C.; Waterland, R.; Sohlerk, K. Prediction of charge mobility in amorphous organic materials through the application of hopping theory. J. Chem. Theory Comput. 2011, 7, 2556–2567.
(29) Mason, M.; Hung, L. S.; Tang, C.; Lee, S.; Wong, K.; Wang, M. Characterization of treated indium−tin−oxide surfaces used in electroluminescent devices. *J. Appl. Phys.* 1999, 86, 1688−1692.

(30) Hush, N. Distance dependence of electron transfer rates. *Coord. Chem. Rev.* 1985, 64, 135−157.

(31) Wang, L.; Nan, G.; Yang, X.; Peng, Q.; Li, Q.; Shuai, Z. Computational methods for design of organic materials with high charge mobility. *Chem. Soc. Rev.* 2010, 39, 423−434.

(32) Wu, C.-c.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chen, Y.-M.; Chien, Y.-Y. Unusual nondispersive ambipolar carrier transport and high electron mobility in amorphous ter (9, 9-diarylfuorene) s. *J. Am. Chem. Soc.* 2003, 125, 3710−3711.

(33) Cornil, J.; Brédas, J. L.; Zaumseil, J.; Sirringhaus, H. Ambipolar transport in organic conjugated materials. *Adv. Mater.* 2007, 19, 1791−1799.

(34) Yin, S.; Yi, Y.; Li, Q.; Yu, G.; Liu, Y.; Shuai, Z. Balanced carrier transports of electrons and holes in silole-based compounds a theoretical study. *J. Phys. Chem. A* 2006, 110, 7138−7143.

(35) Guo, Y.; Wang, W.; Shao, R.; Yin, S. Theoretical study on the electron transport properties of chlorinated pentacene derivatives. *Comput. Theor. Chem.* 2015, 1057, 67−73.

(36) Li, Y.; Zhang, Y.; Ma, Y.; Ren, T.; Wang, L.; Zhang, J. Effects of π-conjugation on electrochemical properties within hole-transporting materials for perovskite solar cells from first principle and molecular dynamics. *Org. Electron.* 2017, 43, 96−104.

(37) Irfan, A.; Chaudhry, A. R.; Muhammad, S.; Al-Sehami, A. G. Exploring the potential of boron-doped nanographene as efficient charge transport and nonlinear optical material: a first-principles study. *J. Mol. Graphics Modell.* 2017, 75, 209−219.

(38) Duan, Y.-A.; Geng, Y.; Li, H.-B.; Tang, X.-D.; Jin, J.-L.; Su, Z.-M. Theoretical study on charge transport properties of cyanovinyl-substituted oligothiophenes. *Org. Electron.* 2012, 13, 1213−1222.