Effect of defect-enhanced molecular oxygen adsorption on the imbalance of hole versus electron mobility in conjugated polymers

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The generally observed higher hole mobility relative to electron mobility in conjugated polymers is explained with the defects and adsorbed molecular oxygen. Adsorption of the extrinsic molecular oxygen leads to that electrons are bound more tightly than holes by the traps in the originally symmetric electronic system. Hence, the mobility imbalance emerges from the asymmetric binding energies. Besides, the defects are the favored adsorption sites because the intermolecular attraction is enhanced due to stronger induced dipole-dipole interaction when gap defect levels appear.

I. INTRODUCTION

Organic semiconductors, including conjugated polymers and small molecules, have attracted great attention in the past two decades partly due to remarkable optoelectronic applications.[1,2] Moreover, their physics is strikingly different from the well-established inorganic counterpart and proper understanding of many observations remains absent. The imbalance between the electron and hole mobilities is widely accepted as one of the most outstanding open questions.[3–5] The hole mobility is commonly observed to be larger than electron mobility for several orders of magnitude, despite of quite symmetrical electronic structures for valence and conduction bands.[6] On the application side, such electron-hole imbalance has been a major limit for the efficiency of organic light-emitting diode where balanced current injection is required. Transport measurements and comparisons with theoretical models suggest that there are much more electron traps than hole traps.[7] The asymmetry of traps could result from extrinsic effects such as the unintentional background p-doping by chemical impurities and oxidation.[8] In reality the mobility imbalance, however, persists even for samples with very high purity. Besides, the oxygen effect was recently found to be reversible,[9] so the dominant effect of oxidation is ruled out.

In this work, we demonstrate that the ubiquitous molecular oxygen is the ultimate entity which breaks the electron-hole symmetry even without any chemical reaction. The highest occupied orbital of O_2 is half-filled and ready to partially accept an electron from the organic semiconductor once physically adsorbed. We show that the electronic structures of the originally symmetric defects are significantly altered by the physically adsorbed O_2, and the trap binding energy for electron becomes much larger than holes. Difference in binding energy naturally leads to imbalanced carrier mobilities. The huge mobility difference is a consequence of the presence of traps and the adsorption of O_2; thus, the idea can be generalized to all the disorder organic semiconductors. To be specific, we investigate the carrier excitations in π-conjugated poly(p-phenylene vinylene) (PPV) chain whose backbone contains a single defect which leads to two-gap energy levels. The conductions for electron and hole are supposed to be completely the same because the two emerging defect levels are symmetric. However, this symmetry is broken when O_2 is close to the defect and provides a pathway only for the electron in the antibonding polymer defect level. The asymmetry results in larger binding energy for trapped electrons than that for trapped hole by a few hundreds of meV. Transport model shows that the mobility can be made different by 2–3 orders of magnitude at high adsorption density. Since no chemical reaction takes place, this effect is reversible once oxygen is removed.

II. GAP STATES IN PPV

Adopting the resonance integrals of $t_1 = -2.2$ eV, $t_2 = -3.0$ eV, and $t_3 = -3.1$ eV in the inset of Fig. 1, one can fit the valence- and conduction-band structures obtained by more sophisticated computations.[8] The defect levels are obtained by introducing a one-bond defect in one single repeating unit with all other units remaining perfect. This can be caused by the reduction of the vinyl double bond t_2 due to structure distortion.[8] The electronic structure is shown schematically in the inset of Fig. 1, where CB and VB, respec-
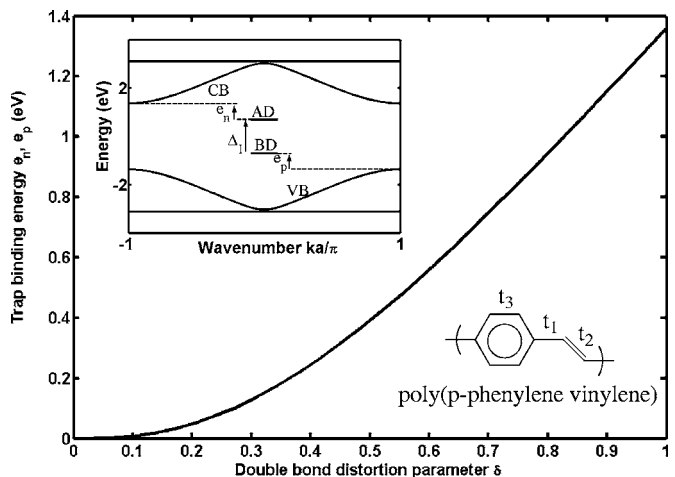

FIG. 1. Shown in the right inset is the chemical structure for PPV as well as its tight-binding parameters t's. The left inset shows the schematic band structure of the PPV chain with one defect unit (see the text for the details of the levels).
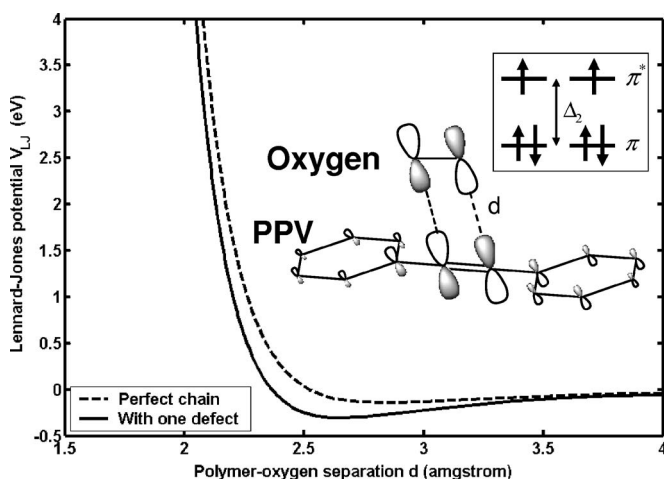
FIG. 2. The Lennard-Jones potential between PPV chain and O_2. The dashed and the solid lines are for perfect and defect chains, respectively. Also shown is the geometry for adsorption and the MOs for the oxygen π^* level and the localized AD level. The box inset gives the ground-state electronic configuration for O_2 in which the energy Δ_2 represents the difference between π and π^* MOs. The gray and white colors indicate the negative and positive lobes of the atomic orbitals.

tively, denote the conduction and valence bands, and the band gap for perfect chain is $E_g = 2.8$ eV. The defect levels labeled by AD and BD refer to the fact that their corresponding wave functions have antibonding and bonding symmetries with respect to the center of the reduced double bond. Now, the BD and AD are, respectively, the highest occupied molecular orbital and the lowest unoccupied molecular orbital. Their difference is designated by Δ_1. The energy gaps e_n and e_p stand for binding energies for the trapped electron and hole, respectively. $e_n = e_p$ is guaranteed by the electron-hole symmetry. Denoting $t_2' = t_2(1 - \delta)$ for the reduced double bond, the equal binding energies are plotted as a function of δ in Fig. 1. As δ increases toward unity, the binding energies increase and their wave functions become more localized around the reduced double bond.

III. DEFECT-ENHANCED O_2 ADSORPTION

It was suggested that O_2 and PPV can form reversible charge-transfer complex, and the probable adsorption site is the carbon-carbon double bond.[10] In fact, the band-edge Bloch state wave function has a major contribution from the vinyl double bond. Therefore we expect that O_2 can adsorb onto the PPV chain, as shown in Fig. 2. The empirical Lennard-Jones 6-12 potential $V_{LJ} = A/d^{12} - B/d^6$, fitting the interactions between small gas molecules, is used as the interaction between polymer and oxygen for separation d. Such form is responsible for the combined effect of a dipole-dipole attraction and a repulsion from respective core electrons. Besides, the fact that both contributions are mainly from the local carbon atoms near the adsorption site justifies its validity here. The potential minimum E_0 and the corresponding separation d are given by $A = E_0 d^{12}$ and $B = 2E_0 d^6$. Based on the second-order perturbation due to dipole-dipole

interaction, we assume that B only depends on the energy difference between the ground state and the lowest excited state of the two-molecule system. The lowest excited state is that one electron is excited from BD to AD in PPV and one electron is excited from π to the singly occupied π^* in oxygen. Such state has energy higher than the ground state by $\Delta_1 + \Delta_2$. Consequently, $B = \frac{\alpha}{\Delta_1 + \Delta_2}$. Δ_2 in O_2 is determined by the gap between π and π^* which gives 4.35 eV.[11] α is roughly the same for all oxygen-conjugated carbon system. Coefficient A for the short-ranged repulsion is also assumed to depend only on the local atomic arrangement. Since the intermolecular interactions between carbon nanotubes and oxygen have been studied extensively,[12] we can determine our unknown coefficients from them due to local similarity between the vinyl double bond in PPV and the carbon bond in nanotube. The fact that the nanotube is curved while PPV is not does not affect the validity of this determination since the intermolecular force is short ranged and depends only on the atomic arrangement near the adsorption site. The separation d and potential minimum E_0 have been reported to be 2.7 Å and 0.25 eV using *ab inito* calculation.[12] Then A and B are 37 500 (eV $Å^{12}$) and 193.7 (eV $Å^6$), respectively. $\alpha = 1046$ (eV^2 $Å^6$) is obtained by the π-band gap of 1 eV in carbon nanotube. The resultant separation and potential minimum for perfect PPV-O_2 system are 2.8 Å and 0.14 eV using $\Delta_1 = 2.8$ eV. Consider the case for $\delta = 0.9$ corresponding to $\Delta_1 = 0.4$ eV. As shown in Fig. 2, the attraction is enhanced for the chain with one defect and the corresponding $d = 2.66$ Å and $E_0 = 0.30$ eV. It is therefore energetically favorable for the molecular oxygen to be adsorbed onto the defect sites.

IV. ELECTRONIC STRUCTURES OF OXYGENATED DEFECTS

The Hamiltonian H for such a system is $H = H_p + H_o + H_{po}$. H_{po} stands for the interaction. For isolated PPV, $H_p = \Sigma_{n,k,\sigma} \epsilon_{n,k} b_{nk\sigma}^\dagger b_{nk\sigma} + \Sigma_{\alpha = \pm, \sigma} \epsilon_\alpha b_{\alpha\sigma}^\dagger b_{\alpha\sigma}$. σ and k are spin and momentum index, respectively. $\epsilon_{n,k}$ is the nth band energy. The subscripts $\pm$, respectively, stand for BD and AD levels and with corresponding energies $\epsilon_\pm$. For O_2, H_o must possess the property of spin-triplet ground state as well as the large on-site repulsion responding for the large difference between electron affinity (EA) (0.45 eV) and ionization potential (IP) (12 eV) in its gas phase.[13] If we denote the degenerate π^* orbitals in O_2 as π_x^* and π_z^*, the Hamiltonian can be written as $H_o = \Sigma_{\alpha = \{x,z\}\sigma} (\xi a_{\alpha\sigma}^\dagger a_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma}) - \frac{J}{2} \vec{S}_{\pi_x^*} \cdot \vec{S}_{\pi_z^*}$, where ξ means the energy for the two degenerate levels and $a^\dagger$ (a) are the corresponding creating (annihilating) operators. U is the direct Coulomb repulsion when two electrons occupy the same orbital, and the positive J describes the exchange effect between the degenerate orbitals. The energy lowering by the exchange effect manifests the more stable spin-triplet $^3O_2$ than the singlet $^1O_2$. The vector operator $\vec{S}$ is the total spin on each degenerate orbital. The values for U and J can be obtained by definitions of EA and IP: $(2\xi - \frac{J}{2}) + IP = \xi$ and $(3\xi + U) + EA = 2\xi - \frac{J}{2}$. ξ is O_2^+ energy and $2\xi - \frac{J}{2}$ is the $^3O_2$ en-
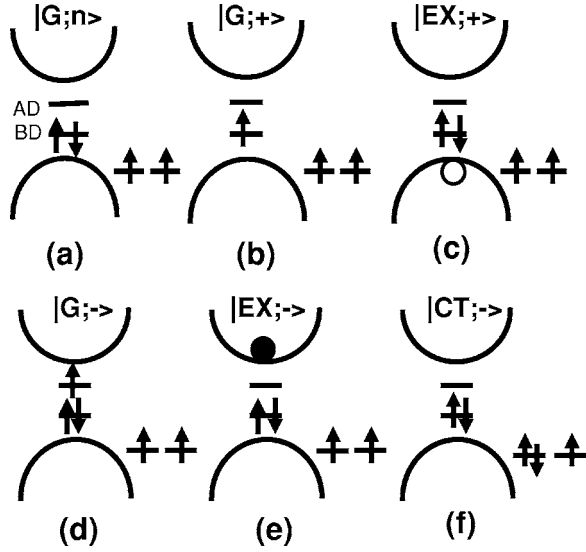
FIG. 3. Electronic configurations for one extra electron and one extra hole in the hybrid system (see the text for the details of the states). Note that there is no charge-transfer component for hole.

ergy. $3\xi+U$ is the energy for O_2^-. J is about 1 eV.[12] Hence, the repulsion $U=IP-EA-J=10.6$ eV.

Hybridization between two molecular orbitals (MOs) of different symmetries is zero. Therefore, the O_2 π_x^* orbital is not involved in the hybridization. Furthermore, BD and all the valence-band states cannot hybridize with the O_2 π_z^* either since they have different parity symmetries with respect to the plane vertically cutting the center of the reduced double bond and center of internuclear line of oxygen. Consequently, O_2 orbital can only hybrid with AD and the conduction-band states. However, the conduction-band states are negligible since their MOs are extended and have relatively little components on the sites near the oxygen. Keeping the only term gives $H_{po}=-t(a_z^{\dagger}b_-+b_-^{\dagger}a_z)$. The spin indices are neglected. The value of t can be determined from the resonance integrals β_{CO} between individual carbon and oxygen atoms. Namely, $t=\frac{1}{\sqrt{2}}(c_1-c_2)\beta_{CO}$. c_1 and c_2 stand for the MO components of AD on the two carbon atoms defining the reduced double bond. The resonance integral β_{CO} between the oxygen and carbon p_z separated by a distance d can be expressed as $\beta(d)=\frac{1}{4\pi\epsilon}\int d^3\mathbf{r}\varphi(\mathbf{r})\frac{1}{r}\phi(|\mathbf{r}-\mathbf{d}|)$. The wave functions φ and ϕ stand for the respective p_z atomic orbitals on carbon and oxygen atoms. The resultant β_{CO} can be simplified if one approximates the atomic orbitals as s orbital with effective Bohr radii r_C of 0.77 Å and r_O of 0.65 Å, respectively.[13] The dielectric constant is chosen to reproduce β_{CC} used in the tight-binding model. When d equals the single bond length of 1.4 Å, β_{CC} is about -3 eV, consistent with the values commonly used for conjugated polymers.

V. ASYMMETRIC TRAP BINDING ENERGIES

Even though a full electron transfer is inhibited by the large repulsion energy U, the mixing of a small charge-transfer component into the ground state is enough to break the binding-energy symmetry. Figure 3(a) shows the ground

state, denoted by $|G;n\rangle$, for the neutral system. For later convenience, we set this configuration as reference, that is, $\langle G;n|H_p+H_o|G;n\rangle=0$. The one-hole configurations in Figs. 3(b) and 3(c), respectively, stand for the trapped-hole ground state and the lowest free hole state, where the hole occupies the valence-band minimum. They are labeled by $|G;+\rangle$ and $|EX;+\rangle$. The matrix elements of H within this subspace is simply

$$\begin{pmatrix} \epsilon_+ & 0 \\ 0 & E_v \end{pmatrix},$$

where E_v denotes the hole energy for the valence-band minimum. Note that we exclude the configuration in which the last electron in BD for $|G;+\rangle$ is transferred to oxygen, because such configuration has very high energy due to the mutual Coulomb repulsion between the two localized holes. Even such state is considered, it is irrelevant since H_{po} does not contain hopping between BD and oxygen. Consequently, the excitation for hole to free continuum takes energy of $E_v-\epsilon_+=e_p$, which is the same as the O_2-free case. The situation for one electron is very different. Figures 3(d)–3(f) denote the trapped-electron ground state, free-electron state, and the charge-transfer state, respectively. They are labeled as $|G;-\rangle$, $|EX;-\rangle$, and $|CT;-\rangle$. The matrix elements for H within the three-state subspace is

$$\begin{pmatrix} \epsilon_- & 0 & -t \\ 0 & E_c & 0 \\ -t & 0 & -EA \end{pmatrix},$$

where E_c is the energy for the conduction-band minimum. The diagonal energy for charge-transfer state is $\xi+U+J/2$ and we replace it with -EA by definition. Similarly, the quantity $e_n=E_c-\epsilon_-$ denotes the unperturbed binding energy for the trapped electron. Then, the ground-state energy is shifted downward by the following expression:

$$(\epsilon_- - EA)/2 - \sqrt{t^2 + [(EA + \epsilon_-)/2]^2}. \tag{1}$$

Note that the hopping term t represents the overlap between the defect and O_2 quantitatively. The energy of the free-electron state $|EX;-\rangle$ is unaffected by t. Therefore, the extra electron in the ground state is bound more tightly when the adsorbed O_2 appears. The resultant binding energy for trapped electron is larger than that for trapped hole, and the difference is written as

$$\Delta_b \equiv e_n - e_p = \frac{t^2}{|\epsilon_- + EA|}, \tag{2}$$

and is plotted versus various EAs of oxygen and coupling t in Fig. 4. The lowering of the ground-state energy comes from the stabilization due to the resonance between the trapped state and the charge-transfer state. Experimentally, such lowering had been observed from the increase of the activation energy of electron trap and its level filling in MEH-PPV by exposing to air.[14] The true ground state becomes a superposition of $|G;-\rangle$ and $|CT;-\rangle$. The absolute square of the coefficient for $|CT;-\rangle$ is also shown in the inset of Fig. 4. As expected, the asymmetry becomes more appar-
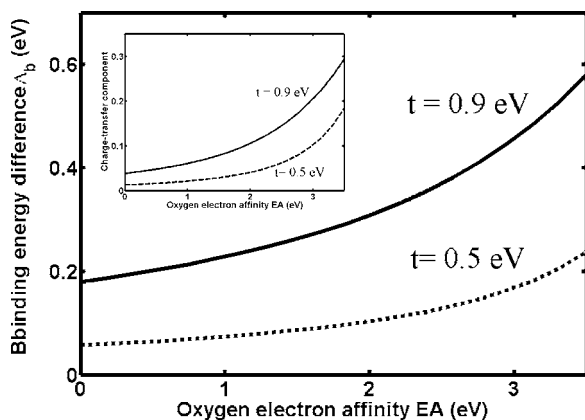
FIG. 4. Binding-energy difference Δ_b between trapped electron and trapped hole for $\delta=0.8$ is plotted for various carbon-oxygen couplings t and EAs of oxygen. The larger binding energy for trapped electron is the origin for the mobility imbalance. Shown in the inset is charge-transfer component in the true ground state for one electron.

ent for stronger coupling t when separation d is shorter. Reduced repulsion U or larger EA in O_2 also enhances the charge transfer and the asymmetry. Actually, the value of EA in solids may be higher than the gas phase value due to polarization effects and structural relaxation. Consider the trap binding energy of 1.0 eV corresponding to $\delta=0.8$. Choosing oxygen EA as the gas phase value of 0.45 eV, the binding energy is 1.16 eV for trapped electron and 1.0 eV for trapped hole. The difference is close to the deep level measurements for MEH-PPV,[15] in which the trap levels AF1 and DF1 have binding energies of 1.0 and 1.3 eV, respectively. Note that such deep trap in PPV may correspond to an almost broken bond since δ is close to 1.

VI. MOBILITY IMBALANCE

Now we use the asymmetric binding energies to quantitatively explain the mobility imbalance. The carrier mobility μ in the disorder organic semiconductor depends on the number of trapped carrier n_T and free carriers n_F, and it can be expressed as $\mu_n=\mu_{PF}/\left(1+\frac{n_T}{n_F}\right)$.[8] μ_{PF} is the free polaron mobility which follows the Poole-Frenkel laws. In the case without any doping, the population ratio $\frac{n_T}{n_F}$ at low field is determined by the trap density x_t per repeating unit and the binding energies e_n and e_p. Thus, the electron-hole mobility ratio can be expressed as

$$\frac{\mu_e}{\mu_h} = \frac{x_t + e^{-\beta e_p}}{x_t(1-\chi) + x_t\chi e^{\beta\Delta_b} + e^{-\beta e_p}}, \quad (3)$$

where χ represents the ratio of the defect sites with an O_2 adsorbed on it. Consider the case for symmetric binding energy of 0.3 eV corresponding to $\delta=0.4$. The resultant separation d and coupling t are 2.79 Å and 0.8 eV, which leads to the electron binding energy e_n of 0.4 eV and the unchanged hole binding energy e_p of 0.3 eV. Assume that each defect site now has an additional oxygen molecule adsorbed on it, or simply $\chi=1$. If the trap density $x_t=10^{-5}$, then the electron
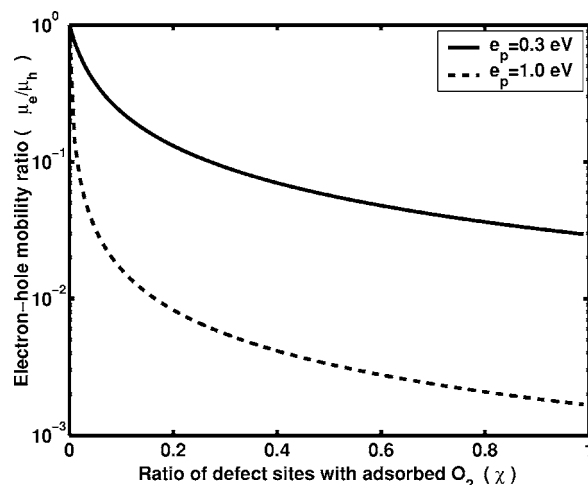

FIG. 5. The ratio μ_e/μ_h of electron-hole mobility versus the ratio χ of defect sites which have adsorbed O_2. As χ increase, or more O_2 adsorbed onto the defect sites, the degree of mobility imbalance increases. The asymmetric effect is more apparent for trap with larger binding energy.

mobility is about $1/50$ of the hole mobility, which is close to the experiment.[4] Figure 5 shows the mobility ratio μ_e/μ_h as a function of O_2 adsorption ratio χ according to Eq. (3). The mobility imbalance is stronger as more O_2 are adsorbed onto the defect sites.

VII. DISCUSSION AND CONCLUSION

So far, we consider only the case that the axis of the oxygen molecule is parallel to the carbon double bonds shown in Fig. 2, where the symmetry excludes the wave function overlap between the oxygen orbital and the bonding defect level (BD level) which could act as the hole trap. The symmetry may be broken in real systems. However, even for the oxygen molecule adsorbed in configurations which enable the tunneling between oxygen and the bonding BD level, the hole binding energy will not be increased by the perturbation of oxygen because of the high-energy cost for the hole to be transferred to the oxygen. On the other hand, as Eq. (2) suggests, the electron binding energy will always increase by the presence of the mixing with the electron-transfer state in Fig. 3. Furthermore, energy consideration suggests that the absorption with high symmetry is preferred. Another symmetrical adsorption configuration is that the oxygen axis is perpendicular to the carbon double bond. Such perpendicular configuration is equivalent to the oxygen-free case since the overlap with the antibonding defect level (AD level) becomes zero. However, the parallel adsorption is supposed to have lower total energy. Consequently, it is reasonable to assume that the parallel adsorption is the predominant one in the ensemble of configurations. Such preferred symmetrical adsorption alone is enough to explain the electron-hole imbalance.

In addition to be the primary site of physical adsorption, the distorted double bond may also be most susceptible to chemical reaction with oxygen to form the carbonyl group.

However, such reactions usually take place only in the presence of some external energy such as light illumination. Oxidation does cause an electron trap and may contribute to the imbalance.[8] However, experimentally, the imbalance is at least partially reversible when the oxygen is pumped out. Physical adsorption instead of chemical reaction must play the major role in the mobility imbalance.

In conclusion, the presence of localized defect levels in the gap of conjugated polymers is shown to enhance the intermolecular attraction between the polymer and the O_2 molecules. The originally symmetric electronic configuration is broken by the coupling with adsorbed O_2, which results in a huge difference between the electron and hole mobilities. The highly imbalanced charge transport widely observed in organic semiconductors is hence explained by the universal defect oxygenation.

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