The Pennsylvania State University

The Graduate School

Department of Materials Science and Engineering

# **DOPING OF SEMICONDUCTING POLYMERS FOR**

## **ELECTRONIC APPLICATIONS**

A Thesis in

Materials Science and Engineering

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

August 2014

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## ABSTRACT

One branch of modern electronics requires avoiding the high processing costs associated with inorganic semiconductors in order to create novel low-cost, mechanically flexible, and low-profile devices for the next generation of consumer devices. Organic semiconductors can be doped to improve their charge mobility and carrier density towards creating better polymer-based photovoltaics, organic thin-film transistors, and organic light-emitting diodes. Dopants offer one route to improved device performance, but the specific interactions between the dopant molecule and the semiconductor must be designed for the desired function.

This work explores the effects of sulfonic acid groups on the behavior of the common organic semiconductor poly-(3-hexylthiophene) (P3HT). P3HT was chosen for its ubiquitous use in photovoltaics and other organic electronic applications. The doping of P3HT by sulfonic acidcontaining moieties was explored initially as a method to replace the poly(3,4ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) electron blocking later at the photovoltaic transparent indium tin oxide electrode. Measurements of doped thiophene-based polymers were conducted in organic thin-film transistor geometries to measure the charge carrier densities. Additionally, spectroscopic evidence of doping complemented the transistor and photovoltaic studies. This work explores the extent to which P3HT can be doped at the highest density and how it may be used in modern organic electronics such as transistors, photovoltaics, and light-emitting diodes.

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## ACKNOWLEDGEMENTS

Firstly, I would like to thank my advisor Dr. Hickner. You have shown interminable patience with my slow progress through graduate school, and I truly value the support and teaching you have given me over my three years at Penn State. I will always owe a portion of my future success to you and the environment you created. Thank you.

I also owe a great deal to my friends and coworkers in the research group. I thank Stephanie, Melanie, and especially Brian and Tim for their early help. I thank the people that came after for putting up with my constant and sudden questions and especially their friendship. Doug, TJ, Changwoo, and Sarah: I wouldn't have made it this far without you.

I would like to thank Thinh Le for excellent scientific conversations and for being there through it all. You were the main person I went to when I couldn't figure something out, and you helped with a great deal of this document over the years whether you know it or not.

I also thank my committee for graciously agreeing to help me with this last step along the way through Penn State given their support and teaching over the past few years. Dr. Gomez, I especially owe you for help outside the Dow project and your willingness to listen.

Finally, I thank my family for their continual support during my time in graduate school. You've been there for me the whole time, and I look forward to returning home more often than I have been.

### Res severa verum gaudia

## Chapter 1

# **Semiconducting Polymers**

## **1.1 Introduction**

Since the discovery of an increase in conductivity of over eights orders of magnitude in polyacetylene, conducting polymers have been a focus of significant research.<sup>1,2</sup> Research that eventually won MacDiarmid, Shirakawa, and Heeger the Nobel Prize in Chemistry in 2000 for their initial discovery has catalyzed efforts in the decades since, and now encompasses both conducting and semiconducting polymers with a current focus on structure-property relationships and functional devices. Polymers tailored for their electrical properties are engineered to compete with inorganic materials in solar panels, to drive down costs in thin film transistors, and to enable flexible electronics.<sup>3–9</sup> In order to fabricate the next generation of these devices, more must be understood about polymers with unique electronic properties, especially regarding their interaction with dopants and metallic contacts.

Historically, doping has been required to enable high conductivity in conjugated polymers. The initial work by Heeger, MacDiarmid, and Shirakawa involved doping polyacetylene with chloride, bromide, iodine, or arsenic pentafluoride vapor resulting in an unprecedented increase in conductivity.<sup>1,2</sup> The polymers used for electrical applications since that discovery have a variety of structures and are not all doped in the same manner, though all share a degree of conjugation in their molecular bonds. Carbon

sp<sup>2</sup> bonds in close proximity enable conduction by stabilizing charge density which is added or removed from the polymer backbone. Changes in charge density are delocalized across many atoms in conjugated systems without large disruptions to the molecular structure.<sup>10–12</sup> The more delocalized the charge, the more metallic the polymer and the higher its charge mobility and conductivity.<sup>10,13</sup> Unlike inorganic materials where the mobility of charge carriers is generally constant, doping can significantly increase both the mobility and conductivity of organic semiconductors.<sup>5,14,15</sup>

High conductivity in organic semiconductors is enabled through two main mechanisms. The first is charge transfer between the organic and another molecule, which is the mechanism behind the discovery of high conductivity in polyacetylene.<sup>1,2</sup> The polymer chain in polyacetylene consists entirely of alternating double and single carbon-carbon bonds. While the neutral structure can tolerate the addition of electrons, the material cannot easily form triple bonds. Electron removal from the polyacetylene structure requires less molecular rearrangement than electron addition and is much more energetically favorable. Holes which are created in the material can travel easily from one carbon to the next. Each electron withdrawn effectively creates a free charge carrier which contributes to the conductivity. Other examples of this kind of improvement in conductivity include the doping of graphene sheets with boron or nitrogen as a replacement for carbon, which either donates or removes an electron from the neutral system to improve the free carrier density. <sup>16,17</sup>



Figure 1-1. Increase in conductivity for trans-polyacetylene on doping with iodine vapor. Increasing concentrations of iodine vapor were introduced during the test for conductivity at specific times. The conductivity increases by more than  $10^7$  to a maximum of 38 S cm<sup>-1</sup>.<sup>1</sup>

The second form of doping which improves conductivity is that which extends the number of atoms in conjugation. Electrons become more delocalized as adjacent atoms or molecules come into conjugation and turn the material more metallic. One of the main examples of this kind of doping interaction is between polyaniline and an acid, which converts the amine groups to imines within the backbone.<sup>18–20</sup> The structure of polyaniline is shown in Figure 1-2. Because the benzene rings are aromatic, converting the amine linages to imines allows the nitrogen double bond to extend conjugation between rings. The conductivity of the polymer increases significantly as the fully protonated (leucoemeraldine) state is deprotonated.<sup>18</sup> The two forms of conductivity enhancement described here relate to the main structural factors that determine the conductivity of organic semiconductors.



Figure 1-2. Structures of polymers discussed in this work. Clockwise from top left are transpolyacetylene,<sup>1</sup> polyaniline in its protonated (blue) and deprotonated (red) forms, polythiophene, polystyrene sulfonate, and poly(3,4-ethylenedioxythiophene).

There are many different polymer structures which are used for electronic applications. Despite the first polymeric semiconductor consisting entirely of sp<sup>2</sup> bonded carbon, polymers used for modern electronics incorporate many structures such as aromatic rings and sidegroups added to modify the bandgap, control the conjugation, and enable solubility.<sup>21–27</sup> The most commonly used polymers incorporate structures which have many monomers in conjugation while also maintaining solubility. Polymers which are fully in conjugation with no side groups typically exhibit low solubility in common organic solvents.<sup>1,2,18</sup> In order to achieve solvent processability as well as the extended conjugation necessary for low processing costs, structures typically used for modern electronics feature aromatic rings with side groups such as short alkyl chains to enhance solubility.<sup>12,22</sup> The structures most relevant to this work include the polymers poly(3,4ethylenedioxythiophene) (PEDOT), polystyrene sulfonate (PSS), and poly-3hexylthiophene (P3HT).

#### **1.2 Relevant Polymers and Physics of Conduction**

The organic semiconductor PEDOT is one of the most commonly used polymers in modern electronics today.<sup>28–30</sup> The structure, shown in Figure 1-2, features thiophene rings partially oxidized by attached oxygen atoms on the monomer unit. The thiophene rings offer strong conjugation between the monomer units, while the ether linkages on the rings offer improved solvent processability with water.<sup>31,32</sup> The effect of the modified thiophene rings in PEDOT are compared against polythiophene in their absorbance spectra below, Figure 1-3. The plots show that the main absorption peak in PEDOT is blueshifted relative to the polythiophene due to electron density withdrawn from the thiophene ring by the oxygen atoms.<sup>33,34</sup> PEDOT mixed with PSS is referred to as a transparent conductor due to the main absorption peak located at 400 nm.<sup>35</sup> One of main uses for PEDOT:PSS is as a transparent layer in optical devices, due to its high conductivity.



Figure 1-3. UV-Vis absorbance of thiophene-based polymers. The absorbance of PEDOT is shown on left, with a maximum in the absorbance at 420 nm.<sup>33</sup> On right, the absorbance of polythiophene with a maximum in absorbance at 490 nm for the unoxidized spectra.<sup>34</sup>

PEDOT is commonly used in industry and in research because it easily forms a charge transfer complex with PSS. The macromolecular salt formed between PEDOT and PSS withdraws electron density from PEDOT and increases its conductivity.<sup>29,36,37</sup> The PEDOT:PSS commonly sold in industry has a very high conductivity for organics (> 100 S cm<sup>-1</sup>) depending on its processing conditions.<sup>38</sup> PEDOT:PSS is widely used as a charge transport layer in organic optical devices due to its high conductivity and transparency which will be discussed further in later chapters.

The focus of this work is on the polymeric semiconductor P3HT. Like PEDOT, it is composed of thiophene rings connected at the 2 and 5 positions as shown in Figure 1-2. The polymer has short hexyl chains attached to each thiophene ring to enhance the polymer's solubility. As the conductivity relies on many rings held in conjugation, the alkyl tails are arranged in a head-to-tail configuration during synthesis. Head-to-head and head-to-tail regiochemistry results in a "regiorandom" polymer while precisely controlled regular regiochemistry during synthesis leads to a "regioregular" polymer. Regioregular P3HT is generally more useful in devices than regiorandom P3HT due to their respective mobilities of  $3*10^{-4}$  and  $2*10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> as measured by Ko, et al.<sup>12</sup> The difference in mobilities is due to the steric interference of the alkyl tails with each other which hinders the conjugation between adjacent thiophene rings and reduces the conjugation length.<sup>39</sup> Brown, et al. determined that charge mobility for the regiorandom polymer is primarily maintained through interchain transport while regioregular P3HT exhibits both inter- and intra-chain transport thanks to its longer conjugation length.

In addition to having an important effect on the charge mobility, the fraction of chains in P3HT in a head-tail conformation also affects the polymer's absorption of light

through the extended conjugation.<sup>39</sup> Figure 1-4 shows the normalized absorbance spectra of both regiorandom (rraP3HT) and regioregular (rrP3HT) polymer. The absorption of the rrP3HT is significantly redshifted due to the extended conjugation which splits the energy bands of the bandgap. As the energy bands split more and more with extended conjugation the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gets smaller which effectively lowers the bandgap and redshifts the absorbance. The effect of conjugation can be more clearly seen in the UV-Vis absorbance of oligothiophenes shown in Figure 1-4 below. Each additional thiophene added to the oligomer redshifts the absorbance by roughly 50 nm at low numbers of rings in the molecule.<sup>40</sup> Subsequent ring additions redshift the absorbance less and less as for two reasons: the relative change of adding one ring to a conjugated region is reduced and there is a limit to the number of rings able to be held in conjugation. As oligomeric thiophene rings are lengthened, their absorption peak can continue to redshift as thiophene rings  $\pi$ -stack with each other between chains. Interchain stacking leads to the absorption peak differences between varying molecular weights of P3HT, as seen in Figure 1-5 below.<sup>41</sup>



Figure 1-4. UV-Vis absorption of thiophene based polymers. On left, absorption of regioregular P3HT (rrP3HT) and regiorandom P3HT (rraP3HT) showing redshifted absorption with increased conjugation length in P3HT.<sup>39</sup> On right, redshifted absorption of oligothiophenes using 3-octylthiophene monomer as oligomer length increases linearly from 1 to 6 monomer units (4, 6a, 6b, 6c. 6d, 6e).<sup>40</sup>



Figure 1-5. UV-Vis absorption of P3HT at two molecular weights with varying temperature. At room temperature, the main  $\pi$ - $\pi$ \* absorption peak shifts from 2.4 eV to 2.3 eV with a molecular weight increase from 9200 M<sub>w</sub> (g mol<sup>-1</sup>) in (a) to 35800 M<sub>w</sub> shown in (b).<sup>41</sup>

Redshifted absorption peaks are well understood in conjugated polymers, and was reported by Guillerez, et al. with their work in oligothiophenes shown in Figure 1-4.<sup>40</sup> Their work covers the main  $\pi$ - $\pi$ \* absorption for thiophene, but does not include the crystallinity seen in Figure 1-4 at the arrow.<sup>39</sup> The arrow pointing to the shoulder at

around 2.1 eV or 600 nm is known to be due to crystalline regions of P3HT where many thiophene rings are in conjugation via  $\pi$ -stacking as well as conjugation along the backbone. The absorption peak at 600 nm is widely attributed to semicrystallinity in P3HT. These salient features of P3HT in UV-vis are important for characterization of external stimuli to the polymer via spectroscopy.

Photoluminescence (PL) spectroscopy has also been used extensively to characterize P3HT, and is useful for probing the excited state of the thiophene rings. The excited states of the molecules can yield information both of the molecular structure as well as the process by which excited states decay. The authors Xu and Holdcroft used photoluminescence spectroscopy extensively to determine the effects of regioregularity on P3HT's excited states.<sup>42</sup>



Figure 1-6. Photoluminescence and UV-Vis absorption spectra of P3HT with varying regioregularity. Spectra correspond to the percent of P3HT with alkyl tails organized in a head-tail fashion (with 100% head-tail corresponding to full regioregularity). The labels (a), (b), and (c) correspond to 80%, 60%, and 50% head-tail organization within the sample for UV-Vis measurements while the primed (a'), (b'), and (c') correspond to the same head-tail fractions for photoluminescence measurements.<sup>42</sup>

Figure 1-6 shows the photoluminescence spectra of P3HT at varying amounts of regioregularity in the curves labelled with a prime (') notation.<sup>42</sup> It is clear from the figure that solutions of regioregular polymer exhibit roughly double the amount of fluorescence than a more regiorandom polymer. This increase in fluorescence is attributed to differences in conjugation length. Much like the quenching of fluorescence that occurs when excited states are given a new decay pathway, fluorescence is quenched on disruption of conjugation in the polymer. In solution, fluorescence is also quenched as the P3HT crystallizes and becomes insoluble.

Many polymeric semiconductors have been under intense scrutiny for the past several decades due to their desirable qualities such as low cost and processability. This work focuses primarily on the organic semiconductor P3HT due to the polymer's strong use in solar devices and its interaction with sulfonic acid. Other polymeric semiconductors which include thiophene rings will also be investigated in order to characterize how organics interact with a dopant which has not been extensively studied in literature.

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# **Chapter 2**

## **Organic Electronic Devices**

### **2.1 Introduction**

Photovoltaic devices, light emitting diodes, and thin film transistors are driving the majority of research in polymers with electronic transport properties.<sup>1–5</sup> Conducting and semiconducting polymers are being used to lower the costs associated with device manufacture and increase device functionality such as flexibility or touch sensitivity.<sup>6</sup> Traditional manufacture of inorganic devices requires expensive processing steps like polishing, epitaxial layer growth, and lithography which are all much more expensive and time consuming than the few seconds required to deposit a polymer layer via solution coating.<sup>4,6</sup> Flexible electronics are also a growing focus of the consumer electronics industry, and inorganics are typically ill-suited to being repeatedly flexed at a small radius of curvature.<sup>7,8</sup> Polymers can address the growing industrial needs for these applications, but several vital scientific questions must first be answered in order to do so, such as the exact nature of charge transport in organics.

The low mobility of charges in semiconducting polymers has been one of the main historical challenges to the applicability of polymers in devices.<sup>6</sup> The charge carrier mobility,  $\mu$ , is defined as  $\mu = \left(\frac{q}{m^*}\bar{\tau}\right)$  where q is the elementary charge,  $m^*$  is the effective mass of the charge carrier, and  $\bar{\tau}$  is the average carrier lifetime. Because inorganic materials were being used to create devices before the discovery of polymers,

the industry grew used to charge mobilities in the range of  $1500 \left(\frac{cm^2}{V*s}\right)$  for electrons in Si wafers at room temperature to as high or higher than  $80000 \left(\frac{cm^2}{V*s}\right)$  for electrons in InSb.<sup>4</sup> While many inorganic materials have been fabricated with mobilities at and above those ranges, the only organic material to even enter the range is carbon in specialized allotropes. Graphene and diamond have charge carrier mobilities that are roughly infinite and over  $1000 \left(\frac{cm^2}{V*s}\right)$  respectively, but are entirely unsuitable in most devices due to their bandgaps and processing requirements.<sup>9,10</sup> The organic structures that are actually in use have much smaller charge mobilities on the order of 0.01 to  $10 \left(\frac{cm^2}{V*s}\right)$ .<sup>6</sup> These low mobilities for polymers and small organic molecules lead to much lower conductivities and slower device operation relative to inorganic materials.

#### 2.2 Thin Film Transistors

Transistors made with organic molecules and polymers use an organic thin-film transistor (OFET) architecture due to device designs accommodating the material features of organics; specifically referring to their low mobilities, bandgaps with deep traps, and generally high resistivity when compared to inorganic materials.<sup>6</sup> These organic devices are attractive thanks to the low processing costs of organics which are enabled by the solubility of the polymers or small molecules and high-speed coating operations. OFETs operate by varying the amount of current passing through a semiconducting medium as modulated by three separate terminals. A semiconductor is attached to two conductive contacts, the source and drain, and is separated from the third contact, the gate, by an

insulating layer. With no voltage applied between the source and drain contacts ( $V_{SD}$ ) there is typically very little current passing through the device unless the channel between the source and drain is doped. Even with a  $V_{SD}$  applied, a voltage needs to be applied between the source and gate contacts ( $V_{SG}$ ) to shift the semiconductor's HOMO and LUMO levels enough to enable current flow in the device.

There are two classes of metal-semiconductor contacts which apply to organic devices. Ohmic contacts exhibit linear current-voltage characteristics, and a schematic of their band structure is shown in Figure 2-1.<sup>4</sup> Ohmic contacts typically have the Fermi levels of the metal and either HOMO or LUMO in the semiconductor very closely aligned, such that there is no barrier to conduction across the material interface. A small voltage applied between the metal and semiconductor will result in a small flux of current, unlike with Schottky contacts. Shottky contacts are characterized to have nonlinear I-V curves, and their band structure is shown in Figure 2-1. These contacts arise from surface states in the semiconductor which "pin" the Fermi energy of the contact to a specific level relative to the metal and are generally unchanged by doping. These contacts do not exhibit a current on application of a small voltage, and require higher V<sub>SD</sub> or V<sub>SG</sub> to show appreciable current relative to Ohmic contacts. In order to achieve significant current flow across the energy barrier in Schottky contacts, the semiconductor interface needs to be heavily doped to enable charge tunneling across the barrier. Tunneling is controlled by both energy and length barriers, but for transfer between equivalent energy levels a length barrier of generally less than 50Å is necessary to allow appreciable tunneling across the barrier.<sup>4,6</sup> Inorganic materials exhibit both kinds of contacts depending on the materials used and their processing. Organic materials

generally exhibit only Shottky type contacts due to the lack of matched crystal lattices and high disorder in the materials. Ohmic contacts in organics are desirable for their high efficiency and lower threshold voltages, and have been the subject of significant research for device improvement.



Figure 2-1. Schottky and Ohmic contacts. Schematic diagrams of the work functions of the materials involved in p-type semiconductors. The depletion region, W, is the region where mobile charges are distributed out of the region to equilibrate the charge imbalance at the contact-semiconductor interface.

Organic transistors have three metal-semiconductor contacts. The relevant architecture is the metal-insulator-semiconductor (MIS) field-effect transistor (FET) shown in Figure 2-2. The source-semiconductor and drain-semiconductor contacts typically have no intentionally applied insulating layer, while the metal-insulatorsemiconductor architecture at the gate requires a strongly insulating material as the gate dielectric. Current flow in the device occurs over a very thin channel adjacent to the gate electrode and is described by two regimes of operation: the linear regime and the saturation regime. The linear regime refers to ohmic behavior in the semiconductor, and saturation refers to the carrier density in the conduction channel reaching a maximum where higher V<sub>SD</sub> results in carriers being lost to a nonconductive channel rather than increasing  $I_{SD}$ . The current in both regimes was originally described for inorganic materials and the equations of operation remain in use for organics despite the change of domain. Current in both regimes is described by equation 2-1 and equation 2-2.<sup>4</sup>

(2-1) 
$$I_D = \frac{\mu C_{diel} W}{L} \left( (V_{GS} - V_{th}) V_{DS} - \frac{V_{DS}^2}{2} \right) \text{ for } |V_{GS} - V_{th}| > |V_{DS}| \text{ (linear regime)}$$

(2-2) 
$$I_D = \frac{\mu C_{diel} W}{2L} (V_{GS} - V_{th})^2 \text{ for } |V_{DS}| > |V_{GS} - V_{th}| > 0 \text{ (saturation regime)}$$

The variable  $I_D$  refers to the drain current in amps,  $\mu$  refers to the charge mobility in cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, C<sub>diel</sub> is the capacitance of the dielectric in farads, W and L are the width and length of the channel respectively,  $V_{GS}$  is the gate-source voltage,  $V_{th}$  is the threshold voltage, and  $V_{DS}$  is the drain-source voltage. These equations can be used to determine the carrier mobility in the two regimes.

(2-3) 
$$\mu_{lin} = \frac{L}{C_{diel}WV_{DS}} \frac{\partial I_D}{\partial V_{GS}} \text{ for } |V_{GS} - V_{th}| > |V_{DS}| \text{ (linear regime)}$$

(2-4) 
$$\mu_{sat} = \frac{2L}{C_{diel}W} \left(\frac{\partial \sqrt{I_D}}{\partial V_{GS}}\right)^2 \text{ for } |V_{DS}| > |V_{GS} - V_{th}| > 0 \quad (\text{saturation regime})$$



Figure 2-2. Schematic of the I-V behavior of the transistor architecture used in this work. a) shows the parameters used, while b), c), and d) depict the linear, transition, and saturation behavior respectively.<sup>6</sup>

One early model of an OFET fabricated by Dimitrakopoulos, et al. used pentacene as its semiconducting material.<sup>11</sup> It shows a significant on/off current ratio of  $10^7$ , ohmic contacts at the source and drain, and a low threshold voltage. The on/off current ratio refers to the difference in currents between the on- and off-states of the device found at the extremes of the tested gate voltages. The higher the on-off ratio, the more defined the on- and off-states are for the device and the more reliable the device is over time. The threshold voltage V<sub>th</sub> refers to the V<sub>SG</sub> required to allow current flow in the device, with

small threshold voltages desirable for their small energy costs. Smaller values of  $V_{th}$  describe devices which require less work to maintain in an on- or off- state. The p-type pentacene OFET in Figure 2-3 has an excellent both on-off ratio and charge mobility at  $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$ .<sup>11</sup>



Figure 2-3. Pentacene OFET fabricated on 0.5  $\mu$ m SiO<sub>2</sub> gate using evaporated pentacene in a top-contact bottom-gate device with a -100 V<sub>SD</sub>. The device exhibits an excellent on-off ratio and charge mobility at 10<sup>7</sup> and 0.16 cm<sup>2</sup> V<sup>-1</sup> cm<sup>-1</sup> respectively.<sup>11</sup>

#### 2.3 Organic Photovoltaics

Organic photovoltaics are a second type of modern organic electronic device architecture which currently receives heavy attention.<sup>6</sup> The simplest device design consists of a semiconductor junction sandwiched between two electrodes, one of which is transparent. Light enters the semiconductor through the transparent electrode and excites an electron from the valence band to the conduction band in the absorbing polymer. Excitons reaching the junction in the semiconductor can dissociate into free holes and electrons which may move freely apart from each other into either the electron acceptor or donor material. The dissociated charges are then collected by the contact electrodes enabling extraction of current generated by incident light.<sup>4</sup>

The junction which enables the dissociation and separation of charges in photovoltaics is typically a heterojunction consisting of two materials with different bandgaps.<sup>4</sup> While a classic example of a photovoltaic is a homojunction between n-type and p-type Si, modern devices typically use a heterojunction to take advantage of an electron acceptor and donor material which have different absorbance spectra and can cover more of the solar spectrum. While a large separation in work function between the donor and acceptor aids in exciton dissociation, a large work function separation between the electron donor/acceptor and its electrode results in lost energy as the dissociated charges are less likely to hop into an electrode as the difference in work function increases. Transport layers are often employed when there is a mismatch in work function between the donor/acceptor and its electrode, which is a common use for PEDOT:PSS.<sup>12</sup> The high conductivity and work function (5.2 eV) of a PEDOT:PSS layer allow holes
that reach the interface to easily reach the electrode for collection.<sup>13</sup> Inclusion of PEDOT:PSS in organic photovoltaics is attributed to an improvement in the critical device parameters of the open circuit voltage ( $V_{OC}$ ), short circuit current ( $J_{SC}$ ), and fill factor (FF), as described by Figure 2-4.



Figure 2-4. Representation of I-V curves in solar devices. Left: An ideal cell due to its high fill factor. Right: a cell with poor fill factor and efficiency.<sup>14</sup>

The V<sub>oc</sub> refers to the difference in work function between the two materials comprising the heterojunction. The J<sub>sc</sub> is the maximum possible current that can be collected in the device, and the fill factor is a combination of the V<sub>oc</sub> and J<sub>sc</sub> referring to the nonideality of the device as shown in Figure 2-4 above. Inclusion of PEDOT:PSS has been shown by Weickert, et al. to improve these values from a V<sub>oc</sub> of 0.41 to 0.58 V, J<sub>sc</sub> of 6.29 to 6.32 mA cm<sup>-2</sup>, and FF of 34.1% to 51.7% leading to an increase in photoconversion efficiency from 0.92% to 1.96%.<sup>13</sup> These improvements are attributed to both the modified work function of the material as well as the preferential localization of excess P3HT at the ITO interface leading to more electron donor at the hole collection electrode and more electron acceptor at the counterelectrode.<sup>15</sup> The improvement evident in organic electronics due to the inclusion of PEDOT:PSS is evidence that any material added to organic electronics must take into account the electronic and thermodynamic conditions of the materials used.

#### 2.4 Organic Light-emitting Diodes

Organic light emitting diodes (OLEDs) are another relevant device architecture for organic semiconductors.<sup>4,6</sup> These devices are designed to efficiently emit light under an applied current. Like photovolatics these devices consist of a homo- or hetero-junction with one transparent and one reflective electrode on either side of the junction. The materials used to create the junction are carefully chosen for their work functions such that one side readily accepts holes from an electrode while the other side readily accepts electrons. As these mobile charge carriers diffuse from the electrodes they begin to recombine as they meet at the junction where light is emitted equal to the bandgap of the material which does the emitting. For each recombination event a photon is emitted with energy equal to the bandgap in the material where the recombination took place. While the dyes, materials, and junction properties within the materials around the junction determine the light intensity and color, one of the main relevant drivers for device efficiency is what is termed the hole or electron transport layer (HTL or ETL). This layer is included adjacent to the electrode contacts and has a work function chosen to accept electrons or holes while excluding the opposite charge carrier. The ETL and HTL ensure that charge recombination only occurs at the junction or within the dyes and is not uselessly lost to recombination events away from the desired locations.

Dopants in organic electronics must exhibit several properties to remain viable. For transistors, a dopant must modify the depletion region or contact resistance without moving away from the interface or degrading with time. In photovoltaics, a dopant should provide high conductivity near a contact without modifying the heterojunction to ensure efficient charge transfer. In OLED devices, a doped region should act as a hole or electron transport layer by having a work function high or low enough to exclude holes or electrons.

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### Chapter 3

# **Doping in Organic Semiconductors**

## **3.1 Introduction**

Doping in organic materials is less well understood than doping of inorganic semiconductors. For example, p-type and n-type dopants can be controllably introduced in silicon up to densities of  $10^{22}$  atoms/cm<sup>3</sup> which enables very precise management of homo- and heterojunctions made using lithography because those dopants can be controllably introduced in layers well below 10 nm.<sup>1</sup> Organic materials and processing methods do not allow anywhere near the kind of control of dopant density or spatial distribution featured in inorganics. While a dopant material could certainly be included in an organic semiconductor at equivalent volume fractions to heavily doped inorganics, the dopants themselves are molecular rather than atomic and thus occupy more space in the lattice leaving less volume fraction for the semiconducting phase. For example, in PEDOT:PSS, the sulfonic acid group on the PS backbone acts as a p-type dopant to the PEDOT and is comprised of five atoms in contrast to the one phosphorous atom required in a silicon lattice for a similar effect.<sup>2</sup> The size, amount of charge donated or withdrawn, and spatial distribution of dopants drive the effectiveness of a given dopant in a semiconducting medium.<sup>3–6</sup>

The first dopants for organic semiconductors were atomic in nature. Polyaniline exposed to halogen vapor shows excellent conductivity and is shown in Figure 3-1.<sup>7</sup>

Polyaniline also shows significant boosts in conductivity as the material approaches a state where every other nitrogen is protonated, as shown in Figure 3-1.<sup>8</sup>



Figure 3-1. Conductivity and structure of polyaniline. On left, the conductivity of polyaniline increases by nine orders of magnitude on doping with halogen vapor.<sup>7</sup> The structure of the most heavily doped form of polyaniline shown on right.<sup>8</sup>

#### **3.2 The charge transfer interaction of PEDOT:PSS**

Modern materials to dope organic semiconductors require solvent processability as well as high conductivity, which is not possible with polyacetylene and its original vapor-phase dopants.<sup>7</sup> PEDOT:PSS is commonly used in solar devices as a hole transfer layer adjacent to the transparent conductor ITO.<sup>9-12</sup> Because commonly less than 30% of an ITO surface is conductive, PEDOT:PSS enables hole collection in the ITO by increasing the fraction of holes that are transported to conductive sites as well as excluding electrons.<sup>13</sup> The work function PEDOT:PSS at 5.3 eV matches the ITO work function at 4.7 eV which enables the transfer of charges from the heterojunction in solar devices.<sup>14</sup> The proposed mechanism between the sulfonic acid in PSS and the PEDOT backbone to enable near-metallic conduction is that the acidic proton interacts with the 3,4-ethylenedioxythiophene unit to form a charge transfer complex.<sup>10</sup> The effectiveness of the charge transfer complex is dominated by the crystallite size of PEDOT and concentration of PSS which both control the interfacial area between the dopant and the semiconductor. PEDOT crystals exhibit high mobility while the number of charge carriers is dominated by the amount of PSS in contact with PEDOT. Thus, the overall conductivity is controlled by the competing effects of morphology and miscibility between the two materials. The effect of crystallite size shown by the distance between crystals is shown in Figure 3-2. As the amount of PSS is increased in PEDOT the conductivity is observed to decrease from 2.3 to  $10^{-3} \Omega^{-1} \text{ cm}^{-1}$  as seen in Figure 3-2 below, which is due to the removal of conductive pathways as the conductivity becomes dominated by ions rather than holes in p-type semiconductivity.



Figure 3-2. Conductivity of PEDOT as a function of crystalline spacing and weight fraction of PSS. On left, the conductivity is shown for films cast from varying solvents which modifies the spacing between crystalline domains.<sup>10</sup> On right, conductivity of a PEDOT:PSS film is shown to approach that of pure PSS as its weight fraction increases.<sup>2</sup>

The solvents used with PEDOT:PSS influence its morphology and can have a strong effect on the material's conductivity because morphology plays a significant role in the properties of conducting polymers.<sup>10</sup> Not only is the planarity of the chain important to the conjugation and electron delocalization, as discussed previously, the way chains stack with each other is critically important towards promoting charge mobility and high charge density.<sup>15</sup> So-called secondary dopants are used to achieve the highest

conductivities in PEDOT:PSS which have been shown to modify the microstructure as well as the charge transfer complex. Diethylene glycol added to PEDOT:PSS was shown to increase the current density by more than an order of magnitude by Crispin, et al. and the effect was attributed to breaking up the conducting PEDOT grains embedded in PSS and connecting them in a 3D morphology.<sup>15</sup> Slight changes to the micro- or nano-structure within organic electronics can result in significant improvements in transport properties, as seen in Figure 3-3 below:<sup>15</sup>



Figure 3-3. Increasing conductivity of PEDOT:PSS with increasing diethylene glycol (DEG) fraction and AFM images. On left, the conductivity of a PEDOT:PSS film increases by three orders of magnitude as the secondary dopant DEG is added. An AFM phase scan of PEDOT:PSS is shown in the middle. On right, an AFM phase scan of PEDOT:PSS doped with 5 wt % DEG shows significantly more crystalline domains of PEDOT.<sup>15</sup>

While PEDOT:PSS is one of the main materials used for high conductivity in organic electronics due to its solvent processability, other dopants have been explored with polymeric semiconductors. P3HT has been shown to be doped with a variety of materials, showing performance increases for transistor, solar, and light emitting devices.<sup>3–5,16–18</sup> One of the early illuminating studies on the doping effect in P3HT was performed by Friend and Kim, et al.<sup>3</sup> They doped P3HT with the electron-withdrawing small molecule tetrafluorotetracyanoquinodimethane (F<sub>4</sub>TCNQ). This molecule was

demonstrated to dope several conjugated polymers. In each case, the conductivity of each semiconducting polymer was shown to increase by more than an order of magnitude, Figure 3-4:



Figure 3-4. Increasing conductivity of semiconducting polymers on doping with  $F_4TCNQ$ . The conductivity of P3HT increases by roughly four orders of magnitude as  $F_4TCNQ$  reaches 10 wt %. The effect of  $F_4TCNQ$  is also shown for other semiconducting materials poly(9,9-di-n-octylfluorene-alt-bis-N,N-(4-butylphenyl)-bis-N,N-phenyl-1,4-phenylenediamine) (PFB), poly(9,9-di-n-octylfluorene-alt-(1,4-phenylene-((4-sec-butylphenyl))mino)-1,4-phenylene) (TFB), poly(9,9-di-n-octylfluorenealt-benzothiadiazole) (F8BT), and compared against PEDOT:PSS which is shown here as PEDT:PSS.<sup>15</sup>

As seen in Fig. 3-4, the electron-withdrawing dopant increased the conductivity of each of the tested molecules. The authors concluded that since the conductivity increases more quickly in polymers with lower HOMO levels, the semiconductors are doped via charge transfer between the LUMO of the  $F_4TCNQ$  and the HOMO of the polymer. The authors both did not test a material with a significantly lower HOMO level and also do not consider band splitting between the energy levels of the tested materials. They go on

to check for spectroscopic evidence of doping using Fourier transform infrared (FTIR) spectroscopy, Figure 3-5.



Figure 3-5. FTIR spectra of neat P3HT and P3HT doped with  $F_4TCNQ$ . Neat P3HT is shown in the top spectra, while P3HT doped at 10 wt %  $F_4TCNQ$  is shown in the bottom curve. The doped spectra already has neat P3HT subtracted.<sup>3</sup>

The FTIR difference spectra shows that doping with  $F_4TCNQ$  leads to increased absorbance in the 1300 cm<sup>-1</sup> region.<sup>3</sup> The authors claim this peak is clear evidence for the presence of holes induced by  $F_4TCNQ$  doping, but do not back the claim. Heeger, et al. claims bipolaron activity in P3HT at 1088, 1161, 1200, and 1354 cm which does not match the spectra in Figure 3-5 but is similar.<sup>19</sup>

#### 3.3 Molecular and electrochemical doping of P3HT

Alternative hypotheses for charge transfer and doping in organic semiconductors were later tested by Pingel and Neher using the same small molecule dopant.<sup>6</sup> They show evidence for a both integer and partial charge transfer interactions between the  $F_4TCNQ$  molecule and the thiophene ring in P3HT, Figure 3-7:



Figure 3-6. Schematic of two hypothesized charge transfer states between P3HT and  $F_4TCNQ$ . a) shows integral charge transfer between the energy states of both materials. b) the schematic shows splitting of the adjacent energy states resulting in partial charge transfer.<sup>6</sup>

The two mechanisms shown by Pingel and Neher depict contradictory models for P3HT doping. The integer charge transfer reaction in Figure 3-6(a) would produce a free hole in the semiconductor and raise the charge density evident in the device. The second mechanism in Figure 3-6(b) shows the splitting of orbitals with intimate contact between the P3HT and F<sub>4</sub>TCNQ, changing the ratio between the majority and minority charge carriers in the P3HT. The authors characterize the density of states, conductivity, and spectroscopy of the doped P3HT. Most important among their measurements in relation to this work are the spectroscopic peaks at 1.2 eV in UV-Vis spectroscopy and the charge carrier density measurements as a function of the molar ratio between the polymer and  $F_4TCNQ$ . Transmission spectra of the optical absorbance data normalized by thickness is shown in Figure 3-7:



Figure 3-7. UV-Vis spectra of P3HT doped with  $F_4TCNQ$ . a) optical absorption of P3HT films at varying molar ratios showing significantly increased absorption over undoped P3HT over the 1.2 eV to 2 eV range. b) P3HT doped at a 100-1 monomer- $F_4TCNQ$  ratio with the  $F_4TCNQ$  anion absorption also shown.<sup>6</sup>

Figure 3-7 indicates that the absorbance peaks which do not line up with the neat  $F_4TCNQ$  absorbance arise from the P3HT. Peaks for the  $F_4TCNQ$  appear at 1.45, 1.62, and roughly 1.8 eV which does not include the peak evident at 1.2 eV. The authors attribute the increased absorbance for the entire 1.2 to 1.8 eV region in Figure 3-7(b) to polaronic absorption in P3HT. They claim that the increased polaronic absorption is evidence for a charge transfer interaction between the  $F_4TCNQ$  and the P3HT. While there is strong evidence for a charge transfer interaction from their spectra of  $F_4TCNQ$  molecules and their ions, the evidence is weak for their claim that strong polaronic absorption occurs from 1.2-1.8 eV. Because the strong 1.2 and 2.0 eV peaks in Figure 3-7 only appear with the presence of  $F_4TCNQ$  and the  $F_4TCNQ$  anion absorbs over the 1.25-2.0 range, the only direct evidence for a polaronic peak is at 1.2 and 2.0 eV directly and not over the entire 1.2-1.8 eV range as claimed by the authors. The 1.2 eV peak is especially significant to this work and will be discussed further. The authors conclude

from the spectroscopic measurements that basically all of the  $F_4TCNQ$  molecules undergo charge transfer, and the effects of that charge transfer are shown in Figure 3-8,



Figure 3-8. Charge density and conductivity for P3HT as a function of doping with  $F_4TCNQ$ . On left, the hole density increases by several orders of magnitude on doping with  $F_4TCNQ$ . On right, the conductivity also increases on  $F_4TCNQ$  doping. The inset shows the charge mobility as a function of doping which indicates that as the average dopant-dopant distance decreases the local energy states begin to overlap allowing much greater charge mobility.

The charge carrier density and conductivity are explored in Figure 3-8, showing the effect of a changing doping ratio in detail. As the amount of  $F_4TCNQ$  increases, the hole density is shown to increase linearly above a  $F_4TCNQ$ :thiophene monomer ratio of  $10^{-5}$ as the slope of the conductivity continuously increases. The authors attribute the sublinear-to-superlinear increase in the conductivity to a strong change in the mobility as calculated in the inset graph. They claim that the initial lowering of the charge mobility is due to free charges being attracted to the dopants via a coulombic potential. As more dopants are added the average dopant-dopant distance decreases and the coulombic potentials overlap resulting in a sharp increase in the mobility and thus the conductivity. While the spectroscopic evidence points to near-complete charge transfer between dopant and semiconductor, the authors point out that only roughly 5% of the dopants result in dissociated carriers free to contribute to the overall conductivity. The complexity of the charge transfer interaction prevents easy attribution to a specific mechanism, which is acknowledged by the authors. Alternative explanations for the features described are only indirectly addressed. Morphology is shown by other works to be roughly unchanged up to a doping ratio of 1:200 despite higher ratios being tested in this work and used for their conclusions. While this work offers strong characterization, it acknowledges that it cannot propose a strong mechanistic explanation for semiconductor doping.

In OLED devices, iron(III) chloride was used to dope P3HT and modify the obtained current density in the device.<sup>17</sup> Romero, et al. fabricated OLED devices with an ITO/(polystyrene-poly-3-hexylthiophene diblock)/(Al or Ca) architecture. FeCl<sub>3</sub> was mixed with the PS-P3HT in xylene and spun onto the ITO for the doping procedure. The fabrication proceeded with three levels of dopant concentration at 0.5, 3.0, and 6.0% wt. Fe(III)Cl<sub>3</sub> to PS-P3HT. Electric field between the electrodes versus the current density travelling between them is plotted in Figure 3-9.



Figure 3-9. Current density in OLED devices with P3HT doped with FeCl<sub>3</sub>. The top graph shows P3HT doped with FeCl<sub>3</sub> at 3.0 wt % while the bottom graph shows P3HT doped with 6.0 wt % FeCl<sub>3</sub>. The bottom graph shows symmetric I-V behavior attributed to doped energy states in close proximity.<sup>17</sup>

The curret density shown in Figure 3-9 increased by orders of magnitude as the dopant level increased.<sup>17</sup> This large increase is attributed to a reduced tunneling barrier within the device on doping. The authors suggested that the dopants produce mobile charges on association of the dopant with the P3HT which distribute themselves in accordance with an applied electric field. As the dopant concentration increases, the mobile charges reach a sufficient concentration to neutralize the field applied which results in the symmetric current versus field plot for the most highly doped device which is not present for another doping level. The results imply that FeCl<sub>3</sub> is capable of doping P3HT, but the authors do not sufficiently characterize the semiconductor-dopant

relationship they report. Capacitance-voltage measurements would have revealed how the OLED is affected by mobile charges and could have determined the effect of any mobile ions which may have been present.

Doping in semiconductors is intimately related to the effects of free charges and electric fields. Armstrong, et al. performed a series of rigorous studies to explore the behavior of charges within P3HT.<sup>22</sup> Their UV-Vis and XPS data show how the energy levels of the P3HT change with an applied electric field and are displayed in Figure 3-10:



Figure 3-10. UV-Vis and XPS spectra of P3HT with applied voltages. On left, UV-Vis spectra are shown over a wide range of applied voltages. Spectra are labelled from 1 to 12 corresponding to stepped through voltages of (1) -0.1 V, (2) 0.0 V, (3) 0.1. V, (4) 0.2 V, (5) 0.3 V, (6) 0.4 V, (7) 0.5 V, (8) 0.6 V, (9) 0.7 V, (10) 0.8 V, (11) 0.9 V, and (12) 1.0 V. Spectra are normalized to the absorbance in the inset graph. On right, XPS spectra are shown over varying applied voltages shown in on each graph. With increasing applied voltage the binding energy shifts to higher eV indicating that the sulfur is oxidized.<sup>22</sup>

Figure 3-10 shows the UV-Vis behavior of a P3HT film as a function of voltage applied across the sample.<sup>22</sup> The numbered spectra refer to an increasing voltage applied across the film and it is apparent that the main  $\pi$ - $\pi$ \* transition of the P3HT is quenched during the application of a voltage. This quenching is attributed to the oxidation of the P3HT. Importantly, the sub-bandgap absorption is seen to increase with the applied electric field. At the highest field applied, a strong increase in the absorption around 1000 nm is observed, which is important to the results observed in this work. The authors claim that polaronic absorption occurs at 850 nm and is evident with the P3HT's response to an applied field. As the field is increased, the authors observe a multipolaronic state absorbance from 800-1100 nm which they note has also been associated with quasimetallic behavior and the highest degree of conductivity for a P3HT film. The observation from Armstrong et al. is supported by a similar experiment from Brown. Et al., who published varying absorbances of neat P3HT with an applied voltage in the 1.2-1.5 eV region shown in Figure 3-11.<sup>20</sup>



Figure 3-11. UV-Vis spectra of P3HT with a varying applied voltage.<sup>20</sup> The spectra show changes in the 1.2 eV range on varying the applied voltage. These results agree with other published data.<sup>22</sup>

The UV-Vis data shows the behavior of an oxidized organic semiconductor and is correlated with XPS data to confirm the trends. The XPS data, Figure 3-11, shows a small oxidative shift to higher binding energies for the sulfur which increases with increasing applied voltage.<sup>22</sup> The XPS data confirms that the P3HT is oxidized on application of an external voltage as it becomes more conductive, and suggests that a method for determining the extent of doping is in the sub-bandgap absorption of P3HT under UV-Vis spectroscopy.

The most relevant study to this work was conducted by Kim, et al. which explored the effect of sulfonic acid acting as a dopant to P3HT.<sup>4</sup> The authors performed UV-Vis, XPS, and electrical measurements to characterize the doping effect. The authors used 2-ethylbenzenesulfonic acid (EBSA) as a dopant, which is extremely similar to the small molecule dopant used in this work. The relevant data from the paper is reproduced in Figure 3-12 below:



Figure 3-12. Schematic of P3HT doped with EBSA and solutions with increasing EBSA content. On left, a schematic showing the acidic proton interacting with the lone pair of electrons on the sulfur atom. On right, the solution color darkens on increasing EBSA content, with weight percentages of EBSA at (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.7, and (f) 1.0.<sup>4</sup>

Figure 3-12 shows a schematic for interaction between the sulfonic acid added to the system and the P3HT.<sup>4</sup> The authors hypothesize that the proton from the acid interacts with the lone pair of electrons on the sulfur atom in the thiophene ring. The authors observed a darkening of the solution color with doping content after being held at 60 °C for 48 hours. The authors did not distinguish between other forms of solution darkening such as P3HT crystal formation. The authors go on to characterize the light absorption properties of the doped material. Their spectroscopy data is shown in Figure 3-13(a) and Figure 3-13(b):



Figure 3-13. UV-Vis and photoluminescence spectra of P3HT doped with EBSA. (a) UV-Vis absorbance of P3HT doped with EBSA, with the inset graph showing increased absorbance at 945 nm and 1.0 wt. %. (b) Photoluminescence spectra of P3HT with increasing EBSA content as outlined in the graph. As the EBSA content increases the intensity decreases with quenching.<sup>4</sup>

Figure 3-13(a) shows the UV-Vis absorption data for P3HT as it is doped with EBSA. The authors report a slight increase in absorption at around 1.3 eV which only appears on doping. The evidence for a doping effect is confirmed by the photoluminescence spectra, which shows strong quenching of the main fluorescence peak for the P3HT and is a characteristic of a new relaxation pathway for excited states in a doped material. While another pathway for charge relaxation can also be crystallization seen in the solid state photoluminescence in Figure 3-13(b), the photoluminescence data from Kim, et al. is also correlated with XPS spectra showing oxidation shifts of the sulfur in the thiophene ring as shown in Figure 3-14 below.<sup>4,21</sup>



Figure 3-14. XPS spectra and hole mobility for P3HT with increasing EBSA content. (a) XPS spectra show an oxidative shift on doping with EBSA. (b) increasing hole mobility with EBSA content in P3HT. The hole mobility increase is attributed to a mixed-band charge transport mechanism.<sup>4</sup>

The XPS spectra show a shift to higher core-electron binding energies on doping, which eliminates crystallinity of the P3HT as the sole cause of the results seen in the photoluminescence data and solution color.<sup>4</sup> Results from multiple sources confirm that P3HT is doped by sulfonic acid. The authors also test transistor devices in order to determine the effect of a dopant on the charge mobility of the polymer. The hole mobility for the device as a function of doping is shown in Figure 3-14. Doping with EBSA is observed to increase the charge mobility by orders of magnitude, the cause of which is not discussed by the authors. The work presents a convincing case for the doping of P3HT by sulfonic acid, showing how the material properties change, but does not go far enough to determine the mechanisms involved in the doping process. From this review of the literature, the most promising methods to determine the extent of doping in P3HT is in the FTIR spectra, UV-Vis spectra at 1.2 eV, and for quenching on addition of the dopant in PL spectroscopy. One of the main aims of this work is to expand on these results and offer a more mechanistic explanation for the doping effect of sulfonic acid on P3HT.

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### Chapter 4

# **Interfacial Effects of Dopants**

## 4.1 Introduction

Efficient operation of electronic devices is often limited by charge transport through the materials making up the device. For example, power generation in photovoltaics requires charge transport between the heterojunction in the middle of the device and the metallic contacts bounding it. If the excited and dissociated charges cannot be collected by an electrode they dissipate their useful energy through recombination. Efficient charge collection is enabled by charge transport layers such as PEDOT:PSS which modify the work function of the device to exclude electrons for greater hole transport.<sup>1,2</sup> Changing the materials at interfaces leads to control over the electric fields, charge transport mechanisms, and efficiency of devices.<sup>3–5</sup>

The Fermi levels of two materials align when they come into contact, creating an electric field at the interface to bring the two charge levels to equilibrium.<sup>6</sup> The simplest example of this effect is seen when n-doped and p-doped silicon come into contact. Electrons diffuse across the interface to fill the energetically favorable vacancies in the p-doped region in accordance with the electric field. As the mobile charge carriers diffuse across the interface they are depleted from their region of origin, leading to a "depletion region" where no mobile charge carriers are located until the electric field from the interface encompasses enough material to ensure charge neutrality.<sup>6</sup> For

Al/polyaniline/ITO diodes, doping the polyaniline with para-toluene sulfonic acid (p-TSA) leads to a current density increase of roughly one order of magnitude along with a reduction in the depletion region from 357 Å to 118 Å.<sup>7</sup> Minimizing the depletion region allows efficient charge transfer at the contact-heterojunction interface by promoting the presence of mobile charges near the electrode. Various materials have been applied at the interface to enable charge transfer both by introducing new energy states and promoting tunneling as a mechanism for charge transfer.<sup>8–10</sup>

### 4.2 PEDOT:PSS

Work function modification at interfaces can improve charge transfer through aligning the electron affinities of the electrode and semiconductor.<sup>11</sup> In the case of OLED devices using PEDOT:PSS as a charge transfer layer in ITO/PEDOT:PSS/poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT)/MoO 3 /Ag, the charge density of the device was shown to increase by an order of magnitude on treatment of the ITO interface by methanol. Friend and Sirringhaus, et al. perform x-ray photoelectron spectroscopy (XPS) measurements to determine the work function of the material before and after methanol treatment. They find that methanol acts to remove surface –OH groups and increases the work function of the PEDOT:PSS from 5.2 to 5.4 eV. The increase in work function reduces the energy barrier to charge transport for holes into the device. The OLED and UPS measurements are shown in Figure 4-1.



Figure 4-1. Modification of the interface between PEDOT:PSS and F8BT. On left, the current density as a function of voltage across a ITO/PEDOT:PSS/F8BT/MoO 3 /Ag device increases by two orders of magnitude on treatment with methanol. In middle, the XPS spectra show a shift in work function for the PEDOT:PSS interface with F8BT. The change in work function is shown in the schematic on right.<sup>11</sup>

### 4.3 Charge Transfer at Interfaces

Charge injection between a metallic contact and a polymer semiconductor is problematic due to several factors. One factor is that there is often very little mobile charge in an organic semiconductor, expanding the depletion region up to the entire length of the semiconducting channel.<sup>12</sup> As the depletion region expands, mobile charges in the semiconductor do not favorably approach the contact and require large voltages applied to enable thermionic emission at the interface. Tunneling allows the thermionic emission barrier to be bypassed, but requires a thin barrier along with a depletion region on the order of angstroms for transfer from the polymer into the contact. Figure 4-2 shows a schematic of tunneling compared against thermionic emission.<sup>13</sup> Thermionic emission is primarily governed by the height of the energy barrier, while tunneling is limited by the barrier width.<sup>6</sup>



Figure 4-2. Schematic of charge carrier tunneling between neighboring energy states.<sup>13</sup> Thermionic emission (solid red line) requires enough energy to promote an electron above the energy difference between the two states. Tunneling (dashed red line) is dependent on the rate of decay of the electron's wave function through the region where the electron is not allowed between the states. It is dependent on the rate of decay as well as the physical distance between states, approaching the highest rate of transmission as the barrier width decreases to zero.<sup>6,13</sup>

An improvement in organic field effect transistors was investigated by modifying the thickness of a self-assembled monolayer (SAM) interposed between a gold contact and P3HT.<sup>14</sup> Samori, et al. demonstrated that the contact resistance increased from 23 k $\Omega$ to 75 k $\Omega$  to 98 k $\Omega$  on changing the SAM component from phenylthiol to biphenylthiol to terphenylthiol as shown in Figure 4-3. Because tunneling is dependent on the distance of charge carriers from the contact, increasing the SAM thickness strongly inhibits tunneling which is observed in the contact resistance. Modifying the depletion region width has a similar effect to SAM thickness changes because both directly modify the electrodecharge carrier distance.



Figure 4-3. Increasing SAM thickness for a P3HT transistor. The contact resistance is increased on increasing the number of phenyl rings in the SAM component.<sup>14</sup>

The major aim of the work in this thesis is to explore how dopants affect the P3HT-contact interface. Towards that end, literature presented here implies that a high density of dopants held at the interface should thin the depletion region while interrupting the semiconductor in bulk the least. Mixing the dopant with the semiconductor at the electrode interface is expected to show a greatly reduced contact resistance relative to a separate layer architecture with dopant adjacent to the contact and semiconductor deposited on the dopant. Polymeric dopants will be explored because they will be kinetically trapped where deposited unlike small molecule dopants such as iodine or the EBSA explored by Kim, et al.<sup>15</sup>

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## Chapter 5

# **Experimental Procedures**

# 5.1 Doping

The process for doping P3HT and depositing the material were carefully considered and have changed over the course of this work. Unless otherwise stated, the practices explained here are the default practice. This section describes how the P3HT was doped and the processes that allowed samples to be fabricated and tested using the doped semiconductor.

As discussed in Chapter 3, doping is enabled by heating the P3HT and dopant together in solution before depositing the material on ITO, glass, KBr, or a transistor device. The most reliable method for doping P3HT in solution while avoiding oxygen contamination is preparing the samples in a glove box. For all samples the appropriate amounts of material were weighed in their dry state outside of a glove box, transferred into the chamber, and then dissolved by dry solvents in an oxygen-free environment. An MBraun glove box was used for all experiments. The standard amount of P3HT dissolved in solution yielding defect-free films from spincasting was 10 mg mL<sup>-1</sup>. This concentration was used for all solutions unless otherwise stated. All materials were weighed in glass vials cleaned via solvent rinsing before drying. In cases where the appropriate amount of dopant to add was lower than the precision of the scale, the material was dissolved in solution using a precisely known quantity and accurately

dispensed from pipettes into the vial before the solvent was dried away and the vial was placed into the glove box. The practice of dissolving materials for delivering precise quantities of material to the glove box was never necessary for P3HT and only used for delivering dopant material, which means that the P3HT was only ever dissolved once. Finally, a clean magnetic stir bar was included with the undissolved materials before their transfer into the glove box.

Once within the glove box, the undissolved polymer contained within the vials was dissolved by dry solvents specifically for use in the oxygen-free environment. Samples were never processed above an oxygen concentration of 80 ppm. All materials were dissolved in solutions consisting of 80% chloroform and 20% methanol by volume. While chloroform is a good solvent for neat P3HT, this solvent ratio was used because the dopants used were typically insoluble in pure chloroform. As such, even the neat P3HT was dissolved in the mixed solvent for consistency. Once the solvent was added to the dry materials, the vials were placed on a hot plate for 48 hours at 60° C to promote doping.

# **5.2 FTIR**

After being held at temperature for two days, the dissolved semiconductor and dopant were deposited onto a substrate for analysis. For FITR spectroscopy, the solutions were drop cast onto KBr pellets. The pellets were pressed using 60 mg of KBr powder and were not used if optical imperfections such as cracks or poorly compressed regions were present. The pellets were 7 mm in diameter. Films were deposited via drop casting,

using single or multiple depositions depending on the concentration of solution. Films were deposited using 20 uL of solution which were sufficient to cover the pellet. At 1 mg mL<sup>-1</sup> seven castings were required to produce film thicknesses sufficient to acquire spectra, which were optically opaque and purple-black in color. Films on KBr pellets were analyzed using a Bruker V70 spectrometer in transmission mode.

### 5.3 UV-Vis

UV-Vis spectroscopy was performed with KBr pellet substrates as well as glass and ITO substrates. KBr pellets were used when directly correlating UV-Vis and FTIR data, while ITO and glass substrates were used for all other work. To acquire high-quality UV-Vis spectra, film thicknesses needed to be much smaller than for FTIR spectroscopy. Films were optimized to be optically transparent with a purple hue. On KBr pellets, three castings at 1 mg mL<sup>-1</sup> created a film of appropriate thickness for spectroscopy. The solution was spuncast on ITO and glass rather than being dropcast to create more uniform films. Material was deposited using solutions at 3 mg mL<sup>-1</sup> and 600 RPM, while solutions at 10 mg mL<sup>-1</sup> were deposited at 1000 RPM. The cast films were measured using a Perkin Elmer Lambda 950 UV-Vis NIR spectrometer in transmission mode. For films cast on ITO, the ITO was cleaned first. The ITO was cleaned in a multi-step procedure. First, the ITO was scrubbed using a strong cleaning soap while alternating scrubbing with a deionized water rinse. After three rinse/scrub cycles, the slides were rinsed a final time in deionized water and dried with pressurized air then exposed to UV-Ozone for ten minutes. The slides were sonicated in acetone for ten minutes and exposed to UV-Ozone

for another ten minutes. Finally, the slides were sonicated in isopropyl alcohol and exposed to UV-Ozone for a final ten minutes before being ready for spincasting.

#### **5.4 Photoluminescence**

Photoluminescence spectroscopy was performed on solutions in quartz cuvettes which were prepared in the glove box and tested while sealed. The cuvettes were sealed to prevent contamination of oxygen. The concentration of the solution in the spectrometer was optimized for signal-to-noise ratio at 3 mg mL<sup>-1</sup> which was the concentration used for all PL spectroscopy tests. In order to test the effects of crystallinity on the fluorescence of P3HT, a series of heating studies were performed. Cuvettes were filled with heated solution within the glove box, sealed, removed from the glovebox, and immediately tested in the spectrometer. The solutions were then scanned repeatedly in the spectrometer until crystallization slowed significantly, then removed to be reheated. The cuvettes were heated on a hot plate without stirring for a specified amount of time before being removed for further spectroscopic measurements. This procedure allowed the effects of solvent quality and crystallinity of P3HT on fluorescence to be studied in an inert environment. The wavelength of excitation light was 470 nm.

#### **5.5 Transistors**

Transistor measurements were performed by spincasting thin films onto silicon substrates patterned with gold. Silicon substrates were prepared by taking silicon wafers with 3 kÅ thermal oxide. Wafers were then patterned with 1 kÅ of evaporated gold. Before polymer casting onto the wafers the substrates were first cleaned extensively. The wafers were rinsed thoroughly with iso-propyl alcohol using a steady stream from a wash bottle. The rinsed wafers were then exposed to UV-Ozone for twenty minutes. Wafers were then rinsed in deionized water from a Millipore purifier and exposed to UV-Ozone for another twenty minutes. Before finally being transferred to the glove box for spin casting, wafers were exposed to trichloro(octadecyl)silane (OTS) for twelve hours for contact modification. The OTS treatment was performed by filling cleaned vials with 16 mL hexadecane, setting the cleaned wafers gold side up at the bottom of the vial, and adding 20  $\mu$ L OTS to the vial. The vials were briefly given gentle agitation to disperse the OTS and were removed after 12 hours. The vials were cleaned by rinsing with methanol and placed in an oven at 120 °C for four hours.

After being exposed to the OTS solution for twelve hours, wafers were removed and rinsed with iso-propyl alcohol and dried with an air gun then immediately transferred to the glove box for spincasting. Solutions of 10 mg mL<sup>-1</sup> P3HT were used for each transistor wafer tested and spun at 600 RPM. The solution concentration was always calibrated to be 10 mg mL<sup>-1</sup> for P3HT and any dopant was simply added to the solution. After spincasting, the wafers were prepared for testing on a Micromanipulator probe station. Preparation consisted of scratching the nonpatterned side of the wafers with a diamond stylus to ensure good contact with the probe station's gate electrode. Devices were also electrically isolated from their neighbors by scratching away the polymer film around the tested device. With good contact made between the bare silicon and the probe station gate, electrical probes were placed on the source and drain pads for each device and I-V sweeps were conducted for testing.
### Chapter 6

# FTIR, UV-Vis, and Photoluminescence Spectroscopy of P3HT/Sulfonic Acid Complexes

### **6.1 Introduction**

The charge transfer interactions between an organic semiconductor and its dopant can be detected spectroscopically, as reviewed in Chapter 3. Typical effects of adding the dopant include an increase in the number of free carriers and charge transfer between the semiconductor and the dopant. While the dopant-semiconductor interaction does not include breaking or forming covalent bonds, charge transfer interactions will shift the vibrational frequency of the characteristic peaks of the nearby covalent bonds which can be investigated with FTIR spectroscopy. The literature has shown that doping also modifies the visible-light absorption of the organic semiconductor due to the modification of its conjugated bonds. The excited states of the materials are modified on crystallization and charge transfer, which can be examined with photoluminescence spectroscopy. This chapter examines the doping interactions between P3HT and sulfonic acid, explored through FTIR, UV-Vis, and photoluminescence spectroscopy.

The proposed charge transfer interaction between a sulfonic acid dopant and P3HT is an association between the acidic proton of the sulfonate and the lone pair of electrons on the sulfur in the thiophene ring. A schematic of their interaction is outlined in Figure 6-1 and is in agreement with literature.<sup>1</sup>



Figure 6-1. Proposed mechanism of the dopant-thiophene interaction. The acidic proton is hypothesized to associate with the lone pair of electrons on the sulfur on dissociation from the  $-SO_3^-$  anion.

As the proton dissociates from the sulfonate group, it may either re-associate with the negatively charged anion or stabilize itself by withdrawing electron density from a nearby molecule. With only P3HT and sulfonated Radel (S-Radel) in intimate contact, it is hypothesized that the most readily available source of electron density is the sulfonate or the lone pair of electrons on the sulfur atom of the thiophene. Withdrawal of electron density from the thiophene ring allows the material to carry more holes than when under neutral conditions. This hypothesis excludes the formation of new covalent bonds, and as such the evidence for doping in FTIR is expected to result in shifts in the characteristic spectra for the sulfonic acid and new polaronic peaks for the thiophene rings.

#### 6.2 FTIR measurements of charge transfer interactions

The interaction between a dopant and thiophene was examined through casting thin films of polymer and dopant from chloroform and methanol as described in Chapter 5. The spectra in Figure 6-2 show how the behavior of sulfonic acid changes when it is introduced to P3HT and heated. As shown by Kim, et al. in Chapter 3, heating is required to enable the charge transfer interaction between 2-ethylbenzenesulfonic acid (EBSA) acid and P3HT in chloroform. Thus, if acid is incorporated into P3HT films, there should be some change in the IR absorption spectra of the P3HT and/or S-Radel from their charge-transfer interaction. The peaks of interest associated with S-Radel are the symmetric singlet and antisymmetric doublet located at approximately 1050 cm<sup>-1</sup> and between 1130 cm<sup>-1</sup> and 1230 cm<sup>-1</sup>, respectively. Table 6-1 shows how the peak centers and splitting of characteristic  $-SO_3^-$  anion stretches shift in wavenumber with varying charge density on the counterion. Thus, when a proton dissociates from the  $-SO_3^-$  anion to interact with the thiophene ring, a shift in the characteristic peaks and a change in splitting should be observed. To detect this phenomenon, solutions of P3HT and p-TSA were dropcast onto KBr pellets according to the procedure in Chapter 5. The FTIR spectrum of the sample was measured in transmission mode then the sample was heated in an oven at 60° C for 30 minutes and the FTIR spectrum was measured again. Next, the sample was heated a final time at the same temperature for 90 minutes and the FTIR spectrum was measured. The FTIR spectra in Figure 6-2 show some shifting of the symmetric and antisymmetric stretch of sulfonic acid with heating, but because the signals from sulfonic acid are mixed in with those of P3HT shown in Figure 6-2, it is

difficult to draw strong conclusions from the data. A further experiment was attempted to expose the doping interaction using FTIR spectroscopy.

	Symmetric Singlet	Antisymmetric Doublet		Splitting
Li+	1030	1134	1203	69
Na+	1042	1188	1226	38
K+	1037	1191	1223	32
Rb+	1036	1194	1219	25
Cs+	1031	1194	1219	25

Table 6-1. FTIR peak assignments for the symmetric singlet and antisymmetric doublet stretches for sulfonic acid as a function of counterion. The splitting between the two doublet peaks is also shown. The peak shifts seen with varying counterions indicate that a sulfonic acid whose proton associates with the lone pair of electrons on a thiophene ring should result in a detectable shift in the characteristic peaks though the amount of shift expected is unknown.<sup>2</sup>



Figure 6-2. FTIR spectra of doped P3HT films on heating. The same cast film was used for all three spectra in both plots, removed from the spectrometer between FTIR measurements to be placed in an oven at 60 °C for the specified time. Spectra show the cast film with a 100-1 ring-acid ratio using S-Radel 2.2 IEC. a) Symmetric stretch absorbance region for the  $-SO_3^-$  anion on heating at 60 °C. b) Antisymmetric stretch absorbance region for the  $-SO_3^-$  anion on heating at 60 °C.

While the earlier experiment relied on tracking the characteristics of the sulfonic

acid groups, another experiment was conducted to look for evidence of free carriers

within the P3HT. Kim, et al. observed changes in the FTIR spectra of P3HT doped with  $F_4$ TCNQ which was discussed in Chapter 3 and whose critical plot is reproduced in Figure 6-3 below.



Figure 6-3. Comparison of polaronic absorption in P3HT to doped P3HT spectra from Kim, et al.<sup>3</sup> On left, Absorbance spectra of neat P3HT compared to P3HT doped with 10 wt.%  $F_4TCNQ$ . The bottom spectra has the absorbance from neat P3HT subtracted and only shows the features of  $F_4TCNQ$  and the  $F_4TCNQ$ -P3HT interaction. The peaks at 1100 cm<sup>-1</sup> and 1300 cm<sup>-1</sup> are attributed to polaronic absorption in P3HT. On right, FTIR absorbance of neat P3HT (grey spectra) and P3HT doped with S-Radel 2.2 IEC at a 10-1 ring-acid ratio without heating (black), heated at 95 °C for 60 min (red), and measured after cooling for four hours (green). The same cast film was used for all three doped spectra and was removed from the spectrometer between FTIR measurements for heating in an oven and cooling in air.

The data from Kim, et al. shown in Figure 6-3 is compared against spectra of both neat P3HT and P3HT doped with S-Radel 2.2 meq/g IEC at a 10-1 molar ratio of thiophene rings to sulfonic acid groups. The P3HT was expected to be doped by the S-Radel and thus show similar spectroscopic features to the published spectra from Kim, et al. in the P3HT small molecule sulfonic acid system. The doped sample was also heated in an oven for various lengths of time at 60 °C to ensure that doping interactions occurred. Unfortunately, none of the peaks observed correlated well with the literature data in Figure 6-3, suggesting but not proving that a doping interaction exists. FTIR

spectroscopy was not pursued further due to the lack of doping evidence in both the P3HT and the S-Radel.

#### 6.3 P3HT/Sulfonic Acid Interaction Measurements with UV-Vis

More significant evidence for doping was observed in the UV-Vis spectra taken of both para-toluene sulfonic acid and S-Radel. Kim, et al. show a slight increase in the absorbance spectra of P3HT blended with EBSA, as referenced in Chapter 3. The increase in adsorption they observed at around 975 nm was found to be replicated on doping P3HT with p-TSA and S-Radel, Figure 6-4.



Figure 6-4. Recovery of the characteristic doping peak after heating. Both p-TSA and S-Radel are compared against neat P3HT with specific amounts of heating. Samples were cast on KBr and transferred immediately between glove box, spectrometer, and oven. On left, P3HT doped with p-TSA at a 10-1 ring-acid ratio. On annealing the p-TSA doped film the doping peak disappears and does not recover over three days left in glove box conditions. On right, P3HT doped with S-Radel 2.2 IEC at a 10-1 ring acid ratio which loses and recovers its doping peak. Even with a lower IEC, the doping peak in the S-Radel doped film is stronger, retains its character under heating, and also recovers to original levels after storage in nitrogen conditions.

The increase in absorption is observed to be much more intense than that shown

by Kim, et al. This difference is attributed to the much higher amount of dopant added to

the samples in this study relative to the 1% wt. EBSA in P3HT (solution concentration

was 20 mg mL<sup>-1</sup> of P3HT in chloroform) used by Kim, et al. The absorption is shown to not be specific to the EBSA molecule; rather it is specific to sulfonic acid due to the absorption features being similar for two different sulfonic acid-bearing moieties. There are two important features in the doping spectra shown in Figure 6-4, only one of which is referenced by Kim, et al. The authors attribute the 975 nm absorption to EBSA-doped thiophene rings, but the authors do not address the increased absorption shown from approximately 700 to 900 nm observed in Figure 6-4. This increased absorption is attributed to both the sub-bandgap absorption due to the introduction of the dopant as well as increased polaronic absorption. Dopants introduce more free carriers to a material by creating inter-bandgap energy states close to the LUMO or HOMO of a material which can donate or remove electrons, respectively. These energy states will absorb light with energy less than the bandgap resulting in broad absorption due to the broad HOMO and LUMO energies. In addition, the free carriers introduced by dopant-semiconductor interactions enable more absorbance from non-neutral semiconductor species which also absorb smaller energies than the bandgap.

As outlined by the FTIR and UV-Vis data, sulfonic acid doping of P3HT is affected by heating, both in solution and in films. Heating was shown to influence the doping interaction in FTIR data of thin films, and the UV-Vis data shows an increase in the doping interaction at 970 nm. Each of the films shown in Figure 6-4was heated in solution at 60 °C for two days before being spuncast onto ITO-covered glass. The absorbance from the ITO has already been background subtracted. The spectra of the p-TSA and S-Radel show significant differences on heating. Heating films at the same temperature used to promote doping in solution is shown to have different effects depending on the dopant used. The p-TSA shows weaker doping features while the S-Radel displays a stronger doping peak. The difference between the dopants is attributed to phase separation of the small molecule. In this case, the increase in doping observed with the polymer dopant is credited to a higher number of activated dopantsemiconductor associations enabled by heating. On annealing at a higher temperature, all films show reduced doping character, attributed to the P3HT motion allowing phase separation of any dopant and possible side reactions. This observation is confirmed by the increase in the absorbance of the main undoped P3HT  $\pi$ - $\pi$ \* transition at 550 nm.



Figure 6-5. UV-Vis absorbance of heavily doped P3HT. A sample of P3HT (purple) is compared against P3HT doped with S-Radel IEC 2.2 (black). The neat P3HT film on KBr was deposited with two separate volumes of 20  $\mu$ L at 1 mg mL<sup>-1</sup> P3HT, while the doped film consists of three 20  $\mu$ L castings at the same volume. The doped sample was heated to 150 °C for 10 minutes in an oven then immediately measured again (red dash). Finally, the sample was held in air for four hours then measured (green dot).

Also of note is the ability of the polymeric dopant to recover lost dopant-ring interactions. Figure 6-5 shows a sample of P3HT doped with S-Radel at a 10-1 ring-acid ratio. The sample was removed from the glove box after casting and immediately measured in the UV-Vis spectrometer. After the scan, the sample was immediately placed in an oven at 150 °C for 10 minutes, and then immediately scanned again. A final scan was performed four hours later, with all three runs shown in Figure 6-5. There are three features of note in the figure. First, the sample can recover dopant-ring associations after some fraction have been lost, seen by comparing the red to the green spectra. The recovery of the doping peak is attributed to both spontaneous recovery of acid-ring associations as well as some amount of formed oxygen-ring interactions which are possible due to the sample being held in air for all testing. Second, the scan taken immediately after the annealing step shows significantly higher P3HT  $\pi$ - $\pi$ \* absorbance. The feature indicates that there is more P3HT in the undoped state on removal from the oven. Third, the reduced  $\pi$ - $\pi$ \* absorbance observed in the scan four hours after annealing reflects a combination of three sources: restored acid-ring interactions, new oxygen-ring interactions, and degradation of the polymer from photodegradation or chemical reactions with the environment. Nevertheless, it can be inferred that the acid-ring association is occurs at room temperature assuming that the materials have not undergone significant phase separation which is evident from the p-TSA doped material in Figure 6-4. S-Radel is able to recover characteristics of doping due to the dopant polymer being immobile relative to the p-TSA.

In summary, the UV-Vis data has shown that there is an association between sulfonic acid and P3HT which can occur at room temperature to maintain P3HT in the doped state. Phase separation is more common in small molecule dopants because they are much more mobile than the polymers, and the resulting reduction in P3HT-acid surface area makes small molecules unsuitable as dopants in any significant concentration. Polymeric dopants are much more stable and as a result can dope more effectively than small molecules on average for the same ring-acid ratio. The tested S-Radel material is robust to heating and stable for many combinations of heating and solvent conditions.

#### 6.4 Excited State Interactions via Photoluminescence

To confirm the data observed in the UV-Vis, photoluminescence spectroscopy was employed. The goal was to investigate how the P3HT behaves with dopant in solution before being cast as a film. Films cast from solutions were not tested beyond initial probes due to low signal and were not pursued further or reported here.

The role of the solvent in promoting the acid-ring doping interaction was investigated by varying the ratios of solvent in the mixture and observing the resulting spectroscopic peaks. The referenced peaks under scrutiny are at 600, 650, and 680 nm which were introduced in Chapter 3. Figure 6-6 shows the results of dissolving neat P3HT in chloroform, chlorobenzene, and a mixture of chloroform and methanol:



Figure 6-6. Photoluminescence spectra of P3HT solutions at 3 mg mL<sup>-1</sup>. On left, photoemission of P3HT dissolved in chloroform (red), chlorobenzene (blue), and a mixture of chloroform/methanol at 95/5 vol.%. Given identical concentrations of P3HT for all solutions, the negligible photoemission for the chloroform/methanol mixture is attributed to P3HT crystals precipitating from solution. The inset shows the solution color. On right, three spectra show the relationship between P3HT and solvent. With spectra collected after each step, P3HT was dissolved in chloroform (black), 1 vol.% methanol was added to the same solution, and the solution was heated to 60 °C. The solutions lose photoemission on addition of methanol due to precipitation but become soluble in a heated solution. The lower intensity of the solution dissolved in chloroform relative to the heated chloroform/methanol solution indicates that crystallites of P3HT are present even in pure chloroform and are dissolved with heating.

The three cases with different solvents shown in Figure 6-6 were tested for their ability to dissolve P3HT. As described in Chapters 3 and 5, P3HT is commonly dissolved in chlorobenzene or chloroform. When adding sulfonic acid as a dopant at high concentrations, another solvent which can dissolve the acid is required. Methanol was added to all of the solutions presented for the FTIR and UV-Vis data, and is tested here for its effects on the P3HT. When dissolved at 3 mg/mL, by eye the P3HT is solvated equally well by both chloroform and chlorobenzene. Spectroscopically it is observed in Figure 6-6 that the two solvents exhibit different levels of fluorescence. The different fluorescence levels for the solvents are attributed to differing solubility, since P3HT crystals or aggregates have quenched fluorescence as mentioned in Chapter 3. When methanol, a nonsolvent for P3HT, is added at 5 vol % to 95 vol % chloroform, then the fluorescence of the solution is quenched entirely and the solution turns dark and opaque. The dark solution and lack of fluorescence indicates that P3HT crystals precipitate solution when held at room temperature for any length of time. Since the solutions require heating at 60 °C to promote the acid-ring doping interaction, this data indicates that the solutions must be cast while warm in order to deposit a uniform amount of unaggregated P3HT. Since it is unlikely that P3HT and the dopants can co-crystallize,

high degrees of crystallinity in solution before casting are hypothesized to reduce the interfacial area between dopant and semiconductor and result in reduced doping interactions between the acid and the thiophene. As shown in Figure 6-6, adding methanol to a solution of only P3HT and chloroform completely quenches the fluorescence peaks. Only on heating do the aggregates in solution break up, restoring the fluorescence to a greater degree than initially found in the room-temperature chloroform solution. Figure 6-6 indicates that P3HT forms aggregates even in a good solvent at room temperature. Heating of these solutions appears to be required to break up the aggregates and enable the acid-thiophene interaction. Further experiments were undertaken to test this hypothesis via photoluminescence spectroscopy of heated and doped P3HT solutions.

PL spectroscopy was conducted with dopant in solution. Both p-TSA and S-Radel at 2.2 meq/g IEC were mixed with P3HT and dissolved at varying ring-dopant ratios with P3HT at 3 mg mL<sup>-1</sup>. Chloroform and methanol were used as the solvent at an 80%/20% chloroform/methanol ratio. The PL data was acquired while the solutions were still warm and sealed from heating inside the glove box. The data from the experiment is shown in Figure 6-7 below:



Figure 6-7. Photoluminescence and UV-Vis absorption of solutions doped with both p-TSA and S-Radel. All solutions were tested immediately after being held at 60 °C for at least 1 hour. On left, photoluminescence of P3HT dissolved at 3 mg mL<sup>-1</sup> while doped with S-Radel and p-TSA. P3HT doped with S-Radel IEC 2.2 at a 100-1 ring-acid ratio is compared against P3HT doped with p-TSA at both 100-1 and 10-1 ring-acid ratios. The reduced intensity of the S-Radel relative to both p-TSA concentrations indicates that S-Radel quenches and thus dopes more effectively than p-TSA even at higher concentrations. On right, the same solutions were examined with UV-Vis spectroscopy. A doping peak is evident which is highest in the P3HT doped with S-Radel.

Figure 6-7 shows how the fluorescence of P3HT is modified in solution by the addition of dopant. The neat P3HT shows fluorescence spectra equivalent to published spectra as seen in Chapter 1 Figure 1-6. On the addition of dopant, the fluorescence peaks of P3HT are quenched but not as strongly as observed in the PL spectra published by Kim, et al. The p-TSA dopant at a 100-1 ring-acid ratio shows effectively no quenching, while a much higher concentration of p-TSA in solution significantly decreased the fluorescence intensity of P3HT. Interestingly, the polymeric dopant quenches the fluorescence of the P3HT more than the small molecule. After being removed from the hot plate, each solution had an identical amount of time to cool before the PL was measured, which indicates that each solution should have effectively no crystallinity despite having methanol in the solvent mixture. While the rate of crystallization may

have an impact on the fluorescence quenching for these solutions, the data show that the S-Radel has a significantly different impact on the P3HT than the p-TSA. The polymer dopant appears to be a more effective doping material than the p-TSA even at  $1/10^{\text{th}}$  the acid group-thiophene ring ratio. This significant increase in doping effectiveness is attributed to a cooperativity effect between P3HT and the dopant, where each acid interacting with the P3HT makes nearby acids more likely to bind to the P3HT chain, resulting in intimately connected S-Radel and P3HT in solution which the small molecule p-TSA is not capable of. UV-Vis spectra of the same dopant ratios in solution were also examined, and Figure 6-7 shows a similar trend to the PL data with the S-Radel being the most effective dopant as judged by the intensity of the doping peak at 970 nm. Unlike the data from Kim, et al. the PL data shown here do not display a simple reduction in intensity of the P3HT peaks and instead quench the peak at 590 nm selectively. The 590 peak shown in Figure 6-7 is reduced more than the peak at roughly 640 nm. These results indicate that S-Radel is a more effective dopant than p-TSA per acid group. Further studies were performed to control the amount of crystallinity the P3HT exhibits in solution and remove crystallinity as a confounding variable.

To examine the effects of P3HT's crystallization in solution, spectra of doped solutions of P3HT were acquired repeatedly as the solution cooled. As the solution is allowed to cool, the crystallinity of the P3HT should increase until all of the P3HT precipitates from solution leaving no material to fluoresce. PL spectra of doped solutions were acquired as the solutions were first removed from the hot plate and at time intervals outlined in Figure 6-8 below:



Figure 6-8. Crystallinity of doped P3HT in solution over time. P3HT doped with p-TSA at a 10-1 ring-acid ratio (left) is compared against P3HT doped with S-Radel 2.2 IEC at a 100-1 doping ratio (right). For each plot, one solution was used which was heated for two days at 60 °C and allowed to cool for 10 minutes before acquiring a photoluminescence spectra. Subsequent spectra were acquired at the time points indicated and stored while sealed in a glove box environment in the dark. The insets show the color of solution after the initial spectrum and last spectrum.

The behavior of the doped P3HT as it cools is indicative of the polymer's

crystallinity in solution and the ring-dopant associations. Once the solution is allowed to cool from its initial heating shown in Figure 6-8 several interesting effects can be observed over the experiment's timeframe. For the P3HT doped with p-TSA, the intensity of each peak in the spectrum decreased during cooling. Beyond the overall reduction in intensity brought on by crystallization observed by the solution's change in color, the ratio between the two main fluorescence peaks at 590 and 650 nm changed. The location of the peak also shifted, which is indicative of a new charge transfer interaction. The hypothesis explaining this trend is that as the P3HT crystallizes from solution, the p-TSA can only interact with P3HT remaining in solution because it should be completely insoluble in P3HT crystals. As P3HT crystallizes, the amount of uncrystalized thiophene rings in solution relative to the p-TSA decreases. With the number of acids per thiophene ring increasing well above the initial concentration, each

ring still in solution is expected to be doped. Using the results from Kim, et al., each dopant state is expected to reduce the effective bandgap of the material by up to 0.6 eV, possibly explaining the shift to lower energies of fluorescence with time.

The mixed solvent solution of 80/20 vol. % chloroform/methanol containing S-Radel dopant required a much longer time to crystallize than solutions of pure P3HT in the same solvent mixture. The intensity of the spectra of P3HT doped with polymer decreased only a fraction as much as that doped with p-TSA. The higher intensity is attributed to greatly reduced crystallinity of the sample in the presence of the polymeric dopant which was confirmed by the solution's orange-red color. The reduction in the rate of crystallinity is attributed to cooperativity between the P3HT and polymer dopant. The cooperativity effect should reduce the crystallinity via constant steric repulsion of P3HT chains by the S-Radel backbone. The methanol in the solution provides a driving force for the P3HT to crystallize from solution even in the presence of dopant. While this hypothesis may explain the results seen in the PL spectra above, an alternative hypothesis is that S-Radel can be incorporated into P3HT crystals which would similarly disrupt their formation. However, this type of co-crystallization is not likely.

These experiments show that P3HT is doped by sulfonic acid. The spectroscopic data shown here primarily indicates that S-Radel is a much more effective dopant than p-TSA on a per acid group basis. The absorbance peaks from doping in UV-Vis indicate that S-Radel dopes P3HT 10 times more than p-TSA at a given acid group concentration. Results from PL spectroscopy indicate a similar trend, and hint at the mechanics of the thiophene-dopant interaction and its thermodynamic stability. Field-effect transistors

were fabricated both to support the spectroscopic doping evidence and to quantify the current-voltage characteristics for device fabrication.

# 6.5 References

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## Chapter 7

### **Doping in Organic Field-Effect Transistors**

### 7.1 Introduction

Conductivity, mobility, and the charge transport behavior of how dopants interact with organic semiconductors at contacts must be measured by electrical means to compliment the spectroscopic studies. While top-gate bottom-contact devices are used for some electrical measurements due to the low contact resistance of this geometry, for this work, bottom-contact bottom-gate devices were used for ease of spincasting and fabricating devices. As outlined in Chapter 5, bottom-gate bottom-contact materials are used for all measurements described in this chapter unless otherwise noted. This chapter explores the impact of doping on the electrical characteristics of P3HT.

In order to be useful in devices, specifically at contacts, it is first important to understand if the dopant can even influence the behavior of P3HT in bulk. While the ultimate goal is to include effective dopant selectively at contacts, achieving doping in the bulk is a benchmarking tool. Bulk doping is simpler in terms of sample fabrication and closer to experiments performed in literature. Chapter 5 described the conditions for optimal P3HT testing in the transistor architecture, and those results are shown again in Figure 7-1 for comparison against the bulk-doped material. Bulk doping of semiconductors is investigated here to determine the effectiveness of different kinds of dopants. Initial results comparing neat P3HT to P3HT doped with small molecule sulfonic acid (p-TSA as introduced in Chapter 3) are shown in Figure 7-1



Figure 7-1. Comparison of neat P3HT to P3HT doped with the small molecule acid p-TSA. The channel width is held constant for all transistors at 220  $\mu$ m. The source-drain voltage is -100 V. The top plot shows I-V sweeps of P3HT at varying channel length, showing increasing device hysteresis in forward (device off to device on) sweeps with decreasing channel length while the reverse (device on to device off) sweeps maintain a consistent threshold voltage. The bottom plot displays P3HT doped with p-TSA at a 100-1 ring-acid ratio over a range of channel lengths. The

on- and off-currents in doped I-V sweeps are higher than the neat P3HT at the same channel length in every case, indicative of bulk doping.

Effective dopants should significantly modify the off-current for the device by increasing the number of free carriers. A higher free carrier concentration allows current to flow even when an applied gate voltage should stop the formation of a conductive channel. Thus, a higher off current is evidence of doping. As seen in Figure 7-1, the off current for P3HT is consistently around 10<sup>-11</sup> A which agrees with literature. In the P3HT doped at a 100-1 ring-acid ratio the off current is increased to roughly 10<sup>-8</sup> A indicating that the material is doped in line with the results published by Kim, et al. for a molecule nearly identical to p-TSA. The P3HT is shown to be doped by p-TSA, and further experiments were undertaken to observe whether a polymeric dopant was more effective as suggested by the spectroscopic data presented in Chapter 6.

Hysteresis was observed in most of the devices described in this chapter. Hysteresis in the literature is commonly associated with trapping states or mobile ions in the semiconductor. The difference between the forward and reverse sweeps is commonly claimed to be trapped electrons or holes which affect the rate at which a conductive channel is formed via accumulation of charge carriers adjacent to the dielectric. The rate at which the conductive channel can form is important to hysteresis, as the threshold voltage is strongly dependent on the specific gate voltage where a conductive channel is formed. Mobile charges are observed to linger in each of the p-TSA doped I-V sweeps shown in Figure 7-1 as the device proceeds from an on-state to an off-state. These lingering charges are observed in the slope of the reverse-sweeps in two features: the slope of the linear region and the slope of the sweeps as the gate voltage proceeds past

the threshold voltage. The transition from on- to off-state is much faster in neat P3HT than in the doped material, with the longest transition taking place in the device with the shortest channel. The shortest channel experiences the highest effective electric field, which favors the device remaining in the on state for the longest time in a doped device. In contrast, the longest channel has the sharpest transition from the on- to off-state which is attributed to the stronger relative field applied from the gate. Once the gate voltage has proceeded past the threshold voltage in the reverse sweep, the doped P3HT is observed to have a continually decreasing current. While neat P3HT is absolutely off after the threshold voltage is passed remaining around  $10^{-11}$  A, the doped material allows a continually decreasing current to flow. These observations indicate that the free carriers in neat P3HT form a metallic state for the conductive channel at a specific gate field with the doped material showing some metallic features over a wide range of gate fields. The differences in the behavior between doped and undoped samples indicate that mobile charges are localized around dopant molecules which require some electric field to turn them into free carriers. Once the carriers leave the site of their dopant, they tend to linger in the bulk of the device. This behavior implies that the energy level for the dopants within the conduction band is neither one that forms a deep trap nor one adjacent to the valence band, but is instead between the two as suggested by Kim, et al. and introduced in Chapter 3.To characterize the dopant, in the context of real devices, it is important to know how general the observed doping phenomenon is to materials beyond P3HT. As referenced in chapters 2 and 4, one of the applications for the doping of organic semiconductors is the modification of interfaces for photovoltaic devices. The two main materials used in those applications are an electron acceptor and an electron donator.

P3HT is commonly used as an electron acceptor and is the focus for current doping studies. However, it is important to know whether the sulfonic acid dopant is capable of interacting with other materials and PCBM is one of the materials paired with P3HT most often in photovoltaics due to the favorable matching between their HOMO and LUMO levels. S-Radel was mixed with PCBM and spun onto a transistor substrate to determine what interactions, if any, took place between the electron acceptor and a strong acid.It was hypothesized that there would be no significant electrical interaction between the PCBM and the sulfonic acid due to the PCBM's electron accepting nature and lack of thiophene ring-like conjugation. The results of a test for that hypothesis are shown below in Figure 7-2.



Figure 7-2. Comparison of PCBM with PCBM doped S-Radel with 3.1 meq/g IEC. The PCBM is doped at a 9-1 and 4-1 PCBM-acid ratio. All curves use a 320 µm channel length and a -100 source-drain voltage. The I-V behavior of neat PCBM is shown on left with a threshold voltage dependent on the direction of gate voltage sweep. On right the PCBM doped at the 9-1 ratio with S-Radel shows effectively no conductivity over the gate voltages swept. The 4-1 ratio sweep shows significant currents at negative gate voltages implying a shift from n-type conductivity to p-type conductivity. From "PCBM - Ion Transport - Charge Carrier Density"

The device consisting only of neat PCBM is observed to have a low off current, characteristics of an n-type semiconductor, and good on/off current ratio of roughly  $10^5$ . Several of those behaviors are found to reverse on the inclusion of acid. All tested devices of PCBM with a 9-1 PCBM-acid ratio show effectively no conduction in the transistor architecture. A device made with a 4-1 PCBM-acid ratio shows p-type behavior, as seen by the current engaged by a negative gate voltage in Figure 7-2. Several devices show wide (>80 V) hysteresis and on-off ratio roughly consistent with neat PCBM despite the majority charge carrier apparently changing from electrons to holes. This behavior was not anticipated and underscores the need for a better understanding of the exact behavior of the dopant.

In P3HT, the acid doping mechanism appears to be the withdrawal of electron density from the conjugated rings. If acid has a similar function with PCBM, it appears that low concentrations reduce the population of conducting electrons enough to strongly inhibit current flow. Higher concentrations of dopant are then enough to deplete the majority charge carrier and invert device behavior. It is surprising that the doped device would appear to approach a current density near that of the undoped material. The similar current densities for undoped and highly doped devices imply that charge carrier mobility and concentration are not the limiting factors for device performance, and that the PCBM is barely modified by the inclusion of the acid. However, the reversed hysteresis and switch from n-type to p-type behavior assert that there is a strong interaction between the PCBM and acid. These contradictory assertions combined with the lack of any modification of off-current leave the acid's interaction with PCBM unknown. With significant amounts of PCBM unavoidably trapped at the ITO-PEDOT:PSS interface as the heterojunction is deposited, the interaction between sulfonic acid and PCBM is remains an unknown factor which complicates analysis of solar devices.<sup>1</sup>

The main data detailing the effectiveness of various dopants is a systematic study varying the ring-acid ratio for each dopant. This test was performed because it can quantify the performance of each dopant in a way that spectroscopic methods were unable to. Each dopant is included in P3HT at a 400-1, 100-1, and 25-1 ratio of thiophene rings to sulfonic acid. These ratios appear to cover the useful range of dopant included in bulk P3HT, at concentrations low enough to be barely detectable in I-V measurements to concentrations high enough to approach but not reach significant ion motion in the transistor device. Small molecule acid is compared against different functionalities of S-Radel to test the effect of polymer laden with a range of acid from significantly less than one acid per Radel repeat unit to much higher functionalities. The various acid carriers tested, their IEC, and their functionality are shown in Table 6-1.

From the spectroscopic data, it was expected that an S-Radel sample with less than one acid per monomer unit would be a worse dopant than a small molecule at the same ring-acid ratio. The polymer with low functionality should have lower performance due to having much more inert polymer backboneper acid group. While the polymeric dopant cannot have an IEC approaching that of the small molecule, at higher functionalities it is expected to become more effective than the small molecule by avoiding the small molecule's phase separation and also guaranteeing acids nearby each other demonstrated by the following example. If small molecule acids are assumed to be evenly dispersed at the 100-1 ratio, using a density for P3HT of 1.1 g mol<sup>-1</sup> the average acid-acid distance can be approximated by calculating the volume of 100 P3HT monomers. The approximate radius of a 100 monomer P3HT sphere with is 1.8 nm implying the average acid-acid distance is 3.6 nm. This distance is much larger than the acid-acid distance of S-Radel IEC 2.2, approximated as 1.5 nm via 15 C-C bond lengths separating acids. While these values are estimates and do not take molecular twisting or packing into account, they imply that for the same number of acids the S-Radel forces acids to be in closer proximity than the small molecule can. Assuming that there is no phase separation, a ring-acid ratio of 6.6-1 is required to force the small molecules as close together as the S-Radel IEC 2.2 at a 100-1 ratio. The following study tests these hypotheses and sheds light on the interaction between acid and thiophene which was difficult to characterize with only spectroscopy.

### 7.2 Doping according to concentration and functionality

The comprehensive spectroscopic data in Chapter 6 shows differences between the dopants used. As already discussed, the p-TSA modifies the hysteresis of the P3HT at a ring-acid ratio of 100-1. In addition, the 100-1 ring-acid ratio also allows a higher on current for the device than neat P3HT which is likely due to a combination of trap filling and the generation of more free carriers. The situation changes at lower ring-acid ratios. Samples doped at a 400-1 ratio show an on-current only slightly higher than neat P3HT. The 400-1 data also shows a hysteresis feature in only the reverse sweeps. This hysteresis shows the device turning off in the same manner as other devices tested while showing a significant current even after the apparent threshold voltage is passed. This extended hysteresis is attributed to the slow release of charges which are strongly trapped by the small molecule dopants in the channel. Interestingly, this behavior is also seen for the 100-1 doping data in the sloped off current for the reverse sweep. When a higher doping ratio is measured, however, none of these behaviors are observed due to the effectively linear I-V sweeps which imply purely resistive behavior. The high doping ratio also shows a lower maximum current than the 100-1 samples while still being higher than neat P3HT which is credited to phase separation of the dopant sufficient to block P3HT's conductive channels. The small molecule dopant displays significant modification of the off-current and doping of P3HT while also showing strong charge trapping.



Figure 7-3. Current-Voltage sweeps of neat P3HT and P3HT doped with p-TSA. The channel length and width were 320  $\mu$ m and 220  $\mu$ m with a source-drain voltage of -100 V. On left, forward and reverse sweeps of neat P3HT sweeps are compared against P3HT doped at a 100-1 ring-acid ratio with p-TSA. On right, forward and reverse sweeps of P3HT doped with p-TSA are compared at doping ratios of 400-1 and 25-1.



Figure 7-4. Current-Voltage sweeps of neat P3HT and P3HT doped with S-Radel IEC 2.2. The channel length and width were 320  $\mu$ m and 220  $\mu$ m with a source-drain voltage of -100 V. On left, forward and reverse sweeps of neat P3HT sweeps are compared against P3HT doped at a 100-1 ring-acid ratio with S-Radel. On right, forward and reverse sweeps of P3HT doped with S-Radel are compared at doping ratios of 400-1 and 25-1.



Figure 7-5. Current-Voltage sweeps of neat P3HT and P3HT doped with S-Radel IEC 3.1 meq/g. The channel length and width were 320  $\mu$ m and 220  $\mu$ m with a source-drain voltage of -100 V. On left, forward and reverse sweeps of neat P3HT sweeps are compared against P3HT doped at a 100-1 ring-acid ratio with S-Radel. On right, forward and reverse sweeps of P3HT doped with S-Radel are compared at doping ratios of 400-1 and 25-1.

		Functionality	Ring-		% vol.	Estimated
		(Acids/	Acid	% wt. of	of	acid-acid
Dopant	IEC	repeat unit)	Ratio	dopant	dopant	distance
p-TSA	5.5	1.00	400-1	0.3%	0.2%	5.8
			100-1	1.0%	0.9%	3.8
			25-1	4.1%	3.7%	2.3
			10-1	10.4%	9.2%	1.7

Table 7-1. Concentration, weight, and volume ratios for dopants used.

S-Radel	2.2	1.15	400-1	0.7%	0.7%	1.4
			100-1	2.7%	2.7%	1.4
			25-1	10.9%	10.9%	1.4
			10-1	27.3%	27.3%	1.4
S-Radel	3.1	1.90	400-1	0.5%	0.5%	0.75
			100-1	1.8%	1.8%	0.75
			25-1	7.4%	7.4%	0.75
S-Radel	0.5	0.14	100-1	19.1%	19.1%	10.7

Comparison of dopants used in transistor experiments. The average acid-acid distance was estimated differently for the p-TSA and the S-Radel. For the p-TSA, the volume of monomers containing one acid was calculated using a P3HT density of 1.1 g cm<sup>-3</sup> and the acid-acid distance is estimated as the diameter of a sphere of that volume. For the S-Radel, the number of carbon-carbon bonds between acids on Radel were counted assuming a functionality of one acid per repeat unit at 1.5 nm and adjusted linearly by the functionality of the polymer tested.

The data on the behavior of sulfonic acid is shown in Figures 7-3, 7-4, and 7-5 which shows the effect of different acid functionalities of dopant. The higher the IEC of the dopant the more acid it delivers per monomer unit. A range of IECs of dopants was tested, as outlined in Table 7-1. The data for the 2.2 IEC S-Radel shows a variety of salient effects, the most significant of which is its more effective doping of P3HT per acid. Comparing the 100-1 ratio I-V sweeps for the small molecule and the 2.2 IEC polymer, the off current is observed to increase by roughly five orders of magnitude with a significant reduction of hysteresis. It is observed that the 100-1 ratio data for the 2.2 IEC polymer displays effectively linear I-V characteristics implying that it is sufficiently doped to show purely resistive behavior with very low hysteresis. Both the on- and off-currents are increased from the 100-1 ratio to the 25-1 ratio for the 2.2 IEC polymer dopant. The current increase combined with the further reduction in hysteresis for the 25-1 ratio shows that phase separation is not an issue for the 2.2 IEC polymer even at very high concentrations. In fact, lower concentrations of polymeric dopant also perform much

better than p-TSA, as the I-V sweeps for the 2.2 IEC dopant at a 400-1 ratio show orders of magnitude higher off currents and lower hysteresis than the p-TSA doped at even a 100-1 ratio. This result implies that polymeric dopants are at least roughly four times as effective dopants as small molecules at low concentrations.

The S-Radel with an IEC of 3.1 meq/g is shown in Figure 7-5. Relative to the lower IEC polymer, the 3.1 IEC displays lower off- and on-currents. Only the 100-1 dopant ratio for the 3.1 IEC shows currents near those of the 2.2 IEC polymer with an on-current at roughly 10<sup>-5</sup> A. The 400-1 ratio for the 3.1 IEC polymer shows a reduced on-current than the 2.2 IEC, as does the 25-1 ratio sample. The 3.1 IEC dopant displays a reduced hysteresis compared to the other dopants tested. These results indicate that the lowest hysteresis in doped materials occurs when acidic dopants are in close proximity. However, there is a tradeoff between acid concentration in the dopant polymer and solubility with the P3HT matrix. The higher the IEC, the more the polymer tends to phase separate from the P3HT while also doping the regions near the dopant very heavily.

When comparing the p-TSA dopant to the S-Radel it is apparent that the two display strongly different doping and charge transfer interactions. The p-TSA dopant appears to prefer to trap charges nearby even when the rest of the device has turned off while the S-Radel shows comparatively much lower hysteresis. The S-Radel appears to dope much more effectively than p-TSA while showing significantly less hysteresis in most cases. The most rational argument explaining the difference between the dopants is the average proximity between acids dispersed within the P3HT. The small molecule dopant is insoluble in P3HT at high concentrations, which means that acids will not be well dispersed within the P3HT and will instead phase separate. Unlike the small molecule, the functionality of the polymer dopant determines the minimum average distance between acids. This means that P3HT doped with S-Radel is likely to have a small average distance between dopants, which has been ascribed to the formation of conductive pathways as described in Chapter 3. S-Radel forces dopants to have a strong local concentration without significant phase separation or interruption of the P3HT matrix which accounts for its much higher performance than the small molecule.

The mobility of the charges in the system is a major concern for organic electronic devices, as discussed in Chapter 2. Typical charge mobilities for P3HT are less than 1 V cm<sup>-1</sup>, around 1\*10<sup>-1</sup> V cm<sup>-1</sup>. Doping negatively impacts the charge mobility in semiconductors according to three main causes. First, doping can disrupt the ordering of the semiconductor by interfering with crystallinity and increasing carrier-matrix scattering. Second, dopants introduce more free carriers which increases the amount of carrier-carrier scattering. A third mechanism is by the introduction of traps in the semiconductor which provide an energy barrier to efficient conduction when the energy difference between adjacent conjugated polymer lengths is significantly different. Small molecule dopants reduce the charge mobility primarily from the first and third mechanisms. The p-TSA is shown to have significantly lower off-currents than S-Radel and has been shown to significantly phase separate in P3HT. S-Radel increases scattering events via all three mechanisms because it introduces far more free carriers than p-TSA as judged by the increased off-currents. Of note is the small reduction in the mobility of P3HT doped at low ratios with p-TSA. At ratios 400-1 and 100-1 the material shows only a small reduction in mobility which is attributed to its low doping effectiveness and phase separation which keeps the material from significantly affecting the P3HT matrix. The

similar phase separation of the 3.1 IEC S-Radel at a 100-1 ratio shows a higher mobility than the 2.2 IEC material due to a reduced interference with the P3HT matrix. The differences between the two levels of IEC lead to the conclusion that mobility is affected most strongly by energy differences between neighboring regions in conjugation with each other.

In examining the charge mobilities estimated through the equation for the saturation regime for transistors, the polymeric dopants appear to affect the mobility via roughly equivalent mechanisms. Slight variations in the mobilities for the materials at various doping levels can be attributed to the IEC differences in the materials used as the low IEC materials deliver much more inert material per acid with a larger average acid-acid distance.

### 7.3 Behavior at High Concentrations

Phase separation is an important factor in considering the effect of dopants on P3HT, and experiments were performed to test the upper limit of solubility of dopants in P3HT. Phase separation reduces the interfacial area between the semiconductor and dopant preventing some dopant molecules from undergoing charge transfer. Samples with a ring-acid ratio of 10-1 were fabricated using both p-TSA and S-Radel, which are shown in Figure 7-6. These samples show initial behavior which is vastly different from samples with lower dopant density. The initial and subsequent I-V sweeps indicate significant levels of ionic conduction. Mobile ions should exhibit high initial and low subsequent conductivity as the ions collect at either the source or drain contact, which is

displayed in Figure 7-6. The I-V sweeps in the figure were collected until the behavior did not change with subsequent sweeps. The sulfonated Radel shows significantly more ionic behavior than the p-TSA, attributed to interconnected ionic domains which are not present in samples doped with small molecule.



Figure 7-6. Doping at high concentrations. On left, optical microscope image of P3HT doped at a 10-1 ratio with p-TSA after spincasting onto a transistor substrate. The scale bar denotes 320  $\mu$ m. The film cast on the substrate is not smooth which denotes phase separated p-TSA aggregates. The channel length and width for the transistors were 320  $\mu$ m and 220  $\mu$ m with a source-drain voltage of -100 V. The middle plot shows iterated I-V sweeps of P3HT transistor architecture doped with p-TSA at a 10-1 ring acid ratio. The I-V sweeps for one device are shown as the device is iterated The inset is a magnified view. On right, iterated I-V sweeps for one device are shown as the shown as the device is iterated.

Because the ionic behavior seen in the I-V is only observed at the highest doping ratios tested, it is expected that current flow due to conduction of mobile ions is negligible at the doping ratio 25-1 and below. As seen in Figure 7-6, the wide changes in the behavior of both S-Radel and p-TSA associated with ionic conduction are only evident at 10-1 rings per acid. At an acid concentration 25-1 and below the I-V sweep shows only small changes in the hysteresis and current level, Figure 7-7:



Figure 7-7. Successive iterations of I-V sweeps for P3HT transistors. The channel length and width were 320  $\mu$ m and 220  $\mu$ m with a source-drain voltage of -100 V. The arrows denote the direction of change for successive iterations where significant change occurred. On left, neat P3HT shows increasing hysteresis over successive iterations for the forward sweeps only. The middle plot shows successive iterations of P3HT doped with p-TSA. There is no significant change over iterations for both forward and reverse sweeps. On right, P3HT is doped at a 100-1 ratio by S-Radel. On successive I-V sweeps the transistor shows lower currents at high gate voltages and higher currents on the forward sweeps only.

The plots of iterated I-V sweeps for neat and doped P3HT shown in Figure 7-7 indicate how the P3HT traps interact with charge carriers on doping. There is little overall change in the I-V behavior relative to the large current swings in Figure 7-6, but the device physics are revealed by the small current shifts. In neat P3HT, hysteresis increases in the forward direction only on iterating the I-V sweep while the reverse sweep maintains constant I-V behavior over many sweeps. Sariciftci, et al. describe this behavior as the trapping of minority carriers where electrons fill traps quickly and empty slowly.<sup>2</sup> Minority carrier traps with a long lifetime can remain full over iterations, leading to a low hysteresis which increases over I-V sweeps. P3HT doped with S-Radel at a 100-1 ratio shows the off-currents for both forward and reverse curves falling with successive iterations due to the motion of positively charged ions which counteract the applied electric fields. For P3HT doped with p-TSA at a 100-1 ratio, the hysteresis is expanded as shown in Figure 7-7 but is stable over many iterations unlike the neat and S-Radel-doped P3HT. The stability is attributed to the larger average acid-acid distance in p-TSA doped

samples which inhibits ion motion and prevents the hysteresis effects observed on doping with S-Radel. P3HT doped with p-TSA is more stable to iterated I-V sweeps but exhibits an overall hysteresis larger than neat or S-Radel-doped P3HT attributed to the larger acid-acid distance which prohibits significant charge transfer and conductivity. As shown in Figure 7-3, a larger concentration of p-TSA in P3HT at a 25-1 ratio shows similar current levels to S-Radel as a dopant indicating that that the average acid-acid distance is more significant than acid concentration in determining the electronic properties of doped material. The data in this chapter indicate how contact doping may be maximized in organic electronics. The charge transfer complexes between P3HT and sulfonic acid enable the doping of P3HT while their proximity to one another governs current flow independently of an applied electric field. Thus, to maximize the doping of P3HT within a small region of space the dopants must be functionalized with acid to the highest degree possible without becoming phase separated. These dopants should be included with P3HT in solution before deposition to ensure maximum interfacial area between the two materials. This procedure is expected to ensure a macromolecular charge transfer salt which will not diffuse away from the contact and minimize the depletion region of the polymer semiconductor.

In summary, the electrical properties of P3HT shift from a semiconductor to a resistor as the dopant concentration increases. Polymeric dopants are found to be much more effective per acid group than small molecules at modifying P3HT, despite their lower IEC. Very high IEC materials are found to phase separate from the P3HT which reduce their effectiveness at modifying the off current of P3HT thin film transistors. The most effective dopant for modifying electrical contacts is found to be S-Radel at a 100-1

ring-acid ratio due to this dopant concentration showing the highest off current

modification and no obvious characteristics of ionic conductivity.

# 7.4 References

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## **Chapter 8**

## **Doping of Thiophene Derivatives**

### 8.1 Introduction

It has been demonstrated that sulfonic acid can dope P3HT. In order to prove the hypothesis that the doping mechanism is the association of an acidic proton with the lone pair of electrons in a thiophene ring, thiophene derivatives such as poly[N -9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and [1]benzothieno[3,2-b][1]-benzothiophene (BTBT) with one alkyl chain attached (C<sub>8</sub>BTBT) were combined with sulfonic acid. Their structures are shown in Figure 8-1. PCDTBT was chosen as another material used in solar devices with bulkier side groups than P3HT which provide steric hindrance to doping as well as modified backbone conjugation. C<sub>8</sub>BTBT was chosen as a small molecule semiconductor. These two materials were combined with sulfonic acid in transistors and thin films to observe their electrical and optical properties. If doped, they are expected to show higher off-currents in transistors and a spectroscopic doping peak near 970 nm in UV-Vis spectroscopy.



Figure 8-1. Structure of PCDTBT (left) and C<sub>8</sub>BTBT (right). These materials are doped with S-Radel to test their electrical and optical properties.
# 8.2 Properties of doped PCDTBT

Transistors were fabricated with PCDTBT and S-Radel IEC 2.2 to determine whether the semiconductor can be doped similarly to P3HT.<sup>1</sup> Figure 8-2 compares the doping of the two materials using methods similar to those described in Chapter 5, with PCDTBT dissolved at 10 mg mL<sup>-1</sup> like P3HT before deposition at 1000 RPM. Solutions were heated for two days at 60 °C before being spuncast onto the transistor substrate. The two semiconductors show similar responses to S-Radel, with the off-currents for both devices increasing substantially on doping. These results indicate that PCDTBT is doped by sulfonic acid in a manner similar to P3HT.



Figure 8-2. Comparison of organic field effect transistors fabricated with P3HT (a) and PCDTBT (b).<sup>1</sup> Both semiconductors are doped with varying levels of S-Radel IEC 2.2, using a source-drain voltage of -50 V and channel length and width of 20  $\mu$ m and 220  $\mu$ m respectively. The 10:*x* ratios refer to weight fraction of materials dissolved in 1 mL of a 12-3-1 volume ratio solution of chlorobenzene:chloroform:methanol. (a): The weight fraction of P3HT to S-Radel 2.2 here referred to as SPS varies over three ratios, which correspond to ring-acid ratios of (bottom-to-top) 1-0, 150-1, 75-1, and 50-1. The off current for the device increases by roughly five orders of magnitude from the least doped to the most doped sample, and transitions from transistor to resistor behavior over the same range. (b): The weight ratio of PCDTBT:SPS shown here is also varied, with the three weight ratios corresponding to monomer-acid ratios of 1-0, 100-1, and 10-1 in increasing order.<sup>1</sup>

Optical absorption measurements were also performed on doped PCDTBT films to determine whether a doping peak at roughly 970 nm was present in another thiophene derivative.<sup>1</sup> Solutions of both P3HT and PCDTBT were dissolved in a 12:3:1 ratio solvent mixture of chloroform:chlorobenzene:methanol at 1 mg mL<sup>-1</sup> each, doped at a 10-1 ring-acid (P3HT) or 10-1 monomer:acid (PCDTBT) ratio and deposited onto KBr pellets. Their UV-Vis spectra in Figure 8-3 show doping peaks around 1.2 eV, the same location seen for doping in both electrochemical and molecular doping studies and discussed in Chapter 3.<sup>2,3</sup> The PCDTBT peak is located at roughly 1.4 eV indicating a shift in doping peak relative to P3HT. From these data, it appears that PCDTBT is doped in a manner very similar to P3HT.



Figure 8-3. Comparison of UV-Vis spectra of thin films of P3HT and PCDTBT doped with S-Radel IEC 2.2 at a 10-1 ring-acid ratio. The inset is a magnification of the doping peak region around 1.2 eV. (a) P3HT doped at a 10-1 ring-acid ratio. (b) PCDTBT doped at a 10-1 monomeracid ratio. PCDTBT shows a doping peak at 1.4 eV.<sup>1</sup>

#### 8.3 Properties of doped C<sub>8</sub>BTBT

In addition to PCDTBT, C<sub>8</sub>BTBT was also doped with S-Radel to determine its

ability to be doped. Transistor devices were fabricated without the usual OTS layer.

C<sub>8</sub>BTBT was dissolved in an 80%/20% vol. mixture of chloroform/methanol along with

S-Radel 2.2 IEC and deposited onto a transistor substrate. The device data shown in Figure 8-4 indicates that  $C_8BTBT$  is doped meaningfully at the highest concentration of acid tested, a 10-1  $C_8BTBT$ -acid ratio. The data indicate that a small molecule thiophene can be doped in a manner similar to P3HT, though more acid is required to achieve meaninful modification of the off-current. The fact that more acid is required for doping is attributed to the small molecule nature of  $C_8BTBT$  which cannot extend conjugation along the polymer backbone like with P3HT.  $C_8BTBT$  appears to be doped by S-Radel in a manner analagous to P3HT and p-TSA, where the small molecule requires more acid or semiconductor in proximity to display doping behavior. This hypothesis is substantiated by the similar 10-1 ring-acid doping ratio required for p-TSA to dope P3HT and for S-Radel to dope  $C_8BTBT$ . While more experiments would need to be performed to prove this hypothesis, the doping evident in the small molecule indicates that thiopehene can be doped by sulfonic acid in many forms.



Figure 8-4. Doping of  $C_8BTBT$  by S-Radel 2.2 IEC. The small molecule was dissolved in an 80%/20% vol. mixture of chloroform/methanol along with S-Radel 2.2 IEC and deposited onto a transistor substrate without OTS treatment. The source-drain voltage was -50 V and the channel length and width were 320  $\mu$ m and 220  $\mu$ m respectively.

## 8.4 Conclusions

All forms of thiophene materials tested in this work appear to be doped by sulfonic acid. The most efficient forms of doping occur in mixtures of polymeric semiconductor with polymeric dopant. The charge transfer interaction between the two materials provides enough mobile free carriers to turn the composite material into a resistor. The charge transfer interaction can be detected most easily by the presence of a spectroscopic peak around 1.2 eV in UV-Vis spectroscopy. While the devices tested here consist of only bulk doping, they indicate that the best way to selectively modify electrical contacts is to deposit a film of polymeric semiconductor mixed with polymeric dopant. To create ohmic contacts, the polymeric dopant should be tailored to provide the

smallest average acid-acid distance possible while maintaining miscibility with the semiconductor. I find that lone pair of electrons on the sulfur atom in thiophene enables a charge transfer interaction with sulfonic acid while the acid-acid distance is the most important consideration when optimizing contact doping for organic electronics.

## 8.5 References

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#### Appendix

#### **Continuing Experiments**

To confirm the hypothesized effects of localizing S-Radel at an interface to affect contact doping of P3HT, contact-specific doping must be performed without also doping the device channel. This type of contact doping could be accomplished via advanced lithographic device fabrication but was not performed in this work. C-V or diode measurements would also enable more precise estimation of the depletion region width.

Time resolved photoemission measurements would also be useful to determine the energy states associated with doping and crystallinity. The two effects could not be resolved with the current apparatus, and this type of measurement could test the hypothesis put forward by Kim, et al. that new energy states are formed on doping.