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Identification of the Possible Defect States in Poly(3-hexylthiophene) Thin Films

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The possible origins of a low density of defect states within the highest occupied molecular orbital to lowest unoccupied molecular orbital gap are suggested for regioregular poly(3-hexylthiophene). A number of chemical defects, impurities, and structural defects could contribute to features in photoemission for regioregular poly(3-hexylthiophene), observed within the highest occupied molecular orbital to lowest unoccupied molecular orbital gap of regioregular poly(3-hexylthiophene).

INTRODUCTION

The interplay between carrier charge mobility and photoemission final state screening has for decades attracted a lot of interest [1], but has only recently been applied to conjugated polymers [2–4]. From photoemission and electronic structure calculations [2, 3], undoped conducting polymers are insulators. If this is the case, then conductivity is likely dominated by hopping conductivity and must be mediated by the finite density of states near the Fermi edge [3, 5]. States contributing to the conductivity are rarely discussed but may be the result of impurities [4, 6], defects [3], disorder [7, 8] in the polymer, or p-p intermolecular interactions [6, 9–11]. Impurities and defects may add to the carrier concentration while chain defects can lead to a loss of mobility as a result of wave function localization. Understanding of the role of defects will therefore be important to improve the transport performances of organic field-effect transistors in spite of increases in defect scattering.

A low density of defect states within the highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) gap of poly(3-hexylthiophene) (P3HT) has been observed [2, 3]. Salaneck and coworkers [12, 13] infer from their data that thermally induced conformational defects occur with increasing temperature associated with loss of coplanar orientation of the aromatic rings in the aromatic chain backbone [12, 13]. This configuration-related disorder may be used to explain the changes in carrier mobility in P3HT field-effect transistors at elevated temperature [9]. A decrease in the carrier mobility in P3HT is observed at elevated temperatures (above 300 K) [9]. At lower temperature (<200 K), there is loss of conductivity [2, 3] that cannot be easily associated with thermally induced structural distortions but is likely a result of the finite energy for carrier activation.

A range of "chemical" defects, such as "missing hydrogen" on an aliphatic pendant group, or some chemical impurity, could impart more hole carriers (greater p-type character) to a semiconducting polymer as well as result in an effectively smaller optical band gap, relative to the HOMO-LUMO gap, as noted elsewhere [14]. As the insulating character of P3HT increases, carrier mobility or carrier concentration decreases with decreasing temperature as has been observed in the low temperature range [3], which indicates impurities and/or chemical defects rather than just structural defects alone play an important role in the conductivity of a polymer; furthermore, this conclusion is consistent with the polaronic conduction mechanisms proposed. As with polypyrrole [15], there are very strong indications that the temperature dependence of the conductivity is not directly related to changes in the polymer geometry with temperature, except at higher temperatures (above room temperature). This is based on the observations of temperature-dependent screening effects and thermochromism using high-resolution photoemission [2].

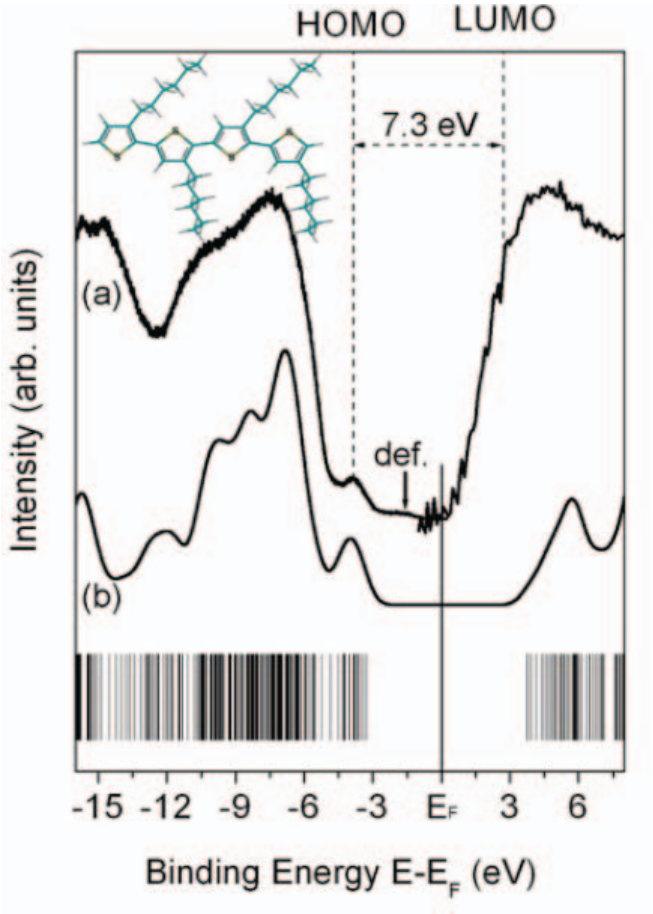

Figure 1. Occupied (left) and unoccupied (right) molecular orbital contributions of regioregular P3HT to the (a) photoemission and inverse photoemission spectra, respectively, are compared with (b) theory. The experimental HOMO-LUMO gap of P3HT (7.3 eV) is indicated as is a defect state (def.) not directly attributable to the molecular orbitals indicated (see text). The inset shows a schematic of a single chain of regioregular P3HT.

Heterogeneous chemical defects (imperfections in the polymer) have already been implicated by conductivity measurements taken of P3HT [3]. Following up on this line of investigation, we suggest the possible origins of a low density of states within HOMO-LUMO gap using model calculations. Both impurities and conformational defects may contribute to the defect state density in the HOMO-LUMO gap.

EXPERIMENTAL AND THEORETICAL DETAILS

Regioregular poly(3-hexylthiophene-2,5 diyl) (or simply poly(3-hexylthiophene) (P3HT)) films were prepared by spin coating techniques, as undertaken elsewhere [12– 16], where the chloroform solvent was allowed to dry between successive casts. The RR-P3HT was purchased from Aldrich (445703) with 98.5% head-to-tail regiospecificity. The schematic of P3HT is shown in the inset to Figure 1. Combined photoemission and inverse photoemission (IPES) were undertaken to study the molecular orbital placement of both occupied and unoccupied molecular orbitals of the adsorbed molecules on Au(111) surfaces. All IPES spectra were obtained with the electron gun at normal incidence and the detector positioned at 45° off the surface normal, as described elsewhere [17, 18]. The high-resolution ultraviolet photoemission spectroscopy (UPS) were carried out at the Center for Advanced Microstructures and Devices synchrotron radiation facility using a Scienta 200 hemispherical electron analyzer with a combined resolution better than 10 meV [19]. The photoemission spectrum was taken with unpolarized He I (21.2 eV), with the photoelectrons collected normal to the surface. All angles (both light incidence angles as well as photoelectron emission angles) reported herein, are with respect to the substrate surface normal. The binding energies are referenced with respect to the Fermi edge of gold or tantalum, and all photoelectrons were collected normal to the substrate surface and at normal incidence for IPES ($k_{||} = 0$ or $\bar{\Gamma}$) to preserve the highest possible local point group symmetry.

Theoretical calculations of the electronic structure of regioregular P3HT were undertaken by PM3-NDO (neglect of differential overlap) with the HyperChem package [20, 21]. The applicability of such simple semi-empirical molecular orbitals calculations to large molecular systems is well established [2, 3, 22–27]. The model calculations were undertaken on short chain length (10 repeat units) that was hydrogen-terminated to prevent excessive folding as is typical of such calculations [2, 3, 14, 24]. We have avoided the "state-of-the-art" modern density functional (DFT) calculations here in this work because of the well-recognized failures of DFT in providing an accurate description of the electronic structure as determined by photoemission and IPES. DFT generally results in a HOMO-LUMO gap smaller by as much as a factor 2 or more. Both photoemission and IPES are final state spectroscopies, so that comparison with this simple semi-empirical ground state molecular orbital energies for 10 monomers of a single chain regioregular P3HT, which includes neither excitations, multiconfigurational final states, matrix element effects nor finite temperature effects to UPS (and IPES), must be considered as only qualitative.

RESULTS AND DISCUSSION

Electronic Structure

Assuming all molecular orbitals contribute equally to the experimental density of states, we obtain a calculated density of states by applying equal Gaussian envelopes of 1 eV width to each molecular orbital (to account for the solid state broadening in photoemission) and then summing. This calculated density of states, together with a rigid energy shift of 5.3 eV applied to the calculated electronic structure, is compared with the combined photoemission and IPES, and shown in Figure 1. The shift of 5.3 eV between theory (referenced to the vacuum

level) and the experimental binding energies (referenced to the Fermi level) is typical as observed for with other conducting polymers [14, 23], insulating polymers [24], and molecular adsorbates [22, 25–26, 28].

From the combined photoemission and IPES spectra as shown in Figure 1, we see there is good qualitative agreement between experiment and calculated density of states. The experimental molecular HOMO-LUMO gap is 7.3 ± 0.2 eV for P3HT, which is consistent with 7.05 eV gap from the molecular orbital theory. These values are similar to the value of 6.4 eV estimated from the gas-phase X-ray photoelectron spectroscopy on the P3HT monomer [29]. Optical excitations can probe excitons, injected charge excitations, intermolecular excitations, and interstate excitations, and are thus not always directly comparable to the ground state. While photoemission is also an excitation spectroscopy, with care this seems to compare better to the ground state.

Many features of P3HT, from the photoemission and IPES spectra (Figure 1), can be assigned to groups of molecular orbitals, except that the lowest unoccupied molecular orbitals underestimates the binding energy, as is typical [2, 3, 14, 22–28]. However, the very weak feature at –1.7 eV binding energy (denoted as "def." in Figure 1) cannot be assigned to any corresponding molecular orbital in our molecular orbital calculations. The existence of this occupied density of states at low binding energy, because of defects, imparts p-type character to the polymer, i.e. places the Fermi level closer to the occupied density of states and could create a hole carrier concentration as well as lead to defect state trapping and hopping conductivity to the P3HT. In fact we note that this state occurs at a energy close to a strong optical absorption band, at 1.8 eV, believed to be due to injected carriers and assigned to polarons [30–32] in this system. In this regard, we believe that impurities could result in states within the HOMO-LUMO gap.

Modeling of Possible Defect States

There is evidence that structure changes in the relative orientation and configuration of the aromatic ring backbone occur over a wide range in temperature for P3HT [2]. There is indeed a strong correlation between the backbone conformation and electronic structure of conjugated polymers [2, 3, 12, 13]. The photoemission feature at –1.7 eV binding energy (Figure 1) could be a consequence of structural defects accompanying the ordering of the aromatic chain backbone, as shown in Figure 2a, d, and e. The rotation of isolated arene rings, along the aromatic P3HT backbone, as schematically shown in the inset to Figure 2a, could create the defect state seen in photoemission at –1.7 eV binding energy. This would effectively close (diminish) the HOMO-LUMO gap of P3HT. The given geometry (Figure 2a) is associated with twist and tilt of one monomer out of the conjugation plane. The extent of such geometric distortions is directly related to the number of defect states within HOMO-LUMO gap; too much loss of regioregularity of P3HT will result in several defect states while moderate loss of regioregularity of P3HT may not create defect states within HOMO-LUMO gap.

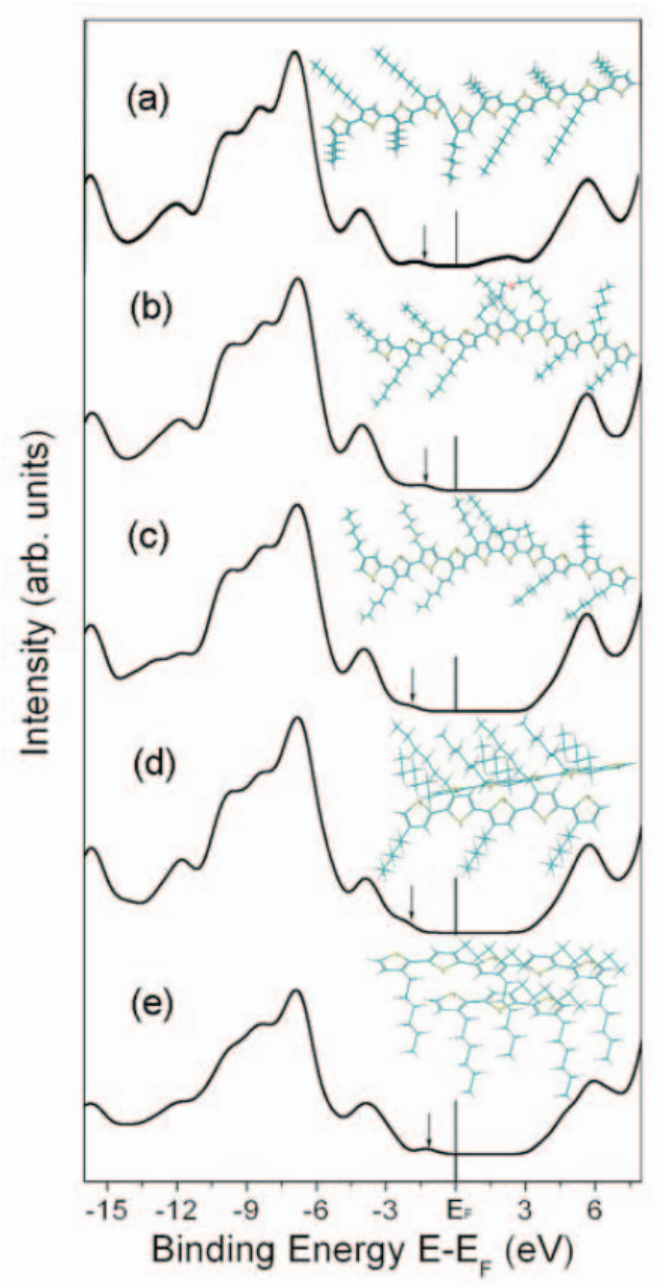

Figure 2. The calculated density of states (DOS) for several types of structural defects as might occur for 10 monomers chain length regioregular P3HT. These structural and chemical defects include isolated rotation of the arene rings (a), an oxygen bridging two pendent groups (b), selected dehydrogenation resulting in a pendant group linking two adjacent thiophenes (c), and loss of p-p stacking either through tilting of adjacent polymer chains (d), or as a result of a lateral displacement of adjacent polymer chains (e) in regioregular P3HT thin films.

The interpolymer packing density affects electronic properties [33], as expected from the π-π interchain interactions [6, 9–11]. We have adopted in our model calculations an interchain spacing around 1–4 nm, with too large a separation between chains, and few features within HOMO-LUMO gap can be created from the interchain interactions. π-π interchain stacking is certainly believed to play an important role in determining the band gap and the film conductivity [6, 9–11], and any change in the chain-to-chain conformation leads to modification of the so-called effective conjugation length. Calculations were undertaken for loss of π-π stacking geometry either through tilting of adjacent polymer chains (Figure 2d) or as a result of a lateral displacement of adjacent polymer chains (different conjugation length) (Figure 2e). As expected, theoretical calculations based on these artificially fixed geometries could result in defect states around –1.7 eV. It is difficult to exclude many possible contributions to the defect-related density of states within the HOMO-LUMO gap based on the present data, although the structure shown and modeled in Figure 2d is unlikely, based on the published polarized light dependent photoemission, which suggest that the P3HT films are highly orientated [2].

All the conformational defect models shown in Figure 2 could lead to a greater carrier concentration; however, the disordered conformation will lead to a barrier to transport and decrease the mobility [9]. The transport properties of organic field-effect transistors will be determined by a balance of these effects. In the case of temperatures at or above room temperature, the mobility decreases with increasing temperature, which indicates that defect scattering is a more dominant effect as temperature increases [9].

It may be that very small numbers of chemical defects, rather than just structural defects alone, play dominant a role in determining the conductivity below room temperature, as suggested by Refs. [2, 3]. As shown in Figure 2b and c, an oxygen bridging two pendant groups (Figure 2b) and selected dehydrogenation resulting in a pendent group linking two adjacent thiophenes (Figure 2c) certainly can result in defect states within the HOMO-LUMO gap consistent with the photoemission (Figure 1).

Along with these introduced "chemical" defects, twisting of aromatic backbone of the polymer can occur even without a tilting or displacement of arene monomer out of backbone plane, as a result of interaction of aliphatic hexyl group. Such distortions are certainly consistent with the fact that the aliphatic hexyl groups do not have a direct influence on the electronic structure of the aromatic rings [34, 35]. We have undertaken a number of model calculations to explore the influence on the electronic structure of such alterations of the aliphatic hexyl groups. Using our simple model calculations, other chemical defects on an aliphatic pendant group or the thiophene alone, such as missing hydrogen on an aliphatic pendant group or thiophene, replacement of a "carbon" atom with an "oxygen" atom on an aliphatic pendant group or thiophene, an oxygen bridging two carbon atoms on an aliphatic pendant group or thiophene, even, in the extreme case, omission of an aliphatic pendant group, will not result in major changes of backbone conformation of P3HT, and do not create density of states within HOMO-LUMO gap. These latter distortions and chemical defects only seem to result in a small change of the HOMO-LUMO gap. Interestingly, even the combination of all these types of alterations of the aliphatic hexyl groups or the addition of oxygen, mentioned earlier, (all together) also do not induce a suitable density of states in the HOMO-LUMO gap. Such chemical defects might exist and might impair the mobility of the carriers, but cannot explain the high-resolution photoemission.

Similarly, the interplay between aliphatic pendant group and thiophene does not necessary create density of states in the HOMO-LUMO gap, despite the resulting possible distortions to the aromatic backbone. The model simulations suggest that interactions between the aliphatic pedant groups and the same monomer site of a thiophene will not create defect density of states in the HOMO-LUMO gap. Surprisingly, dehydrogenation bridging two pendant groups (such as might occur by replacing an oxygen atom in the structure shown in Figure 2b with double carbon bond) will not create a suitable density of states in the HOMO-LUMO gap, although similar twisting is imparted to the thiophene backbone, as was described earlier. Similarly shorter polymer chains lengths lead to an increase, not a decrease, in the HOMO-LUMO gap [2] and are unlikely to increase conductivity.

We must infer that certain acceptor state defects, in the vicinity of the aromatic ring backbone, contribute to the p-type character to the polymer and will enhance conductivity. These defects can contribute carriers as long as the temperature is sufficient to "activate" the carriers. Not all defects, chemical impurities, and distortions to P3HT will affect the conductivity at a given temperature; however, although they may contribute states to within the HOMO-LUMO gap. Defects that lead to changes in the electronic structure, within the HOMO-LUMO gap, will not necessarily alter the conductivity significantly and change the density of states near the Fermi level. Some of the few defects that are possibly pertinent to contributions to a density of states within the HOMO-LUMO gap are summarized in Figure 2. As noted earlier, we cannot assign a specific photoemission feature within the HOMO-LUMO gap to a specific defect type nor can we assess, a priori, the impact of a given defect upon the conductivity, from the photoemission data alone. It is very unlikely that the carriers in P3HT have a homogeneous origin.

If one looks at the overall conductivity [3], for all intents and purposes, this material is an insulator in the native undoped state, as the conductivity is very low for a metal or semimetal (nA or less). The temperature dependence of the conductivity is characteristic of a two-dimensional hopping model [3], consistent with the presence of defects.

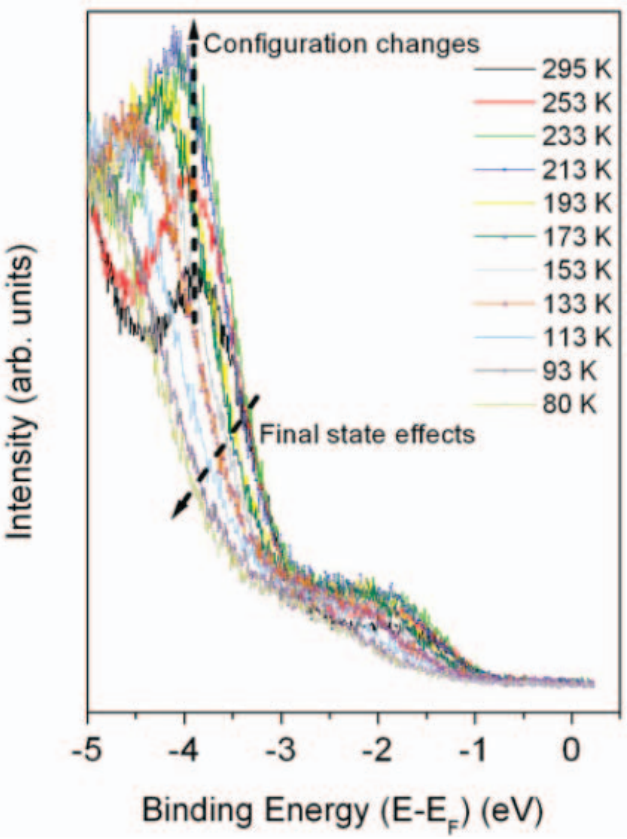

Figure 3. Temperature-dependent photoemission spectra of regioregular P3HT. Notice that as temperature decreases the photoemission features attributed to the P3HT molecular orbitals increase in binding energy for the temperature range of 80–233 K, while change of orbital peak intensities is significant in the region of 213–295 K.

Screening Effect in Temperature

A gradual, but unambiguous temperature-dependent change of the valence band was found in the photoemission between 80 and 300 K, as summarized in Figure 3. There is a gradual increase in the binding energy of the valence band with decreasing temperature over the temperature range of 80–233 K. The observed increased insulating character of P3HT with decreasing temperature is characterized by a general decrease in photoemission final state screening because of electron and hole localization (i.e. an observed increase in the photoemission binding energies with decreasing temperature), a loss of carrier conductivity, and a decrease of carriers (increased carrier trapping). The fact that the charge localization due to temperature-dependent trapping and mobility is gradual implies that the chemical defects are heterogeneous, which is consistent with the theoretical indications, as well as our assignment of the small binding energy photoemission feature to different defects states, including impurities, chemical defects (missing hydrogen, unsaturated bonds), and structural defects. Studies of related polythiophenes suggest that the transport is dominated by variable range hopping [5], which is certainly consistent with the heterogeneous nature of defects suggested by the photoemission.

The configuration changes are more significant than final state effects in the temperature range of 213–295 K (Figure 3), as is evident from the increase in some of the photoemission peak intensities with decreasing temperature. The increasing intensity of the photoemission feature at –1.7 eV binding energy suggests increasing carrier density or a thermally (and reversible) defect density; however, the conductivity actually decreased with decreasing temperature in this temperature range [3]. The changes in photoemission intensity are likely due to the increased twisting of the aromatic polymer backbone with increasing temperature [3]. While the loss of regioregularity of P3HT and coplanar thiophene orientation increases the effective defect scattering and decreases mean free path for the charge carriers resulting in lower conductivity and mobility [9], carrier concentrations may actually be increasing at higher temperatures.

CONCLUSIONS

In summary, we suggest that impurities, “chemical” defects and “structural” defects are the origin for a small density of states within the HOMO-LUMO gap of P3HT. These heterogeneous defects impart p-type character to the polymer, although they may limit charge mobility. Chemical defects and structure defects associated with the geometry change of the backbone may also contribute significantly to the transport properties. Nonetheless, we believe that defects leading to a small change in carrier concentration near the Fermi level will significantly increase conductivity, even though the same defects may lead to a decrease in carrier mobility.

The change in dielectric properties, mediated by defect states, is gradual with temperature as seen from the photoemission, which is consistent with the theoretical suggestion that there is a heterogeneous contribution of defect states even in regioregular P3HT. Considering the gradual change of binding energy and photoemission intensities with temperature, the distribution of defects contributing to the semiconductor properties of P3HT must be fairly isotropic. As temperature drops, some of these heterogeneous defect states are frozen out while others are not at each temperature interval. The indications of heterogeneous defect states are consistent with the photoemission. Such defect states might extend from the conduction and valence-band edges all the way to the Fermi level, but at such a low density that their contribution to the photoemission and IPES is generally minimal.

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