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Intrinsic Charge Trapping in Organic and Polymeric Semiconductors: A Physical Chemistry Perspective

L. G. Kaake, P. F. Barbara, and X.-Y. Zhu*

Energy Frontier Research Center, and Department of Chemistry & Biochemistry, University of Texas, Austin, Texas 78712

ABSTRACT We aim to understand the origins of intrinsic charge carrier traps in organic and polymeric semiconductor materials from a physical chemistry perspective. In crystalline organic semiconductors, we point out some of the inadequacies in the description of intrinsic charge traps using language and concepts developed for inorganic semiconductors. In π-conjugated polymeric semiconductors, we suggest the presence of a two-tier electronic energy landscape, a bimodal majority landscape due to two dominant structural motifs and a minority electronic energy landscape from intrinsic charged defects. The bimodal majority electronic energy landscape results from a combination of amorphous domains and microcrystalline or liquid-crystalline domains. The minority tier of the electronic density of states is comprised of deep Coulomb traps embedded in the majority electronic energy landscape. This minority electronic energy landscape may dominate transport properties at low charge carrier densities, such as those expected for organic photovoltaic devices, while the bimodal majority electronic energy landscape becomes significant at high carrier densities, that is, in organic field effect transistors.
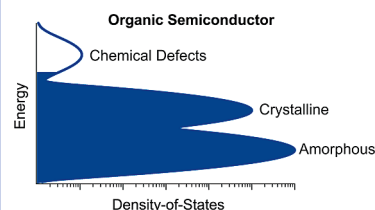
Disordered Semiconductors. Organic semiconductors are being explored for a number of exciting applications, such as organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs), and organic photovoltaics (OPVs). A salient feature distinguishing organic (including polymeric) semiconductors from their inorganic counterparts is the strong tendency of charge carrier localization in the former. The effects of carrier localization are reflected by the dominant role of polarons due to electronic–nuclear coupling. The inherent tendency for carrier localization is enhanced by the presence of energetic disorder, which is the result of structural inhomogeneities and chemical impurities, leading to charge carrier trapping in some cases. Thus, we can view organic semiconductors as members of the disordered semiconductor family.

> In crystalline organic semiconductors, we point out some of the inadequacies in the description of intrinsic charge traps using language and concepts developed for inorganic semiconductors.

Theoretical description of charge transport in disordered materials is based on the central idea of Anderson localization,[1] whereby disorder in the electronic energy landscape causes a carrier wave function to become confined to a small region (site) within the semiconductor material. The concept of a localization site enters the treatment of disordered semiconductors often in the form of percolation theory; however, a clear connection between a localization site and the atomic details of a material only exists for inorganic semiconductors. For example, in a lightly doped crystalline semiconductor, randomly distributed dopant atoms serve as localization sites. In these disordered systems, conductivity is calculated from modeling transport between sites as activated tunneling.[2]

A useful concept in understanding transport in disordered systems is the mobility edge (ε_M), which is the energetic position separating localized sites from delocalized sites; electrons above the mobility edge participate in band transport while those near the mobility edge ($\sim kT$) can be thermally ionized into delocalized states. Deeper into the localized density of states, current can still be carried, but only through thermally activated tunneling and hopping, while localized electronic states too deep to be thermally activated into current-carrying states are effectively considered as static. The former are usually referred to as shallow traps and the latter as deep traps. Deep traps, once charged, will tend to remain so for extended periods of time and, thus, alter device performance parameters. Note that traps and dopants are both energetically located in the band gap; they are

distinguishable based on their relative energetic positions relative to the valence band maximum (VBM) or the conduction band minimum (CBM).[3] When electron donors are located near the VBM, they serve as hole traps. Conversely, electron acceptors near the VBM act as dopants. Similar arguments naturally apply to the CBM.

While transport models developed from disordered semiconductor theory have been successfully applied to describing temperature and field-dependent transport in organic semiconductors,[4,5] little is known about the microscopic origins of localization sites and charge carrier traps in these materials. Chemical impurities are obvious culprits, but there are confusions and misconceptions on structural origins of localization sites and traps. In addition, one must remember that disordered semiconductor theories are developed originally for transport on an electronic landscape with disorder mainly in the electronic coordinate. Site energies are considered fixed and are not subject to change via nuclear polarization. This is true for most inorganic semiconductors but inappropriate for molecular materials where strong electron−nuclear coupling is the norm. Strong electronic−nuclear coupling is responsible for not only the formation of polarons (i.e., charge carriers dressed by nuclear deformation)[6] but also the possibility of dynamic trapping.[7,8] The latter refers to a self-trapping process as a localized charge carrier digs deeper below ε_M with increasing time due to extensive molecular rearrangements or chemical reactions. While strong electronic−nuclear coupling is expected for the flexible and disordered polymeric semiconductors, even in crystalline semiconductors of small organic molecules, the inherently narrow electronic bandwidth and the susceptibility of these soft materials to both static and dynamic deformation can contribute to carrier localization at noncryogenic temperatures. The prevalence of strong electron−nuclear coupling qualifies organic and polymeric semiconductors as new classes of disordered semiconductors.

Synopsis of Charge Carrier Traps in Organic Semiconductors. Charge carrier traps have been observed from the beginning of model organic semiconductor device research; they affect the device performance of OLEDs, OTFTs, and OPVs. For example, the presence of shallow traps is evidenced in thermally activated transport and in carrier-density-dependent charge mobility. Deep traps can cause charges to remain fixed within an organic semiconductor film after the device is turned off. The presence of fixed charges modifies the electrostatic landscape of the material and leads to changes in e−h recombination efficiency in OLEDs and shifts in the threshold voltage for transistor turn-on in OFETs. The latter came to be known as bias stress and is characterized by a temporally evolving shift of the threshold voltage with a continuously applied gate voltage.[9]

On the basis of microscopic origins, we divide charge traps into two categories, extrinsic traps due to impurities or chemical defects and intrinsic traps from structural inhomogeneity. Extrinsic traps are sites within the band gap and are associated with species of different chemical composition than the organic semiconductor. For example, impurities in the source material can cause traps.[10] This is likely an important consideration as the chemical purification of

organic semiconductor materials lags far behind what has been achieved in silicon. In addition, intermolecular interactions in an organic semiconductor film are dominated by the relatively weak van der Waals force, making organic semiconductor materials particularly susceptible to the incorporation of chemical impurities, such as solvent and ambient gas molecules.[11,12] Another source of extrinsic traps is chemical instability; many conjugated organic molecules are reactive toward oxygen or water.[13] Finally, in conjugated polymers, certain structural motifs, such as twisting of a conjugated polymer chain, have been suggested to create immobile electron−hole pairs that could contribute to low mobility and charge trapping.[14]

Extrinsic charge carrier traps likely play dominant roles on the transport properties of organic semiconductors when their purities are less than desirable or when they are subject to chemical attacks by, for example, oxygen, water, or organic solvents. While reducing extrinsic traps will remain a chief goal in the practical application of organic semiconductors, one must also cope with the inevitability of chemical impurities. This is especially true in the context of low-cost and large-scale manufacturing where the much-touted advantages of organic materials are apparent. Extrinsic traps will not be discussed in depth throughout the remainder of the article. We will instead focus on the microscopic origins of intrinsic traps that result from structural inhomogeneity in organic semiconductors. In doing so, we will consider two types of organic semiconductor materials, small molecules and polymers.

Intrinsic Charge Traps in Small-Molecule Organic Semiconductors. Small-molecule organic semiconductors are characterized by a high degree of crystallinity. While transport in single crystals has been demonstrated for a number of small molecules, most organic semiconductor materials of practical importance are in the form of polycrystalline thin films. The morphology of thin film organic semiconductors is characterized by large concentrations of domain boundaries and other structural defects. A reoccurring scheme in the literature is the comparison of polycrystalline organic semiconductor thin films to their inorganic counterparts, especially polycrystalline or amorphous silicon. However, there is a danger in this comparison. As is well-known, defects and surfaces of inorganic semiconductor materials are characterized by dangling bonds, while those of an organic semiconductor are not. The left panel in Figure 1 illustrates the formation of bonding and antibonding orbitals and eventually valence and conduction bands from partially occupied sp^3 hybridized Si orbitals. The most important point to note is that the sp^3 state on a dangling Si bond is located in the middle of the band gap. The midgap dangling bonds can act as both electron and hole traps and therefore must be passivated (by covalent bond formation with H) for optimal device function.

The right panel in Figure 1 shows the formation of valence and conduction bands from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of pentacene molecules. Unlike the covalently bonded Si, the valence and conduction bands of this van der Waals solid are formed from the fully occupied and fully
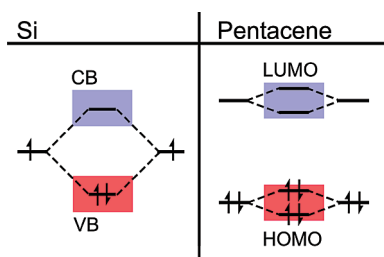
Figure 1. Schematic band structure and molecular orbital diagram for silicon and pentacene as examples of inorganic and organic semiconductors, respectively. The silicon diagram depicts valence and conduction band formation from singly occupied sp^3 hybridized orbitals on Si atoms. Their linear combination gives rise to bonding and antibonding orbitals and eventually valence (VB) and conduction bands (CB) in the infinite solid. Here, the energetic position of isolated atoms is the midgap. The pentacene side of the diagram depicts the formation of HOMO and LUMO bands from the fully occupied and fully unoccupied molecular orbitals, respectively. Note that in this case, both the HOMO and the LUMO on each isolated pentacene molecule are energetically located at the midband, instead of the midgap.

unoccupied molecular orbitals, respectively. As a result, the HOMO or LUMO level of an isolated pentacene molecule is energetically located at the midband, instead of the midgap, and cannot serve as either an electron or hole trap. As a corollary, grain boundaries are not expected to act as traps because the break in the band structure shifts the energy toward the isolated molecular level (i.e., into the band not into the gap). Thus, one must take care when applying heuristics borrowed from the study of inorganic semiconductors to the study of organic semiconductors or, more generally, any van der Waals solid. Note that the above argument is quantitatively modified when one takes into account differences in the charge carrier polarization energy between crystalline domains and domain boundaries (and interfaces).[15]

The above argument suggests that intrinsic charge carrier traps in a polycrystalline organic semiconductor films are most likely sites with the highest degree of electronic coupling, i.e., crystalline domains, not domain boundaries as suggested previously.[16] Another way to understand this seemingly counterintuitive conclusion is to realize that carrier energies are primarily determined by their degree of delocalization. Charges with a greater degree of delocalization will have a lower total energy, primarily because of a lower kinetic energy. Indeed, experiments by Muller and Marohn using Kelvin probe microscopy on operating pentacene OTFTs revealed that charge trapping was inhomogenously distributed and did not appear to be confined to grain boundaries.[17] Frisbie and co-workers[18] carried out concurrent imaging of the domain boundary network and electrostatic potential of ultrathin pentacene thin films deposited on the silicon oxide surface. These authors found that the electrostatic potential of domain boundaries was lower than that in crystalline domains and suggested that domain boundaries are charge traps. However, we believe the opposite is likely true; crystalline domains, not domain boundaries, are charge traps. To explain the discrepancy, one should note that pentacene, like many organic semiconductor materials, is very prone to static charging. During deposition, adventitious charges

(in this case, holes) accumulate within the film and become trapped in the lower-energy crystalline domains, raising their electrostatic potential with respect to domain boundaries. This interpretation is consistent with Kelvin probe microscopy results of Muller and Mahron[17] or Sirringhaus and co-workers[12] that showed increased electrostatic potential from intentionally trapped holes in pentacene.

Single-crystal organic semiconductors have higher field effect mobilities than their respective polycrystalline thin films, virtually without exception. How, then, does one understand the argument that the interior of the crystalline domain can act as charge traps? The answer lies in the grain boundaries that insulate the highly conductive crystalline domains from the remainder of the film. These insulating boundaries can lead to carrier trapping by hindering the removal of charge carriers from a crystallite. In other words, charges are trapped *by* high-energy grain boundaries not *on* them. More generally stated, it need not be the case that the causal mechanism for charge trapping also serve as the location of the trapped charge. In light of this argument, the term trap site can be misleading as it tends to equate the location of the trapped charge with the cause of the charge-trapping phenomenon.

> ## Charges are trapped *by* high-energy grain boundaries not *on* them.

The model of charge trapping presented above is somewhat oversimplified. Morphological complexity of polycrystalline organic semiconductor thin films goes beyond the picture of crystalline domains + domain boundaries. One expects a variety of defects, such as point defects, line dislocations, and so forth. However, not all defects are relevant to the process of charge trapping. For example, neutral point defects are not expected to act as charge traps because the break in crystal packing pushes local carrier energies into the band not into the gap. In general, a neutral defect which decreases the local bandwidth will not act as a charge trap. Conversely, a neutral defect which increases the local bandwidth will tend to act as charge trap. This increased local bandwidth can come from decreased intermolecular spacing due to compressive stress from mismatch in interfacial energy, from the incorporation of electronically neutral impurities, or from other subtle changes to intermolecular arrangements. Calculations preformed by Bredas and co-workers[19] showed that increases in the electronic coupling can result not only from decreasing intermolecular spacing but also from changing the registry along the long molecular axis of neighboring molecules. Note that at domain boundaries, changes in intermolecular registry, and/or distance may incidentally increase electronic coupling, but this may not be sufficient to compensate for the reduced coordination number. As a result, domain boundaries are unlikely to serve as the location of trapped carriers.

An example of such a defect is illustrated by Zhu and co-workers.[20] Figure 2 shows molecular resolution scanning tunneling microscope (STM) images of a pentacene thin film grown on a benzenethiol-passivated Au surface. Compressive
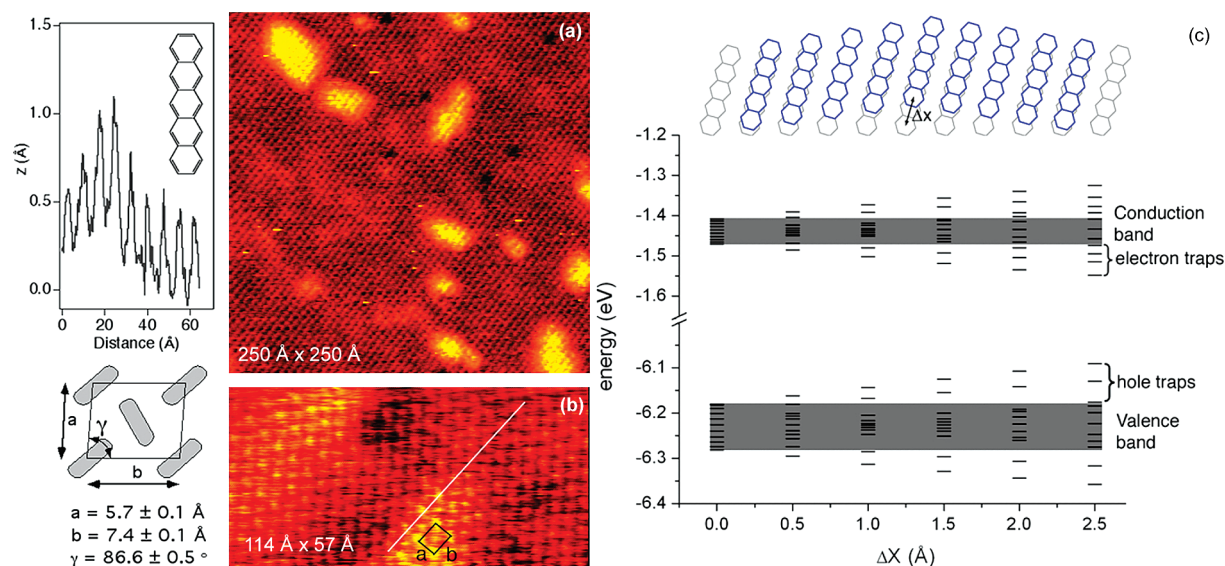
Figure 2. Scanning tunneling microscope images showing a thin film of pentacene grown on a bezenethiol-passivated Au(111) surface. Individual molecules can be resolved. The wide range image (a) indicates that the overall morphology of the pentacene film is not flat but has many low periodicity height variations. The line scan (upper left corner) taken from the zoomed-in image (b) indicates that the height variation is less than that of a single pentacene molecule. Panel (c) shows the result of band structure calculations performed as a function of out-of-plane displacement. States within the gap are observed as a result of increasing wave function overlap between neighboring molecules. After Kang et al.[20]

stress during film growth results in "buckling" defects, that is, sliding of pentacene molecules along their long molecular axis while two-dimensional crystalline packing is maintained. Results from electronic structural calculation on the right confirms that these sliding defects are shallow charge traps with energies ≤100 meV above (below) the valence band maximum (conduction band minimum). Similar buckling defects have been observed recently in STM imaging of pentacene thin films grown on crystalline C_{60} surfaces.[21]

Note that crystalline domains within a polycrystalline thin film may exhibit different defect densities and, thus, different trapping densities. Depending on the quality and purity of the pentacene film, there can be unintentional doping (e.g., from extrinsic dopants). Under equilibrium conditions, more charge carriers are expected to reside in crystalline domains with a higher trapping density. This may explain the subtle differences in electrostatic potential among different crystalline domains, as shown in Kelvin probe microscopy images reported by Frisbie and co-workers.[18]

The "softness" of molecular solids is not only reflected in static defects, as shown above, but also in the form of dynamic trapping, that is, molecular and lattice distortions in the presence of a charge carrier. This is of course equivalent to the widely accepted concept of polarons in most organic semiconductors,[6] with very few exceptions.[22] Polaron formation is a dynamic process occurring on ultrafast time scales, $\sim 10^{-15} - 10^{-14}$ s due to molecular vibrations or $10^{-13} - 10^{-12}$ s from phonon modes. However, dynamic localization in the presence of charge carriers can also occur on much longer time scales due to more extensive molecular movements. As an extreme example, a recent study by Bovesiepan et al. on the solvation of an electron on an ice surface showed

localization dynamics spanning 17 orders of magnitude, from femtoseconds to minutes.[8] Marohn and co-workers showed slow (minutes) self-trapping processes in polycrystalline pentacene in the presence of free carriers by time-resolved electric force microscopy measurements.[23] These authors attributed the slow trapping process to a structural-defect-related chemical reaction in the presence of hole carriers.

Intrinsic Charge Traps in π-Conjugated Polymers. We must realize at the onset that understanding intrinsic charge traps in semiconducting polymers is much more difficult than that in crystalline small molecular semiconductors. This results from the structural complexity of polymeric materials and the susceptibility of these materials to the introduction of charged defects (extrinsic dopants, chemical modifications on polymer chains or terminal groups, and covalent defects). As pointed out by Gregg and co-workers,[14,24,25] conjugated polymers, such as poly(3-hexythiophene) (P3HT), are characterized by high levels of free carriers (10^{15-17} /cm^3) in the absence of photoexcitation or charge injection. Such a high carrier density persists even after extensive chemical purification. These charged defects serve not only to dope the polymeric semiconductor (p-type) but also to introduce trapping sites. These charged traps are present in addition to those resulting from noncovalent structural defects. In view of this complexity, we divide the following discussion into two sections. We first focus on the majority electronic energy landscape resulting from dominant structural motifs in π-conjugated polymeric semiconductors. The majority electronic energy landscape is sampled at very high carrier densities when minority traps are already filled. This is of importance to field effect transistor devices where gate-induced doping occurs predominantly to the first layer of molecules in direct contact with the dielectric. A typical doping

level in the "ON" state of an OTFT is on the order of $10^{11}-10^{13}/cm^2$, corresponding to a volume density of $10^{18}-10^{20}/cm^3$, which is 2−4 orders of magnitude higher than the density of charged defects. Following this discussion, we will briefly address the minority electronic energy landscape due to charged defects. These minority traps play dominant roles at low charge carrier densities, that is, in an organic photovoltaic device.

Majority Electronic Energy Landscape: Bimodality. Microcrystalline polymers such as regioregular P3HT are often characterized by crystalline domains interdispersed in an amorphous matrix. Within each crystalline domain, highly conjugated, planar polymer segments are π-stacked. This leads to the two-dimensional (2D) delocalization of charge carriers and, thus, significant electronic bandwidth perpendicular to the chain axis. In comparison, the amorphous regions are more one-dimensional (1D) in nature and should have a narrower electronic bandwidth. Spectroscopic experiments[26,27] and electronic structural calculations[28] confirmed that charge carriers within the crystalline domains of P3HT possess lower energies than those in the amorphous regions. The tight binding perspective presented in Figure 1 applies equally well to the study of carriers in microcrystalline polymers. Namely, polymer segments in amorphous regions are more electronically isolated and will have electronic energy levels which are midband compared to those in crystalline domains. Thus, 1D amorphous regions serve not as charge traps but as a barrier for charge transport. In contrast, the 2D crystalline regions are energetically more favorable for charge carriers. Note that structural heterogeneity in both 1D and 2D regions will modify the bimodal electronic energy distribution. Similar to the case of pentacene in Figure 2, changes in interchain registry and/or distance may increase electronic coupling, which is perhaps more likely in the 1D amorphous region. However, the incidental increase in electronic coupling in the 1D amorphous regions may not be sufficient to compensate for the reduced coordination number as compared to that in the 2D crystalline region.

To probe this majority electronic energy landscape, we carry out in situ optical absorption spectroscopy measurement on a model device, the interface between a polymeric semiconductor, P3HT, and a polymer electrolyte dielectric consisting of lithium poly(styrene sulfonate) dissolved in poly(ethylene oxide), LiPSS/PEO.[29] We choose this electrolyte dielectric material because the presence of mobile ions allows us to obtain very high capacitance due to the formation of an electrical double layer at the polymer semiconductor and polyelectrolyte interface. As a function of gate bias voltage (V_G), in situ optical spectroscopy reveals a distinct transition from electrostatic ($0 > V_G > -1.8$ V) doping to electrochemical ($V_G < -1.8$ V) mixing.[29] Here, we focus on the electrostatic double-layer charging region. On the basis of a previously measured capacitance density of 20 $\mu F/cm^2$ at the P3HT/PSS interface,[30] we can calculate a maximum charge density of $\sim 2 \times 10^{14}/cm^2$ at the highest bias voltage of $V_G = -1.8$ V. Since this charge density is confined within a few nanometers from the interface, we can convert this 2D density to a 3D carrier density of $10^{20}-10^{21}/cm^3$. Such a high carrier density samples the majority electronic energy
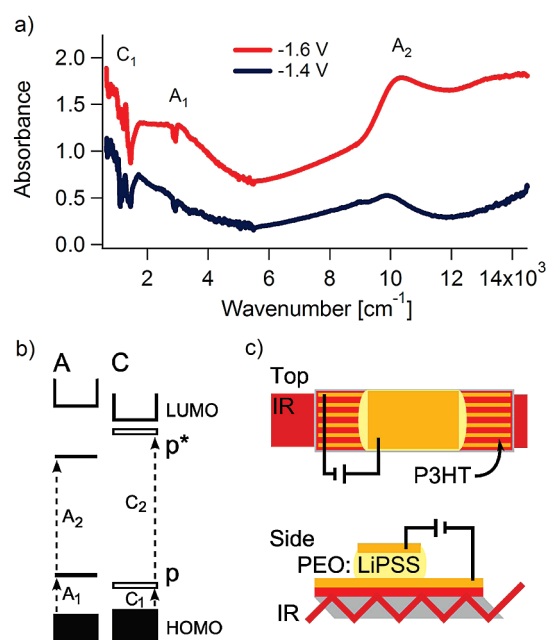

Figure 3. Infrared spectroscopy of charge carriers in P3HT. Panel (a) shows two spectra of a P3HT capacitor structure taken at two different bias voltages. The zero volt spectrum was subtracted to give the spectra of accumulated holes and then scaled and offset to emphasize the change in shape. Prominent peaks are labeled by the morphological region, either amorphous (A) or crystalline (C). Features belonging to amorphous regions of the polymer are more prominent at higher bias voltage. Panel (b) shows a proposed energy diagram for charge carriers in P3HT. Panel (c) shows a schematic of the P3HT capacitor structure used for the voltage-dependent spectroscopy. The dielectric used was a mixture of poly(ethylene oxide) (PEO) and lithium poly(styrene sulfonate) (LiPSS).[29]

landscape and can be observed spectroscopically. The two spectra in Figure 3 are obtained from the model device at two different bias voltages. At the lower bias voltage, charge carriers (hole polarons) predominantly reside in crystalline regions of the polymer. As the bias voltage and thus injected charge density increase, charge carriers start to populate states more associated with the 1D disordered regions. This presents clear evidence for the bimodal electronic energy landscape in P3HT and the preferential population of the 2D crystalline domains at low charge carrier densities.

It is instructive to compare microcrystalline polymers to polycrystalline small-molecule films. In small-molecule thin films, domain boundaries are usually very narrow, of the size of one or a few molecules. In contrast, polymer chains are sufficiently long to inhibit them from forming crystallites with narrow, well-defined grain boundaries. As a result, crystalline domains in polymers tend to be surrounded by wide regions of disordered polymer chains. In fact, the majority of a microcrystalline polymer thin film can often be regarded as disordered. Given the size of the disordered regions, they not only serve as an energy barrier to transport between two crystalline domains but also directly participate in carrier transport. In other words, charge carriers must traverse disordered regions of the polymer to achieve macroscopic
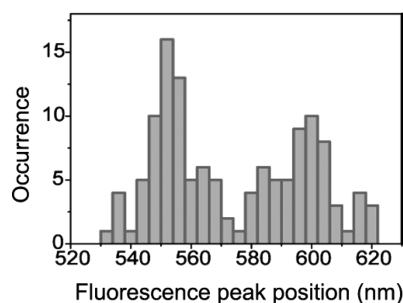
Figure 4. Peak energy distributions of single-molecule fluorescence spectra for MEH-PPV excited with 488 nm at ~20 K. This histogram illustrates a bimodal distribution behavior with average peak energy maxima of ~2.25 eV for the blue-emitting form and ~2.05 eV for the red form. After Kim et al.[33]

transport because the disordered regions are wide and comprise a large percentage of the film. To make this idea more concrete, one can imagine charge transport as occurring through a series of steps. First, a charge carrier can be activated from a low-energy crystalline region and into the high-energy disordered region. Afterward, it will localize on a disordered polymer chain, hop along on the 1D electronic landscape, and eventually fall into another 2D crystalline domain with lower energy.

The bimodality of the electronic energy landscape in semiconducting polymers has been unambiguously established in fluorescence single-molecule spectroscopy (SMS) measurements of not only microcrystalline polymers, such as regioregular poly-3-octyl thiophene (P3OT),[31] but also amorphous polymers, such as poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV).[32,33] Figure 4 shows a histogram analysis of fluorescence peak positions of MEH-PPV single molecules embedded in an inert matrix. The excitonic energy distribution is clearly bimodal, with an energy gap of ~0.2 eV. This kind of bimodal energy distribution has been attributed to two dominant structural motifs within a folded polymer chain, amorphous 1D regions and liquid-crystalline 3D regions. Exciton delocalization within the liquid-crystalline domain leads to the observed red shift in fluorescence emission. Such a bimodal electronic energy distribution should also play important roles in charge carrier transport, as is the case for microcrystalline polymers.

Another major difference between polymers and crystalline molecular thin films is the greater extent of nuclear polarization in the former. The earliest theories of charges in conjugated polymer chains point toward the large role chain distortions play in charge carrier stabilization.[34,35] This perspective has been validated repeatedly in spectroscopic measurements.[36] The extent of nuclear polarization varies inversely with the degree of interchain delocalization.[37] This indicates that the energetic difference between the crystalline or liquid-crystalline domains and the disordered regions is not purely electronic but also requires an account of different polarization effects. Compared to crystalline molecular thin films, polymeric semiconductors are more susceptible not only to extensive structural deformation but also to potential chemical reactions in the presence of charges. Both effects

can result in the dynamic localization of an injected charge into deep traps. Such a deep, self-trapping process has been observed for a single-polymer chain of MEH-PPV following field-induced charge injection from a hole donor.[38] The amount of trapped charge is quantified by the extent of fluorescence quenching in single-molecule fluorescence spectroscopy, and the self-trapping process is revealed in the charging-rate-dependent hysteresis in fluorescence intensity. A similarly slow and dynamic trapping process has also been observed by single-molecule spectroelectrochemistry (SMS-EC) of an electrochemically doped (i.e., charge injection in the presence of a counterion) conjugated polymer nanoparticle of poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT).[7] The SMS-EC experiment revealed a reversible charging process following the initial injection of holes. In addition, there was a small fraction of deeply trapped holes that were formed soon after the injection. The dynamic trapping processes observed can account for much of the hysteresis found in thin film transistor measurements.

Minority Electronic Energy Landscape: Charged Defects. The majority electronic landscape is modified by the electrostatic distribution of the minority charged defects. As discussed above, even in the absence of extrinsic chemical impurities, π-conjugated polymeric semiconductors are not intrinsic semiconductors but rather doped semiconductors at a doping level as high as $10^{17}/cm^3$. Gregg and co-workers hypothesized that the source of such a high intrinsic doping level comes from covalent and charged defects, particularly adjacent cation−anion pairs resulting from the twisting of a planar conjugated polymer backbone.[14,24,25] In support of this hypothesis, chemical treatment of the polymer was found to lead to a reduced free carrier density and longer exciton diffusion length presumably because of the titration of these defects.

Accepting the charged defect hypothesis, we now discuss briefly their role in electronic transport and trapping. First, a charged defect may donate a majority carrier (a hole in the case of P3HT and similar p-type conjugated polymers) to the conduction states, but the remaining opposite charge (e.g., the anion) is localized to the defect site and should serve as a Coulomb trap. This situation is very similar to charge traps in doped inorganic semiconductors. Due to the low dielectric constant of polymeric materials, Coulomb traps are poorly screened, and trapping energies many times k_BT are to be expected. Thus, charged defects are deep traps and may have detrimental effect on transport at low carrier densities, such as those expected in an OPV device. Unlike the majority electronic energy landscape where crystalline domains tend to trap charge while the amorphous regions behave as barriers, the Coulomb traps from charged defects are expected to be predominantly located in the amorphous regions. This is because we expect the presence of covalent and charged defects to be correlated with the greater degree of structural disorder in the amorphous regions.

The presence of the minority electronic energy landscape and charged defects has so far been inferred indirectly from transport measurements. A major problem in understanding the minority electronic energy landscape is the lack of experimental tools that are capable of directly probing them. New spectroscopic and microscopic techniques with much

improved sensitivity and/or selectivity are needed to tackle this problem.

> In π-conjugated polymeric semiconductors, we suggest the presence of a two-tier electronic energy landscape, a bimodal majority landscape due to two dominant structural motifs and a minority electronic energy landscape from intrinsic charged defects.

AUTHOR INFORMATION

Corresponding Author:
*To whom correspondence should be addressed. E-mail: zhu@cm.utexas.edu.

Biographies

Loren Kaake is a postdoctoral fellow in the Energy Frontiers Research Center at the University of Texas—Austin. His research interests include the development of in situ spectroscopic techniques for condensed matter research, most notably in the study of organic optoelectronics and ion transport across interfaces.

Paul Barbara is Director of the DOE EFRC: Understanding Charge Separation and Transfer at Interfaces in Energy Materials. His research interests include nanoscience and nanotechnology of conjugated polymers. He is a Member of the National Academy of Sciences and a recent recipient of the ACS Wilson Award in Spectroscopy.

Xiaoyang Zhu is the Vauquelin Regents Professor of Chemistry at the University of Texas—Austin and Direcor of the Center for Materials Chemistry. He conducts research in two area, (1) electron transfer in molecular and nanomaterials and (2) chemistry and physics of soft interfaces. For further information, see: http://zhu.cm.utexas.edu.

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