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Polymorphism Dependent Charge Transport Property of 9, 10-Bis ((E)-2-(pyrid-2-yl) vinyl) anthracene: A Theoretical Study

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The charge transport properties of three crystalline polymorphs (α, β and γ) of 9, 10-Bis ((E)-2-(pyrid-2-yl) vinyl) anthracene (BP2VA) were investigated at the first-principle level using Density Functional Theory (DFT) method based on Marcus theory, as well as the hybrid quantum mechanical and molecular mechanical (QM/MM) method. The polymorphism dependent charge transport property was explored by 10 the calculation and analysis of the reorganization energy, the transfer integral, as well as the charge carrier mobilities of three different crystalline polymorphs. The results show that 1) β-BP2VA has the highest charge carriers mobility (for hole is 0.988cm^{2}V^{-1}S^{-1} and for electron is 0.053cm^{2}V^{-1}S^{-1}) among the three crystalline polymorphs. 2) Comparison of the reorganization energy between individual molecule in gas-phase and embedded molecule when considering the steric effect of surrounding molecules suggests 15 that the reorganization energy is dependent on intermolecular interaction for BP2VA. The calculated charge carrier mobilities are strongly dependent on the crystalline polymorphs. The enlightenment to us is that during the designing of optoelectronic materials with high charge mobility, we should pay attention to the molecular packing mode in the bulk material besides the molecular structure itself.

INTRODUCTION

20 Organic semiconductors have gained more and more attentions because of their tremendous applications in organic solar cells, light-emitting diodes, field effect transistor, sensors, laser printing, and xerography etc. [1-3] Charge transport property especially charge carrier mobility of organic semiconductors is of great 25 importance due to its direct influence on the performance of the opto-electronic devices. Time of flight (TOF), field effect transistor (FET), carrier extraction by linearly increasing voltage (CELIV), transient current method, and charge decay method have been used to characterize the charge carrier mobility of 30 organic semiconductors. [4-9]Meanwhile, theoretical study has been becoming an important tool to study the charge transport properties and predict the charge carrier mobility [10-14] of organic semiconductors. Up to now, most of the theoretical studies focused on the effects of hetero-atoms and substitutions on 35 charge transport properties.[15-17] With the development and application of organic crystalline materials, there were some investigations on the relationship between the charge transport property and molecular packing structure. Rovira etc. systemically investigated the influence of the crystal structure on 40 the performance of single-crystal OFETs and unveiled the relationship between the crystal structure and the field-effect mobility, showing that the material with the herringbone crystal structure has the remarkably good performance.[18] Shuai and co-workers studied the influences of the crystal packing and 45 molecular size on the charge mobility and found that the high temperature crystal packing phase (two molecules in unit cell)

favors the intermolecular electron coupling through the favorable frontier orbital overlap. [10] Marks reported the effects of the heteroatom and the molecular packing on the hopping transport in 50 organic semiconductors and concluded that the tilted π-stacking with tilt angles of 40-60° could increase the π-overlap (particularly for LUMOs) and facilitate the charge transport.[19] However, there is less reports about the charge transport property of one molecule with different crystalline polymorphs and 55 different molecular packing. Wang studied the isomerism/phase dependent charge transport properties of Tris (8-hydroxyquinolinato) aluminum (Ⅲ) using density functional theory and Marcus charge transport theory, and showed that mer-Alq3 molecules have the stronger electron- transporting ability 60 (n-type materials) compared with the hole-transporting ability and fac-Alq3 molecules possess stronger hole-transporting character than the electron-transporting ability. The detailed theoretical calculations indicate that the reason lies in the differences of HOMO and LUMO distribution states of the two 65 kinds of isomers, and the different molecular packing modes of the charge-transporting pathway for different phases.[20] Here, in this work, we report a comprehensive and detailed study of polymorphism dependent charge transport property of 9, 10-Bis ((E)-2-(pyrid-2-yl) vinyl) anthracene (BP2VA) by the analysis of 70 the reorganization energy, the transfer integral, as well as the charge carrier mobility. We hope to be able to get a better understanding of the relationship between the different crystalline polymorphs and charge transport properties, particularly the scale of the influence of the molecular packing (transfer integral) and 75 the intermolecular interactions (reorganization energy).

THEORETICAL AND COMPUTATIONAL METHOD

Generally, there are two widely used models to investigate the carrier motion: the coherent band model and the incoherent
[5] hopping model.[22] In the coherent band model, the charges (holes and electrons) transfer through valence or conduction bands formed by the overlapping molecular orbital with strong coupling between neighbouring molecules. It is usually suitable for highly ordered organic crystals at very low temperature. Brédas have
[10] demonstrated that when the temperature is higher than 150K, the simple band model is not applicable to describe the charge carrier mobility.[23] In contrast, at room or higher temperature, the hopping model exhibits a dominant mechanism because the dynamic structure disorder invalidates the band model due to a
[15] strong coupling of the lattice phonons with charge motion. [19] Hence we adopt the incoherent hopping model to study the charge transfer process of BP2VA polymorphs.

The drift mobility of charge carriers can be given by the Einstein equation [24] as following:

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

[20] Where e is the electron charge, k_B is the Boltzman constant, and T is the temperature, D is the diffusion coefficient. Given the hopping rate between two neighboring molecules, the diffusion coefficient can be evaluated from the hopping rates as

$$D = \frac{1}{2n} \sum_i r_i^2 k_i P_i$$

Where n is 3, for the charge motion as a random walk in three
[25] dimensions, r_i is the hopping distance between the center-to-center inter-molecule, k_i is the charge hopping rate from the initial charge center to the ith neighboring molecule, P_i is the hopping probability for charge carrier to a particular ith neighboring molecular,

$$P_i = \frac{k_i}{\sum_i k_i}$$

[30] According to the Marcus charge transfer theory, the hopping rate of intermolecular charge can be described by the following equation [24, 25]:

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

Here, h is the Planck Constant, V is the electronic coupling terms for the nearest neighbouring molecules, and λ is the
[35] reorganization energy, ΔG is the difference in free energy between the initial and final molecular sites. For molecular crystals with only one type of molecules, ΔG is generally zero since all molecules in the crystal are equivalent. In our work, there are two inequivalent molecules per unit cell for all the three
[40] crystals, hence we take ΔG into account when calculate the transfer rate. The reorganization energy consists of two parts: the inner and outer reorganization energy. The former is the molecular geometry modifications when an electron is added or removed from a molecule, and the latter is the modifications in
[45] the surrounding medium due to the polarization effects. We neglect the outer part and focus on the inner part [28, 29] due to the contribution to the reorganization energy from electronic polarization of surrounding molecules which is just on the order of a few tenths of an electronvolt. [26, 27] For some crystalline

[50] materials, such as crystalline oligoacenes, the gas phase reorganization energies of individual molecules constitute reasonable approximations for total reorganization energies. [30] Owing to the fairly flexible structure of BP2VA, the molecular reorganization energy could be reliable on the different
[55] polymorphs. For the comparison, we take account of the impact of intermolecular packing on the molecular reorganization energies and calculate the reorganization energy while explicitly considering how the individual molecules interact with, and constrained by, their specific local crystal packing using the
[60] hybrid quantum mechanical and molecular mechanical (QM/MM) method. The accuracy of QM approaches together with the computational efficiency of MM force fields offers an attractive method to studying geometric and electronic reorganization in crystalline and organic solids. In this case, the nearest
[65] neighbouring molecules were fixed at the geometry of the respective crystal, while the centred molecule was allowed to relax. [30, 31]

There are two ways to calculate the electronic coupling of molecules. One is the indirect method of Koopmans' theorem at
[70] the Hartree-Fock mean-field level. [19, 32] The other is direct dimer Hamiltonian evaluation method. [33, 34] Here we use the latter method:

$$V = \langle \psi_i^{0,1} | F^0 | \psi_i^{0,2} \rangle$$

Where $\psi_i^{0,1}$ and $\psi_i^{0,2}$ represent the molecular frontier orbitals (HOMOs for hole transfer and LUMOs for electron transfer) of
[75] isolated molecules 1 and 2. F^0 is the Fock operator for the dimer in a specific pathway. It can be evaluated by

$$F^0 = SC\varepsilon C^{-1}$$

where S is the intermolecular overlap matrix, C is the molecular orbital coefficients, and ε is the energies from one-step diagonalization without iteration. This approach has been widely
[80] applied for organic molecules and gives the best results at the DFT level. [35, 36]

The molecule geometries of neutral and charged states are optimized at the DFT level using (U) B3LYP hybrid functional [37, 38] on the basis set of 6-31G (d, p). All the above molecular
[85] geometry obtained from the crystal structure data. The reorganization energies when considering the steric effects of the surrounding molecules in the crystals are calculated at the QM/MM B3LYP/6-31G (d, p)/UFF level. All the electronic coupling calculations are carried out using the PW91PW91/6-
[90] 31G (d, p) basis set. All the calculations were performed with the Gaussian 09 package. [39]

RESULTS AND DISCUSSION

Molecular Geometries and Reorganization Energies
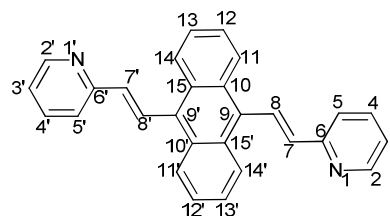
[95] **Scheme 1.** Chemical structure of 9,10-Bis ((E)-2-(pyrid-2-yl)vinyl) studied in this work.

BP2VA molecule as illustrated in scheme 1 was synthesized by our group and three different crystalline polymorphs of α-, β- and γ-BP2VA were obtained. [21]

The initial molecular structures are adopted from the crystalline polymorphs of BP2VA. All the crystalline polymorphs are monoclinic, however, β- and γ-BP2VA are P21/c space group, while α- BP2VA is C2/c space group. α- and β-BP2VA are center symmetrical molecules, however, γ-BP2VA is asymmetrical. The main difference between these polymorphs is the torsion angles, particularly compared β-BP2VA with α- and γ-BP2VA. We carried out the frequency calculations to ensure that the optimized structures are reasonable. The calculated results indicate that α- and γ-BP2VA have the same optimized structure, nevertheless, β-BP2VA gets different optimized structure surprisingly. This could attribute to the neglect of influence of the sterical restrict role of the different packing mode and the apparent difference of the initial structure. The main differences between these optimized structures are the torsions, which show the same trend as in the crystalline polymorphs. (See ESI Table S1)

When a molecule in the neutral state gains or losses an electron, it will be in the cationic or anionic state, and the parameters of the molecular structure change certainly. Compared with the changes of the bond length, the variation of the dihedral from the neutral states to the charged states is obvious. It could be found that the geometry change upon reduction is obviously larger than that occurring upon oxidation, indicating that the hole of the reorganization energy will be smaller than that of electron.

The above calculation was carried out for the isolated BP2VA molecule in gas state based on DFT. In order to consider the influence of the local environmental steric packing of nearest-neighbouring molecules, we further calculate the reorganization energy of BP2VA within different polymorphs. We randomly choose one molecule as embedded molecule and picked up all the nearest-neighbouring (NN) molecules to exhibit the surrounding circumstance, and calculate the reorganization energy. The embedded molecule treated with QM method, while the NN molecules treated with MM method, as shown in Figure S1. The calculated internal reorganization energy using B3LYP functional on the basis set of 6-31G (d, p) for BP2VA with different crystalline polymorphs by adiabatic potential surface (APS) together with the values when considering the steric packing effect based on QM/MM method are listed in Table 1.

Table 1. DFT-B3LYP/6-31G(d, p) calculated reorganization energy for individual BP2VA molecule in crystal structure and in gas state by adiabatic potential surface (AP) and the values for embedded molecule based on QM/MM method.

Crystalline Polymorphs	Hole(eV) (APS)	Hole(eV) (QM/MM)	Electron(eV) (APS)	Electron(eV) (QM/MM)
α	0.242	0.209	0.552	0.497
β	0.260	0.205	0.549	0.472
γ	0.242	0.207	0.553	0.487

For the individual molecule in gas state adopted from the crystalline polymorphs of BP2VA, the reorganization energies for holes is smaller than that of electrons, indicating that BP2VA of all the three polymorphs benefit hole transport when just considering the impact of the reorganization energy, which is consistent with the analysis in the literature.[40] For α- and γ-BP2VA, the reorganization energies are almost the same, though

there is a 0.001eV difference for electron of γ-BP2VA. However, the reorganization energy of β-BP2VA for hole (0.260 eV) is higher than the others, and for electron (0.549 eV) is slight lower than the others. A multitude of researchers hold the view that a molecule with no outside interactions (i.e., in the gas phase) will going to have one minimum ground-state geometry. Here, we obtain varied optimized structures and reorganization energies furthermore for the individual molecule. The difference of the reorganization energy is related to the difference of the optimized molecular geometries because the reorganization energy involved in the electron-transfer process from a neutral molecule to a radical molecule. [41, 42] If consider only the influence of the reorganization energy, without any other factors, we could conclude that β-BP2VA has the best electron transfer ability and the worst hole transfer property among these three crystalline polymorphs.

For the embedded molecule, we got different values of reorganization energy as shown in Table 1. All the reorganization energies are lower than those for the individual molecule. It is apparently evident that with the influence of surrounding molecules, the steric packing restricts the relaxation of the embedded molecule, and gives rise to smaller reorganization energies. The comparison of the reorganization energy between the individual molecule in gas-phase and the embedded molecule considering the steric effect of surrounding molecules suggests that the reorganization energy is dependent on intermolecular interaction indeed. Especially for β-BP2VA, the reorganization energy for hole of the individual molecule is the highest, while that of the embedded molecule possesses the lowest value.

Transfer integral and Charge Mobility

For organic semiconductors, the relative orientations and intermolecular packing motifs play an important role in the charge transport properties.[1, 18] Transfer integral is one of the key parameters in the determination of the charge hopping rate, which dominated by the orientation of the interacting molecules and the interactions between them.
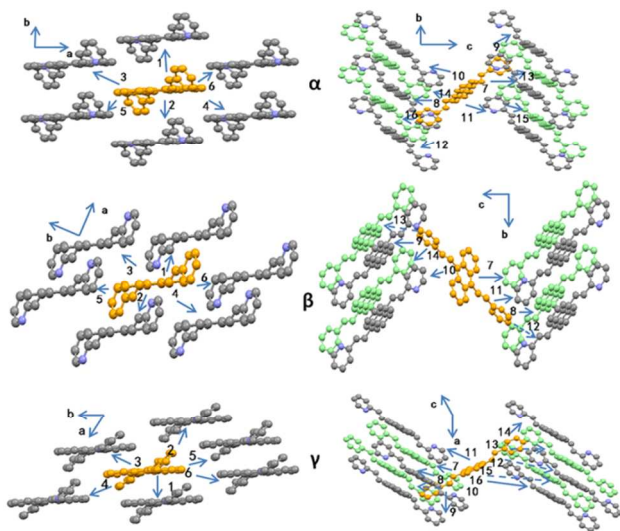

Figure 1. Selected Charge transfer pathways of α-, β- and γ-BP2VA.

To define the charge hopping pathways, we use the single crystal structures of α-, β- and γ-BP2VA to generate all the possible hopping ways. Choosing one molecule as charge donor, all the nearest neighbouring molecules can be regarded as the charge
5 acceptors. The most effective charge hopping routes are displayed in Figure 1.

The intermolecular charge transfer integrals were calculated with the PW91PW91 functional on the basis set of 6-31G (d,p), as showed in Table 2.

Table 2. Charge Transfer Integrals for electron ν(e) and for hole ν(h) for Main Pathways of α-, β- and γ-BP2VA.			
Pathway	Distance/Å	ν(h)/meV	ν(e)/meV
α-BP2VA			
1,2	8.12	2.4	17.4
3,4	8.98	46.1	33
5,6	8.98	14.4	2.9
7, 8	7.78	2.8	0.9
9,10,11,12	11.24	2.0	11
13,14,15,16	11.74	1.0	5.8
β- BP2VA			
1,2	5.74	99.6	101.7
3,4	7.59	30.1	19.1
5,6	9.51	6.9	6.4
7,8,9,10	12.12	3.7	5.8
11,12,13,14	13.29	0.2	1.4
γ-BP2VA			
1	3.89	84.4	28.9
2	8.62	4.5	21.5
3	9.19	1.0	5.7
4,5	10.42	8.2	21.2
6	11.31	0.1	2.6
7,10	8.98	12.5	15.2
8,12	11.88	0.5	2.2
9,16	11.7	4.0	5.3
11,14	12.21	1.9	14
13,15	14.2	0.2	0.7

10 In order to get a better understanding of the difference between these transfer integrals, we further investigated the orbital and weak interactions between the molecules, as shown in Figure 2. For α-BP2VA, the most effective transfer pathways are 3 and 4, the center-to-center distance is 8.98 Å with the plane-to-plane
15 distance of 3.44 Å. The transfer integral for hole is 46.1 meV, and for electron is 33 meV. These values are several times higher than that of the other routes. This kind of shifted-cofacial π-packing with the weak interaction between the molecules should be an effective transfer way and yields the relatively strong electronic
20 coupling. The transfer pathways of 5 and 6 have the same center-to-center distance with 3 and 4, and have the smaller plane-to-plane distance of 2.26 Å. However, we get much lower transfer integrals for the transfer pathways of 5 and 6, which could ascribe to the completely rare overlap between the orbital distributions.
25 In the crystalline polymorphs of β- BP2VA, the largest transfer

integrals for transfer way 1 and 2, is 101.7 meV and 99.6 meV for electron and hole, respectively，which could ascribe to the good overlap of the orbital distribution with the same phase and C-H⋯N and C-H⋯π interactions between the molecules. It is also the
30 biggest transfer integral among these three crystalline polymorphs.
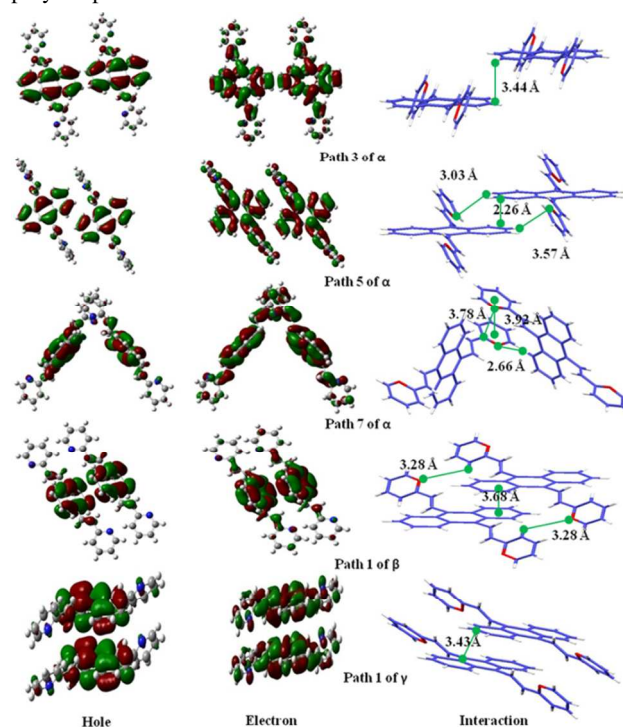

Figure 2. Orbitals (left) and weak interactions (right) in some selected transfer ways in three crystalline polymorphs.

In the situation of γ-BP2VA, for the transfer pathway 1, the
35 molecule has a slide tight face-to-face stack and forms dimers with the center-to-center distance of 3.89 Å, which is the most valuable transfer pathway with the transfer integral of 28.9 meV for electrons and 84.4 meV for holes. The shortest center-to-center distance in these crystalline polymorphs does not conduct
40 the strongest electronic coupling due to the repulsive interaction of the tight face-to-face stacking. The same analysis could apply to the other transfer pathways. We could conclude that in order to obtain the strong electronic coupling, the molecule should be shifted-cofacial π-stacking with the appropriate center-to-center
45 distance, the overlap of the orbital distribution with the same phase, and weak interactions between the molecules.

The theoretical predicted hole and electron mobilities at room temperature (298K) in different polymorphs of α-, β- and γ-BP2VA are listed in Table 3.

Table 3. Theoretical Charge Mobilities [a] (cm^2/V·S) for Hole and Electron of α-, β- and γ-BP2VA.			
Mobilities	α-BP2VA	β-BP2VA	γ-BP2VA
hole	0.487(0.328)	0.988(0.514)	0.325(0.214)
electron	0.008(0.004)	0.053(0.021)	0.004(0.002)

50 [a] Values in parentheses are calculated with the reorganization energy of individual molecule without surrounding interactions.

The theoretical results indicate that, for the three crystalline polymorphs, the hole mobility is about tens of times larger than the electron mobility since in either molecular crystals or conjugated polymers, the highest occupied band is usually wider than the unoccupied band.[40] This indicate that BP2VA is preferable hole-transporting material. The calculated mobilities of β-BP2VA show the largest values of 0.988 cm^{2}V^{-1}S^{-1} for the hole and 0.053 cm^{2}V^{-1}S^{-1} for the electron due to its favorable molecular packing and strong electronic coupling. Due to the smaller reorganization energy of embedded molecule, the calculated charge carrier mobilities are greater than that of the values in parentheses, which was obtained with the reorganization energy of individual molecule without surrounding molecules. This suggests that even in some cases the gas-phase reorganization energies of individual molecule could approximate to the total reorganization energies, [30] however in our study of the BP2VA molecule, we should consider the steric effects of the surrounding molecules in the crystals when calculating the reorganization energy. Nevertheless, all the values show the identical trend that $\mu_{\beta\text{-BP2VA}} > \mu_{\alpha\text{-BP2VA}} > \mu_{\gamma\text{-BP2VA}}$. Noticeably, all the molecules with different polymorphs have similar reorganization energy for hole (the biggest discrepancy is 0.004 eV between α-BP2VA and β-BP2VA), though they illustrate varied charge mobilities. This could attribute to the much more influence of the intermolecular packing than the reorganization energy in this case. Though there is strong electronic coupling in the dimer of charge transfer pathway 1 in γ-BP2VA, on the contrary, there is weak electronic coupling and less interaction between the dimers, and this induce the weakest charge transfer mobility. This means that there is no "efficient" transfer pathways formed in γ-BP2VA.

CONCLUSIONS

In conclusion, we investigated the electronic structure and charge transport properties of BP2VA molecule with three different crystalline polymorphs based on Marcus theory. The BP2VA molecule in all the crystalline polymorphs favours hole transport, and the hole mobility of β-BP2VA reached as high as ~1 cm^{2}V^{-1}S^{-1}. The shifted-cofacial π-stacking with the appropriate center-to-center distance, the good overlap of orbital distribution with the same phase, and the weak interactions could result in the strong electronic coupling and high transfer integral, and high charge mobility furthermore. The comparison of reorganization energy between individual molecule in gas-phase and embedded molecule when considering the steric effect of surrounding molecules suggests that the reorganization energy is dependent on intermolecular interaction for BP2VA. This could shed some light on the better understanding of the relationship between the charge transfer properties and different crystalline polymorphs of organic semiconductors. Additionally, when design new optoelectronic material with high charge mobility, one should become more focused on the effect of intermolecular packing.

ACKNOWLEDGEMENTS

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:10.1039/b000000x/

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