Electronic States at the Interface between Crystalline and Amorphous Domains in Conjugated Polymers

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ABSTRACT: Conjugated polymers exhibit complex structure with interlaced crystalline and amorphous domains. We have investigated electronic structure of the interface between crystalline and amorphous domains in poly(3-hexylthiophene) (P3HT). Two types of the interface were considered: sharp interface and interface composed of extended chains. We have found that HOMO states of both interface types belong to the crystalline domains. States belonging to both domains were not found. We have calculated HOMO and LUMO band offsets between crystalline and amorphous domains. These offsets are close to previous estimates in the case of interface with extended chains. We find that there is no formation of trap states at the investigated interfaces. Regardless of the interface type, amorphous domains present high barriers for charge carriers, which lead to charge transport through crystalline domains.



■ INTRODUCTION

Organic semiconductors based on conjugated polymers have stimulated significant research interest in last decades due to their applications in organic solar cells, organic field-effect transistors, and organic light-emitting diodes.^{1–5} Understanding the electronic and transport properties of conjugated polymers is the precondition for the enhancement of their performance. On the other hand, electronic structure of a material is strongly affected by its atomic structure. Conjugated polymers exhibit complex structure: they contain both crystalline (ordered) and amorphous (disordered) domains.^{6,7} While the electronic structures of single crystalline and single amorphous domains are well understood, there is a lack of knowledge about the electronic structure of the interface between these two regions.

In real conjugated polymers, amorphous and crystalline domains are interlaced. According to previous works,⁶⁻⁹ it is believed that a single polymer chain typically spreads across both amorphous and crystalline domains. There are three types of such chains: bridge chains, which connect different crystalline regions through an amorphous region; folded chains, which connect different parts of the same crystalline domain and extended chains, which are extended out from crystalline and have their end in the amorphous domain.^{6,7} However, chains can also be entirely localized in the crystalline or amorphous domain. Amorphous domains have larger band gap than crystalline due to reduced electronic coupling between monomer units.^{6,7,10,11} Differences in band gaps produce band offsets in the valence and conduction band between crystalline and amorphous domains. Offset in the valence band acts as a barrier for a hole to jump from crystalline domain into amorphous.^{6,11-13} In all previous works, amorphous and crystalline domains in conjugated polymers were investigated separately and the effects of the interface between these two domains were not explicitly taken into account.

To fully understand electronic properties of conjugated polymers, calculations that include both crystalline and amorphous domains are needed. In this paper we perform such calculations and obtain microscopic insights into the electronic states at the interface between crystalline and amorphous regions in poly(3-hexylthiophene) (P3HT). We consider two types of interfaces that we call type A and type B. Type A interface is a sharp interface between an amorphous and an ordered domain where P3HT chains belong exclusively to one of these regions, as shown in Figure 1a. This type of interface is an idealization that is highly suitable to investigate the difference between ordered and disordered regions. On the other hand, it is unlikely that a realistic interface is that sharp. Therefore, we additionally consider the type A' interface, where an intermediate region exists between the ordered and the amorphous regions (Figure 1b). Type B interface consists of two ordered domains whose chains extend into the region between them and form an amorphous region (Figure 1c). It is believed that this type of interface is a reasonably good representation of interfaces that exist in real materials.⁶

In this work, we mainly investigate the energy level alignment between the states in the two regions and the possibility of having interface trap states within the band gap of the material. For all interface types we model the ordered region as an ideal crystal. Realistic ordered regions are not perfect crystals and exhibit the effects of thermal (dynamical) disorder and paracrystallinity. In our previous work,¹⁴ we found that the effects of thermal disorder produce variations of the energy levels in the valence band on the order 0.1-0.2 eV and therefore we do not include them in this work. Along the same

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Figure 1. Atomic structures of interfaces considered in this work: (a) type A; (b) type A'; and (c) type B.

line, we do not expect that the effect of paracrystallinity, when it is reasonably small, will change the main conclusions of our work.

Our results indicate that wave functions of HOMO states are delocalized and belong to ordered domains, regardless of the interface type. Localized states in disordered domains start to appear at the energies few hundreds meV below HOMO in the case of realistic type B interface. In the case of sharp type A interface, the difference between HOMO levels in crystalline and amorphous domains is even larger. Additionally, there is no evidence of the existence of states belonging to both domains. Therefore, disordered regions present barriers for hole transport which, consequently, dominantly goes through crystalline regions.

METHODOLOGY

Atomic structure of the interface between ordered and disordered region was generated using in-house developed Monte Carlo (MC) simulations,¹⁵ while electronic structure was calculated using the charge patching method (CPM)¹⁶ and the overlapping fragments method (OFM).¹⁷ Methods for the electronic structure calculations were described in detail in previous works.^{10,14,16–20} Therefore, in this section we focus on the description of the procedure for generating the atomic structure.

During MC simulations crystalline domains were kept rigid. There are several types of crystalline structures reported in the literature.^{14,21,22} We chose the shifted structure (neighboring chains in the π - π stacking direction mutually shifted by a half of the unit cell in the backbone direction) with interdigitated side chains as representative, since it was shown that this structure is energetically favorable.^{14,21} Lattice constants were obtained from NPT (constant pressure and temperature) MC simulations at zero temperature and pressure of 101.325 kPa, using the OPLS parameters set^{23,24} for nonbonded interactions. These lattice constants are a/2 = 15.55 Å, b = 8.1 Å, and c = 7.77 Å.

The procedure for generation of amorphous domains is different for type A and B interfaces. In the case of type A interface, at the beginning, P3HT chains were randomly placed in the simulation box, which was significantly larger than the final. The box was gradually compressed until the density of amorphous P3HT reached its experimental value of around 1.1 $g/cm^{3.25}$ Type A' interface was generated using the same atomic configuration as for the type A interface, with a difference that several chains in the crystalline domain closest to the amorphous region were allowed to move freely. For type B interface, two different starting configurations were used: one with interdigitated backbone chains and the other where backbone chains were separated by a predefined distance in the backbone direction (denoted as c-direction in figures). In this case, the simulation box was compressed only in the backbone direction until the density in the amorphous region between crystalline domains reached its experimental value. For all types of interfaces, the temperature of 1000 K was used in MC simulations. At the end, when the final density of the amorphous region is reached, the system was cooled down to 0 K. By keeping the crystalline structure rigid and by cooling the amorphous structure, effects of thermal disorder¹⁴ were excluded to keep focus on the difference between crystalline and amorphous region. Energy of the system in MC simulations was modeled as a sum of nonbonded van der Waals and Coloumb interactions and interring torsion potentials. OPLS parameter set was used for nonbonded interactions and torsion potentials of dihedrals within side chains, while thiophene-thiophene torsion potential was taken from ref 10. Periodic boundary conditions were applied in all directions.

Each of the obtained interface atomic structures contains around 10000 atoms. Electronic structure calculations on such systems are not feasible using standard density functional theory (DFT) codes.²⁶ Therefore, CPM was applied instead of DFT. Electronic charge density was calculated directly by adding contributions (called motifs) of each atom in a system.¹⁶ Charge density of motifs was extracted from DFT calculations on a small prototype system, which consists of three thiophene rings. When charge density was obtained, the single-particle Hamiltonian was constructed. The Hamiltonian was diagonalized using OFM, which divides the system into small fragments that consist of three neighboring rings (called trimers) and uses eigenstates of these small systems as the basis set.¹⁷

We note that our electronic structure calculations yield the Kohn-Sham orbitals of a charge neutral system. Therefore, polaronic effects that arise as a consequence of nuclei relaxation in the presence of an additional charge are not included. The changes of energy levels due to polaronic effects were previously estimated to be on the order of 100 meV or smaller (Supporting Information, ref 27), which justifies their neglect. Additional charge also induces polarization charges at the interface of two materials with different dielectric constants. This effect is negligible in our case because we investigate the interface of two forms of the same material. Our calculations are based on local density approximation which does not yield the correct band gap. Nevertheless, the band gap error is expected to be nearly the same for ordered and disordered form of the same material and therefore obtained band offsets are reliable.

RESULTS

As explained, type A interface is a sharp interface between crystalline and amorphous region where each chain belongs to one of these regions. Both regions in the structures that we simulated contain 20 P3HT chains, each 10 thiophene rings



Figure 2. Wave function moduli squared of the (a) highest electronic state in the valence band in the crystalline domain, (b) localized electronic state in the valence band in the crystalline domain and (c) highest electronic state in the valence band in the amorphous domain in the case of type A interface. The inset shows the distribution of the averaged diagonal Hamiltonian elements in the crystalline domain along *b*-direction. Isosurfaces correspond to the probability of finding a hole inside the surface of 75%.

long. In the crystalline region, the chains are arranged in two lamellas, where one lamella contains 10 chains stacked in the $\pi - \pi$ direction (denoted as *b*-direction in the figures). We have calculated energies and wave functions of the electronic states in the valence band for four different random realizations of the system. The results that were obtained are similar for all realizations and indicate that three different types of electronic states exist: (1) delocalized states in the crystalline domain (Figure 2a), (2) localized states at the edge of the crystalline domain (Figure 2b), and (3) localized states in the amorphous domain (Figure 2c). Highest states are delocalized and belong to the crystalline domain. These states have highest energies due to the strongest electronic coupling between thiophene rings (both inter- and intrachain coupling). Localized states in the crystalline domain start to appear at energies of around 0.4 eV below HOMO. These states are localized at P3HT chains, which are nearest to the amorphous region. Diagonal Hamiltonian elements of the rings nearest to the interface are smaller than diagonal Hamiltonian elements of the rings far from the interface, which can be clearly seen from the distribution of the diagonal Hamiltonian elements across bdirection, given in the inset of Figure 2c. Values of the elements are obtained by averaging the diagonal Hamiltonian elements of the rings that have the same *b*-coordinate. Consequently, such states have lower energies than the energy of delocalized HOMO state. Localized states are not possible in ideal crystalline domains, which are periodic in all crystallographic directions. Therefore, localized states in the crystalline domain near the interface are induced by the interface. Finally, localized states in the amorphous domain start to appear at the energies around 1 eV below HOMO. These states fully resemble the states in purely amorphous P3HT.^{10,18}

Band offsets of HOMO and LUMO levels between amorphous and crystalline domains were estimated from local density of states (DOS), given in Figure 3 for one realization of the structure for each interface type. Values of offsets can vary up to 0.2 eV depending on the structure. According to Figure 3a, HOMO band offset for type A interface is around 1 eV. On the other hand, LUMO in the amorphous domain has similar energy as LUMO in the crystalline domain. It is usually assumed that HOMO and LUMO offsets are equal to the half of the band gap difference between crystalline and amorphous



Figure 3. Density of electronic states (arbitrary units, logarithmic scale) of crystalline (red) and amorphous (blue) region in the case of (a) type A interface, (b) type A' interface, and (c) type B interface.

domain. According to previously reported results, this offset is expected to be in the range of 0.1-0.3 eV.^{6,10,11,13} Our results indicate that the presence of disordered domain affects the energy levels in crystalline domains. This can be clearly seen from the distribution of diagonal Hamiltonian elements from different chains in crystalline region (inset of Figure 2c). Difference between the diagonal Hamiltonian elements of the rings furthest from the interface and the rings closest to the interface is around 0.3 eV. Therefore, energy levels in the crystalline domain far from the interface are shifted by approximately 0.3 eV toward higher energies. This shift leads to an increase in HOMO band offset and a decrease in LUMO band offset in comparison to the offsets estimated as half of the band gap difference. The shift may originate from uneven charge distribution at the interface between ordered and disordered chains.

Intermediate region between amorphous and crystalline region (type A' interface) presents a more realistic interface model than the sharp interface. In our simulation it consists of five P3HT chains and there is the same number of chains in crystalline region. As expected, chains closer to the crystalline region are well-ordered and chains closer to the amorphous region are more disordered (Figure 1b). The main difference between electronic structures of type A and A' interfaces is in the localization lengths of the states in the ordered domains. Wave function of HOMO state of the type A' interface is delocalized (Figure 4a), but with significantly lower localization length than HOMO state of the type A interface due to disorder in the intermediate domain. Highest states in the perfectly ordered domains (Figure 4b) have energies only few meV below HOMO. The difference between the HOMO state



Figure 4. Wave function moduli squared of the (a) highest electronic state in the valence band in the intermediate domain, (b) highest electronic state in the valence band in the crystalline domain, and (c) highest electronic state in the valence band in the amorphous domain in the case of type A' interface. Isosurfaces correspond to the probability of finding a hole inside the surface of 75%.

and the highest localized states in the amorphous domain (Figure 4c) is around 1 eV (Figure 3b), similar as in the case of sharp interface.

Type B interface is composed of 20 chains, where each chain contains 20 thiophene rings. Half of the rings in each chain belong to the amorphous, other half to the crystalline region. Results for the hole wave functions and energies were extracted from 8 different realizations (4 for each starting structure). We have found that in such structure two types of states exist: (1) delocalized states in crystalline domain (Figure 5a) and (2) localized states in amorphous domain (Figure 5b). The HOMO state is completely delocalized in the ordered domain. Localized states start to appear at the energies around 0.4 eV



Figure 5. Wave function moduli squared of the (a) highest electronic state in the valence band in the crystalline domain and (b) highest electronic state in the valence band in the amorphous domain in the case of type B interface. Isosurface correspond to the probability of finding a hole inside the surface of 75%.

below HOMO (Figure 3c). This result is more in line with previous expectations due to the fact that this interface type is more realistic, contrary to the sharp type A interface. Wave functions of the states can leak slightly from crystalline domain to amorphous and vice versa, but they are dominantly localized in one of them. Interestingly, states in the amorphous domain can be localized on two chains, which can be explained by the presence of some degree of ordering between disordered chains.

Our results indicate that the interface between amorphous and crystalline domain does not introduce trap states in the band gap of crystalline domain. This is a generally positive feature, having in mind that the presence of such trap centers would deteriorate charge mobility. Moreover, there are no states which belong to both domains. These results are qualitatively different from the results for the electronic structure of grain boundaries between misaligned naphthalene crystals, given in ref 19. At the grain boundaries in polycrystalline naphthalene there are points of both stronger and reduced electronic coupling between molecules. States localized at the points of strong electronic coupling act as traps. On the other hand, electronic coupling between chains in amorphous and crystalline domains in P3HT is always smaller than the coupling between chains in crystalline domains. This coupling is even not able to form the states which belong to both domains. The only type of states which are in some way induced by the interface are localized states at the edge of crystalline domains in type A interface. In type B interface similar states do not exist, because the drop in the electronic coupling between the rings in the direction perpendicular to the plane of the interface is not that high.

In this work electronic states at the interface between crystalline and amorphous domains in P3HT were investigated. We have considered two different interface types: sharp interface and more realistic interface that consists of extended chains. Results can be summarized as follows. Highest states in the valence band are delocalized in the crystalline domains for both interface types. Highest states in the amorphous domains are localized on one or two chains, as in the case of single amorphous domain. Amorphous domain presents a barrier for

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hole transport due to high energetic offset between highest states in the crystalline and in the amorphous domain. This offset is comparable to other reported results in the case of interface that consists of extended chains. In the case of sharp interface, this offset is larger due to the energy levels shift in the crystalline domain. Importantly, we find that none of the investigated interfaces leads to formation of trap states at the interface. These results indicate that in conjugated polymer materials charge transport takes place through crystalline domains. While our results indicate that amorphous domains present barriers for charge transport, we note that paths for fast charge transport through the amorphous domain could exist if well-ordered bridging chains connect the crystalline domains through the amorphous domain, as proposed in ref 6.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; et al. Electroluminescence in Conjugated Polymers. *Nature* **1999**, 397, 121–128.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Light-Emitting Diodes Based on Conjugated Polymers. *Nature* **1990**, *347*, 539–541.

(3) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Light-Emitting Diodes Made from Cadmium Selenide Nanocrystals and a Semiconducting Polymer. *Nature* **1994**, *370*, 354–357.

(4) Dodabalapur, A.; Torsi, L.; Katz, H. E. Organic Transistors - 2-Dimensional Transport and Improved Electrical Characteristics. *Science* **1995**, *268*, 270–271.

(5) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. High-Efficiency Solution Processable Polymer Photovoltaic Cells by Self-Organization of Polymer Blends. *Nat. Mater.* **2005**, *4*, 864–868.

(6) Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A General Relationship Between Disorder, Aggregation and Charge Transport in Conjugated Polymers. *Nat. Mater.* **2013**, *12*, 1038–1044.

(7) Lan, Y.-K.; Huang, C.-I. Charge Mobility and Transport Behavior in the Ordered and Disordered States of the Regioregular Poly(3hexylthiophene). J. Phys. Chem. B 2009, 113, 14555–14564.

(8) Crossland, E. J. W.; Tremel, K.; Fischer, F.; Rahimi, K.; Reiter, G.; Steiner, U.; Ludwigs, S. Anisotropic Charge Transport in Spherulitic Poly(3-hexylthiophene) Films. *Adv. Mater.* **2012**, *24*, 839–844.

(9) Brinkmann, M.; Wittmann, J.-C. Orientation of Regioregular Poly(3-hexylthiophene) by Directional Solidification: A Simple Method to Reveal the Semicrystalline Structure of a Conjugated Polymer. *Adv. Mater.* **2006**, *18*, 860–863.

(10) Vukmirović, N.; Wang, L. W. Electronic Structure of Disordered Conjugated Polymers: Polythiophenes. J. Phys. Chem. B 2009, 113, 409–415.

(11) Tsoi, W. C.; Spencer, S. J.; Yang, L.; Ballantyne, A. M.; Nicholson, P. G.; Turnbull, A.; Shard, A. G.; Murphy, C. E.; Bradley, D. D. C.; Nelson, J.; et al. Effect of Crystallization on the Electronic Energy Levels and Thin Film Morphology of P3HT:PCBM Blends. *Macromolecules* **2011**, *44*, 2944–2952.

(12) Kaake, L. G.; Barbara, P. F.; Zhu, X.-Y. Intrinsic Charge Trapping in Organic and Polymeric Semiconductors: A Physical Chemistry Perspective. J. Phys. Chem. Lett. **2010**, *1*, 628–635.

(13) Sweetnam, S.; Graham, K. R.; Ngongang Ndjawa, G. O.; Heumüller, T.; Bartelt, J. A.; Burke, T. M.; Li, W.; You, W.; Amassian, A.; McGehee, M. D. Characterization of the Polymer Energy Landscape in Polymer:Fullerene Bulk Heterojunctions with Pure and Mixed Phases. J. Am. Chem. Soc. **2014**, *136*, 14078–14088.

(14) Mladenović, M.; Vukmirović, N. Effects of Thermal Disorder on the Electronic Properties of Ordered Polymers. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25950–25958.

(15) Allen, M.; Tildesley, D. J. Computer Simulation of Liquids; Clarendon Press, Oxford Science Publications: New York, U.S.A., 1987.

(16) Vukmirović, N.; Wang, L. W. Charge Patching Method for Electronic Structure of Organic Systems. *J. Chem. Phys.* 2008, 128, 121102.

(17) Vukmirović, N.; Wang, L.-W. Overlapping Fragments Method for Electronic Structure Calculation of Large Systems. *J. Chem. Phys.* **2011**, *134*, 094119.

(18) Vukmirović, N.; Wang, L.-W. Density of States and Wave Function Localization in Disordered Conjugated Polymers: A Large Scale Computational Study. J. Phys. Chem. B 2011, 115, 1792–1797.

(19) Mladenović, M.; Vukmirović, N.; Stanković, I. Electronic States at Low-Angle Grain Boundaries in Polycrystalline Naphthalene. *J. Phys. Chem. C* 2013, *117*, 15741–15748.

(20) Mladenović, M.; Vukmirović, N. Charge Carrier Localization and Transport in Organic Semiconductors: Insights from Atomistic Multiscale Simulations. *Adv. Funct. Mater.* **2015**, *25*, 1915–1932.

(21) Dag, S.; Wang, L.-W. Packing Structure of Poly(3-hexylthiophene) Crystal: Ab Initio and Molecular Dynamics Studies. *J. Phys. Chem. B* **2010**, *114*, 5997–6000.

(22) Poelking, C.; Andrienko, D. Effect of Polymorphism, Regioregularity and Paracrystallinity on Charge Transport in Poly(3hexylthiophene) [P3HT] Nanofibers. *Macromolecules* **2013**, *46*, 8941– 8956.

(23) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. J. Am. Chem. Soc. 1996, 118, 11225–11236.

(24) Cheung, D. L.; McMahon, D. P.; Troisi, A. A Realistic Description of the Charge Carrier Wave Function in Microcrystalline Polymer Semiconductors. J. Am. Chem. Soc. 2009, 131, 11179–11186.
(25) Pfaff, M.; Klein, M. F.; Müller, E.; Müller, P.; Colsmann, A.;

Lemmer, U.; Gerthsen, D. Nanomorphology of P3HT:PCBM-Based Absorber Layers of Organic Solar Cells after Different Processing Conditions Analyzed by Low-Energy Scanning Transmission Electron Microscopy. *Microsc. Microanal.* **2012**, *18*, 1380–1388.

(26) Parr, R. G.; Yang, W. Density-Functional Theory of Atoms and Molecules; Oxford University Press: New York, U.S.A., 1989.

(27) Vukmirović, N.; Wang, L.-W. Charge Carrier Motion in Disordered Conjugated Polymers: A Multiscale Ab Initio Study. *Nano Lett.* **2009**, *9*, 3996–4000.