4914 *Chem. Mater.* **2009,** *21,* 4914–4919
DOI:10.1021/cm902031n

CHEMISTRY OF
MATERIALS
Article

Defect Engineering in π-Conjugated Polymers

Ziqi Liang, Alexandre Nardes,† Dong Wang, Joseph J. Berry, and Brian A. Gregg*

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401. †Also at Department of Physics and Astronomy, University of Denver, Denver, CO 80208.

Received July 6, 2009. Revised Manuscript Received August 24, 2009

The optoelectronic properties of thin films of poly(3-hexylthiophene) (P3HT) are markedly improved by treating the polymer in solution with either electrophiles or nucleophiles. The work function is strongly decreased by treatment with lithium aluminum hydride, consistent with hydride ion addition and the observed ~400-fold decrease in *p*-type defect density. The exciton diffusion length (L_{ex}) doubled to 14 nm, while the bulk carrier mobility (μ) improved by more than an order of magnitude to 2.4×10^{-3} cm^2/(V s). The work function is increased after treatment with dimethylsulfate, which is consistent with methyl cation addition and, again, both L_{ex} and μ are increased substantially. Both treatments greatly improve the polymer's stability against photo-oxidation. We discuss these results in the framework of defect engineering in organic semiconductors, in analogy to defect engineering studies of inorganic semiconductors.

Introduction

The photoconversion of sunlight directly to electricity and/or fuels may be the *only* viable long-term strategy for a sustainable energy future.[1] Organic semiconductors (OSCs) show great promise for future photovoltaic cells, partly because of their almost-unlimited synthetic variability, their low-temperature "plastic" processing, and the possibility of producing lightweight, flexible, easily manufactured, and inexpensive solar cells.[2,3] OSCs have been slowly replacing inorganic semiconductors in applications that require some combination of low cost, large area, and flexibility—but do not require rapid switching speeds. Examples include photocopiers, laser printers, light-emitting diodes (LEDs), and more recently, white light panels for room lighting.[4] It seems likely that OSCs will eventually become competitive with the rather expensive, heavy, and (often) inflexible inorganic semiconductors that now dominate the photovoltaic business.

Defects, especially charged defects, often have a controlling influence on the properties of inorganic semiconductors,[5,6] yet their influence on OSCs is just beginning to attract attention.[7−11] Defect engineering of inorganic semiconductors is a major field of research,[6,12] yet it remains practically unknown in OSCs.[8] The best known example of defect engineering in inorganic SCs is the addition of hydrogen to amorphous silicon, aSi. When first synthesized, aSi had such a high defect density (~10^{19} cm^{-3}) that it was useless for practical applications.[12] However, when grown in a hydrogen atmosphere, many of its dangling bonds were terminated by hydrogen, reducing the defect density by ~4 orders of magnitude and transforming it into a commercially useful material.[12]

We study the prototypical π-conjugated polymer, regioregular poly(3-hexylthiophene) (denoted hereafter as P3HT). If P3HT were truly intrinsic (defect-free), it would have a free carrier density of ~10^5 cm^{-3}.[5,7,10] Yet, P3HT and similar polymers actually have a free hole density of $p_f \approx 10^{15} - 10^{17}$ cm^{-3}.[13,14] There seems little doubt that the

---

*Author to whom correspondence should be addressed. E-mail: brian.gregg@nrel.gov.

(1) (a) Lewis, N. S., Crabtree, G., Eds. *BES Workshop on Solar Energy Utilization*, 2005. (b) Hemminger, J., Ed. Report from the BES Advisory Committee, **2007**.

(2) (a) Gregg, B. A. *J. Phys. Chem. B* **2003**, *107*, 4688–4698. (b) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338. (c) McGehee, M. D. *MRS Bull.* **2009**, *34*, 95–100. (d) MRS Bull. **2005**, *30*, 1 (Organic-Based Photovoltaics Issue). (e) Peumans, P.; Yakimov, A.; Forrest, S. R. *J. Appl. Phys.* **2003**, *93*, 3693–3723. (f) Placencia, D.; Wang, W.; Shallcross, R. C.; Nebesny, K. W.; Brumbach, M.; Armstrong, N. R. *Adv. Funct. Mater.* **2009**, *19*, 1–9. (g) *Organic Photovoltaics: Mechanisms, Materials, and Devices*; Sun, S.-S., Sariciftci, N. S., Eds.; Taylor and Francis: Boca Raton, FL, 2005.

(3) Blom, P. W. M.; Mihailetchi, V. D.; Koster, L. J. A.; Markov, D. E. *Adv. Mater.* **2007**, *19*, 1551–1566.

(4) (a) Jenekhe, S. E. *Chem. Mater.* **2004**, 16. (b) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449–486 (Special Issue on Organic Electronics).

(5) Smith, R. A. *Semiconductors*; Cambridge University Press: Cambridge, U.K., 1978.

(6) Landsberg, P. T. *Recombination in Semiconductors*; Cambridge University Press: Cambridge, U.K., 1991.

(7) Gregg, B. A. *J. Phys. Chem. C* **2009**, *113*, 5899–5901.

(8) Wang, D.; Reese, M. O.; Kopidakis, N.; Gregg, B. A. *Chem. Mater.* **2008**, *20*, 6307–6309.

(9) Liu, A.; Zhao, S.; Rim, S.-B.; Wu, J.; Könemann, M.; Erk, P.; Peumans, P. *Adv. Mater.* **2008**, *20*, 1065–1070.

(10) Gregg, B. A. *Soft Matter* **2009**, *5*, 2985–2989.

(11) Arkhipov, V. I.; Heremans, P.; Emilianova, E. V.; Bässler, H. *Phys. Rev. B* **2005**, *71*, 045214.

(12) Street, R. A. *Hydrogenated Amorphous Silicon*; Cambridge University Press: Cambridge, U.K., 1991.

(13) (a) Jain, S. C.; Geens, W.; Mehra, A.; Kumar, V.; Aernouts, T.; Poortmans, J.; Mertens, R.; Willander, M. *J. Appl. Phys.* **2001**, *89*, 3804–3810. (b) Jarrett, C. P.; Friend, R. H.; Brown, A. R.; de Leeuw, D. M. *J. Appl. Phys.* **1995**, *77*, 6289–6294. (c) Dicker, G.; de Haas, M. P.; Warman, J. M.; de Leeuw, D. M.; Siebbeles, L. D. A. *J. Phys. Chem. B* **2004**, *108*, 17818–17824.

(14) Mozer, A. J.; Sariciftci, N. S.; Pivrikas, A.; Österbacka, R.; Juska, G.; Brassat, L.; Bässler, H. *Phys. Rev. B* **2005**, *71*, 035214.

Published on Web 09/11/2009

© 2009 American Chemical Society

conductivity of P3HT is a function of the *p*-type defect density (P_{def}), rather than an intrinsic property of the semiconductor. Other semiconductor properties such as charge carrier mobilties and exciton diffusion lengths are also expected to be strongly influenced by P_{def}.[7,8] Not all chemical imperfections lead to electroactive defects; some produce electrically invisible states at, or outside, the band edges. However, it is the midgap states—those sites that are either easier to oxidize or easier to reduce than the great majority of sites—that may dominate the semiconductor properties by introducing charges where otherwise few would exist. The chemical nature of these defects is still unknown; however, since they have energy levels in the bandgap, we hypothesize that they should be more chemically reactive than nondefect sites. In support of this hypothesis, we observe that reacting the polymer with lithium aluminum hydride (LAH) or dimethyl sulfate (Me_2SO_4) causes substantial improvements in chemical stability and electrical properties. The total charged defect density decreases for both reactions. Although the exact mechanism responsible for these changes is not yet known, they are consistent with hydride addition in the one case and methyl cation addition in the other. These reactions, and others like them, provide a method to target specific changes in the optoelectronic properties of π-conjugated polymers.

Experimental Section

Materials. P3HT was obtained from Rieke Metals (Lot No. 4002-EE, 90%−93% regioregularity). All chemical reactions and film preparation with P3HT were conducted under a N_2 atmosphere, and the polymer was protected from light as much as possible. Polymer recovery yields were 90% or more.

Reactions. *P3HT_Me_2SO_4.* Four hundred seventy milligrams (470 mg) of P3HT were added to 100 mL of degassed chlorobenzene and stirred for 2 h. One milliliter (1 mL) of dimethylsulfate (Me_2SO_4, Aldrich) was added, and the solution was stirred at room temperature for 18 h. [*NOTE: Me_2SO_4 is a highly toxic reagent!*] Then, 1 mL of triethylamine was added and stirred for 30 min before pouring slowly into 400 mL of stirred methanol. After stirring for 3 h, the precipitated polymer was filtered, washed with copious amounts of methanol, and dried in a vacuum desiccator.

P3HT_LAH. Six hundred four milligrams (604 mg) of P3HT were added to 100 mL of distilled tetrahydrofuran (THF) and stirred for 2 h. Ten milliliters (10 mL) of 1 M LAH in THF was added and allowed to react for 18 h at room temperature. Five milliliters (5 mL) of acetic acid were slowly added, followed by 100 mL of methanol. After filtration and washing with methanol, the precipitate was dispersed in 100 mL of methanol, 15 mL of acetic acid, and 3 mL of concentrated HCl and stirred for 3 h to extract any remaining aluminum salts. The polymer was then filtered, washed with methanol, and dried in a vacuum desiccator.

Devices. Indium tin oxide (ITO) substrates (12 Ω/□, Colorado Concept Coatings) were cleaned sequentially in an ultrasonic solvent bath of acetone, detergent, deionized water, and isopropyl alcohol. After drying, the substrates were cleaned in an oxygen plasma (Technics 500-II Plasma System). A PEDOT-PSS (Baytron P VP AI 4083) layer of ~30 nm was spin-coated onto the ITO at 4000 rpm for 30 s and then baked on a hot plate at 120 °C for 1 h. Polymers (~10 mg/mL) were dissolved in anhydrous chlorobenzene with warming and stirred overnight. Thin films were prepared by spin-coating on a KW-4A spin-coater (Chemat Technology) on ITO glass slides, platinum interdigitated electrodes (IDEs, AbTech Scientific), or highly oriented pyrolytic graphite (HOPG, SPI Supplies) for L_{ex} measurements. Thick films for mobility measurements were prepared by solution casting onto PEDOT/PSS-coated ITO glass slides and left to slowly evaporate overnight. All P3HT films were annealed at 140 °C for 20 min before characterization. For mobility measurements, Ca (20 nm) and Al (100−200 nm) layers were sequentially deposited by thermal evaporation through a shadow mask in a glovebox-integrated deposition chamber (Angstrom Engineering) with a base pressure of 2×10^{-8} Torr at rates of 0.2 and 2 Å/s, respectively.

Measurements. Exciton diffusion lengths (L_{ex}) were measured as described previously.[8] Work functions were measured relative to a stainless steel standard by the Kelvin probe method with a Monroe Electronics Isoprobe (Model 244). Conductivity was measured on platinum IDEs with an electrode spacing of 10 μm with a Keithley Model 236 source measure unit between −1 V and +1 V. Activation energies were measured in a Janis Research VPF-475 cryostat coupled with a temperature controller (Lakeshore Model 330). Hole mobilities were measured by CELIV at room temperature under N_2. A linearly increasing voltage pulse in reverse bias was applied with a function generator (Agilent 33220A). Current transients were monitored through a 50 Ω load on a Tektronix oscilloscope (DPO 7254, 2.5 GHz). Resistance-capacitance (RC) constants were observed to be at least a factor of 1000 smaller than the time scales of interest.

Results and Discussion

Treatments. Analogous to the case of aSi, the defect sites in P3HT may be more reactive than unperturbed sites and, therefore, might be amenable to chemical modification. However, also, in analogy to defect engineering in inorganic semiconductors, it may be difficult to prove the chemical identity and influence of a defect in a solid film that is present only at very low concentrations. The chemical identity of many defects in inorganic semiconductors is still not known; they are characterized only by their density, energy level, and charge states.[5,6,12] The understanding of defects in organic semiconductors is at a much more primitive stage. Here, we propose a probable reaction mechanism for our treatments that is based on the well-known reactivity of the reagents and is consistent with our results. Apparently less than one thiopene unit in 10^4 reacts, as estimated from the change in carrier density; thus, the product, chemically, is almost identical to the starting material. Accurate chemical analyses of such tiny changes are difficult in polymers. Therefore, in this paper, we focus on the large changes in optoelectronic properties of the films caused by the treatments and propose a reasonable, but unproven, chemical mechanism that explains them. The observed optoelectronic changes are entirely consistent with hydride ion addition in the one case, and methyl cation addition in the other.

Electrophiles such as dimethylsulfate (Me_2SO_4) and nucleophiles such as lithium aluminum hydride (LAH) are not reactive enough to modify unperturbed P3HT.

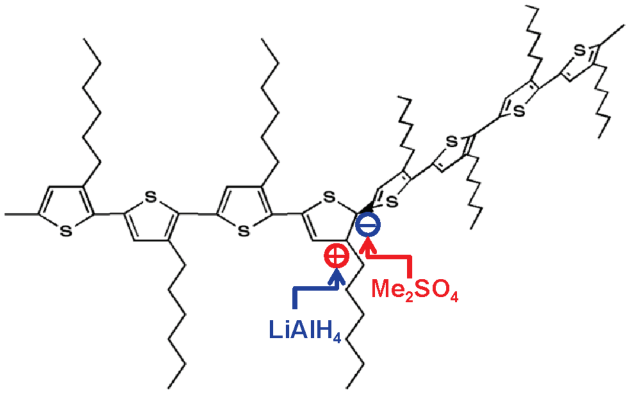

Figure 1. Schematic showing possible charged defects in P3HT and their reaction with Me_2SO_4 or LAH. The addition of a methyl cation or a hydride anion, respectively, converts a strained, charged sp^2 carbon into a neutral sp^3 carbon.

However, they may react at defect sites where sp^2-hybridized carbons, for example, are distorted from their equilibrium positions and thereby destabilized. The polymers were stirred at room temperature in solutions with Me_2SO_4 or LAH, then worked up, purified, and dried (see the Experimental Section). We have reported preliminary results of treating P3HT with Me_2SO_4 directly in the spin-coating solution.[8] We refer to the treated polymers as P3HT_Me_2SO_4 and P3HT_LAH, respectively. Figure 1 shows a schematic of the charged defects in P3HT and the expected points of attack by a methyl cation and a hydride anion. These chemical addition reactions would convert strained, electroactive sp^2-hybridized carbons into electro-inactive sp^3 carbons. When adjacent anionic and cationic sites are removed, which may occur during workup of the initial reaction, the effect is to reduce a (strained) double bond to a single bond and eliminate two charges.

Although we wish to treat the defects in solid films, we use solution-phase reactions because it is not possible to uniformly treat a film with reagents such as LAH and Me_2SO_4. Because polymers in solution must also have morphological defects that are caused by thermal fluctuations, we reasoned that these defects (although transitory) may be similar to morphological defects in the solid and thus reactive toward electrophilic and nucleophilic reagents. We also performed some reactions on thin solid films and confirmed that the results are qualitatively identical to those reactions performed on polymers dissolved in solution. Treatments with sodium borohydride, sodium methoxide, and LAH gave similar results; thus, we report results obtained with LAH. Results with methyl iodide and Me_2SO_4 were also comparable; thus, we describe the latter. Finally, preliminary experiments with poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene), MDMO-PPV, gave results similar to those with P3HT, although we describe only the more complete data set with P3HT. The variety of reagents and polymers studied preliminarily shows that our results are more general than just the solution-phase treatments of P3HT with LAH and Me_2SO_4 described here.

Optical Spectra. The absorption spectra of polymer solutions and thin films were unchanged by either treatment. Photoluminescence (PL) spectra of films were also unchanged. These results are consistent with the very low extent of the chemical reactions. Nevertheless, the PL intensity of films increased ~2-fold after LAH treatment and ~3-fold after Me_2SO_4 treatment.

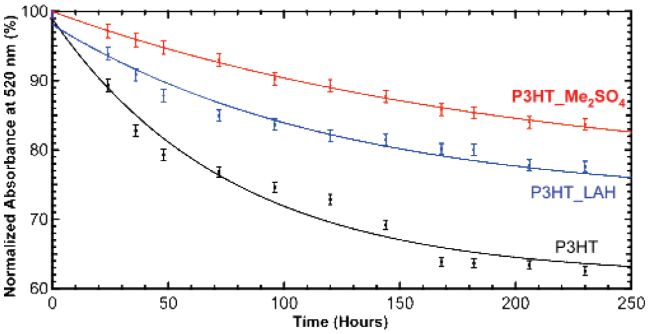

Figure 2. Photobleaching studies of P3HT after chemical treatments indicate improved stability toward photo-oxidization in the following order: P3HT_Me_2SO_4 > P3HT_LAH > P3HT.

Photostability. The photostability of conjugated polymers in air is crucial for long-term applications. The photochemical stability was assessed by the bleaching rate of P3HT films, measured at their absorption maximum, under white light illumination of ~8 mW/cm^2 by a tungsten bulb in air at room temperature. Figure 2 shows that the photostability of P3HT is notably improved by either treatment. P3HT treated with Me_2SO_4 shows the greatest stability to photo-oxidation, decreasing by only ~16% after 230 h of illumination, compared to a 37% loss in untreated P3HT. These data suggest that defects may be a major source of photochemical instability in P3HT.

Work Functions. The work functions (ϕ) of the polymers were measured by the noncontact Kelvin probe method.[15] These values may differ somewhat from those obtained using ultraviolet photoelectron spectroscopy (UPS), because the former yields a value averaged over a substantial area, whereas the latter is a localized measurement. Furthermore, the Kelvin probe technique was employed under a nitrogen atmosphere in a glovebox, rather than under ultrahigh vacuum. The Fermi levels are referenced to that of a stainless steel sample determined by UPS to be located at ϕ = 4.31 eV. Plasma-cleaned ITO was measured at ϕ = 4.7 eV, which is consistent with the literature. The Fermi levels of the P3HT films are shown in Figure 3, compared to its HOMO and LUMO levels, as reported by Chua et al.[16] The work function of pristine P3HT lies ~0.6 eV above its valence band edge, which is consistent with moderately strong *p*-type doping in its native state. Treatment with Me_2SO_4 shifts ϕ positive by 0.2 eV, which is caused by the increase in free hole concentration (see below) and probable removal of anionic sites caused by the addition of

---

(15) (a) Huang, J.; Miller, P. F.; Wilson, J. S.; deMello, A. J.; deMello, J. C.; Bradley, D. D. C. *Adv. Funct. Mater.* **2005**, *15*, 290–296. (b) Johnson, K. B.; Hansen, W. N. *Rev. Sci. Instrum.* **1995**, *66*, 2967–2976.

(16) Chua, L.-L.; Zaumseil, J.; Chang, J. F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194–199.

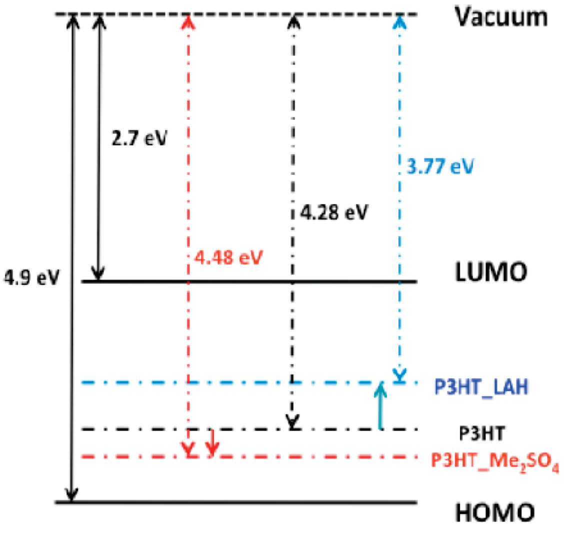

Figure 3. Work functions (Fermi levels are indicated by the dot-dashed lines) measured via Kelvin probe for pristine P3HT and the two treated films, referenced to the HOMO, LUMO, and vacuum levels.

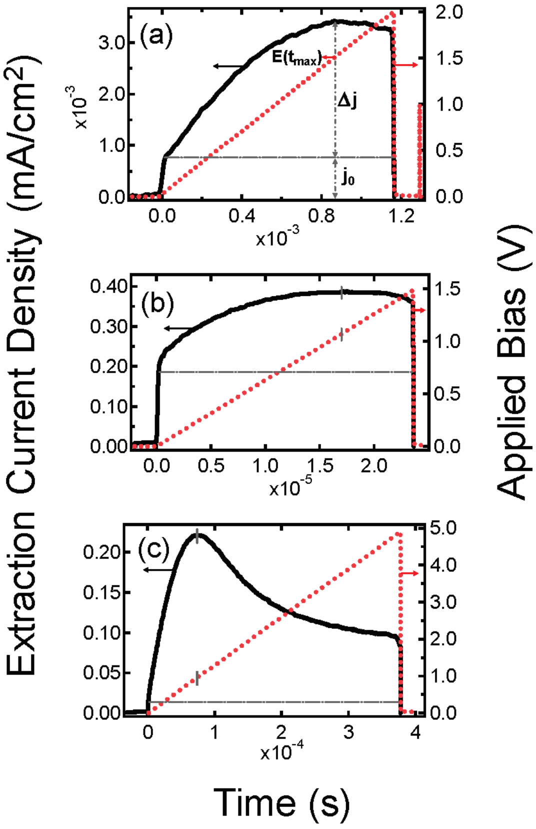

Figure 4. CELIV curves of (a) P3HT (d = 7.4 μm, A = 1.7 kV/s, and $E(t_{max})$ = 2 kV/cm); (b) P3HT_Me$_2$SO$_4$ (d = 1.1 μm, A = 63 kV/s, and $E(t_{max})$ = 10 kV/cm), and (c) P3HT_LAH (d = 4.8 μm, A = 13 kV/s, and $E(t_{max})$ = 2.05 kV/cm).

methyl cations. In P3HT_LAH, ϕ is shifted negative by 0.5 eV, as expected qualitatively from the decrease in hole density (see below) and the probable elimination of cationic sites by hydride ion addition.

Hole Mobilities. The hole mobilities of the polymers are obtained via charge extraction by linearly increasing voltage (CELIV) measurements[14,17] on relatively thick films (1−7 μm). In this technique, a pulse of linearly increasing voltage is applied to the sample in the dark with one blocking contact. The majority carrier (hole) mobility is extracted from the time required for the transient current signal to reach its maximum value at t_{max}, according to[14,17,18]

$$\mu = \begin{cases} \dfrac{2d^2}{3At_{max}^2\,[1+0.36(\Delta j/j_0)]} & (\text{if } \Delta j \le j_0) \\[2ex] \dfrac{2d^2}{3At_{max}^2} & (\text{if } \Delta j > j_0) \end{cases} \qquad (1)$$

where d is the device thickness, A the applied voltage ramp rate, j_0 the displacement current, and Δj the maximum drift current. The $[1 + 0.36(\Delta j/j_0)]$ term compensates for the redistribution of the electric field during charge extraction and is valid for moderately conductive samples. The mobilities obtained in the present work are similar to those obtained previously in P3HT and Me$_2$SO$_4$_P3HT by time-of-flight measurements.[8] Typical CELIV data are shown in Figure 4, and the mobility values are collected in Table 1. Maximum current transients, and thus the effective field at which the mobilities are measured, occur in the range of $F = 2 \times 10^3 - 1 \times 10^4$ V/cm. Little to no field dependence of the mobilities was observed over the range of our measurements, similar to the results of Mozer et al.[14] Pristine P3HT showed a value of $\mu_p = 1.4 \times 10^{-4}$ cm^2/(V s), which was consistent with values reported from other studies.[8,14,19] Both treatments increased the mobility: μ_p in P3HT_Me$_2$SO$_4$ was approximately twice as high as that in untreated P3HT, and in P3HT_LAH, it was 17-fold higher ($\mu_p = 2.4 \times 10^{-3}$ cm^2/(V s)). These results suggest, not surprisingly, that defects are deleterious to carrier transport.[7,11,20]

Free Carrier Density. The dark conductivity (σ) is given by

$$\sigma(T,F) = qp_f(T,F)\mu_p(T,F) \qquad (2)$$

where q is the electronic charge, T the temperature, and F the applied electric field. Once the mobility is known, the zero-field conductivity provides a measure of the equilibrium value of p_f. The value of p_f is expected to increase with both temperature and field.[7,21] The zero-field dark conductivity was obtained from polymer films on interdigitated electrodes (IDEs) from the slope of the current−voltage ($I-V$) curve as it passes through 0 V. The results are collected in Table 1. The conductivity of

---

(17) Juska, G.; Genevicius, K.; Arlauskas, K.; Österbacka, R.; Stubb, H. *Phys. Rev. B* **2002**, *65*, 233208.

(18) Juska, G.; Arlauskas, K.; Viliunas, M.; Genevicius, K.; Österbacka, R.; Stubb, H. *Phys. Rev. B.* **2000**, *62*, R16235. Mozer, A. J.; Dennler, G.; Sariciftci, N. S.; Westerling, M.; Pivrikas, A.; Österbacka, R.; Juska, G. *Phys. Rev. B* **2005**, *72*, R035217.

(19) Choulis, S. A.; Kim, Y.; Nelson, J.; Bradley, D. D. C.; Giles, M.; Shkunov, M.; McCulloch, I. *Appl. Phys. Lett.* **2004**, *85*, 3890–3892.

(20) Feng, X.; Marcon, V.; Pisula, W.; Hansen, M. R.; Kirkpatrick, J.; Grozema, F.; Andienko, D.; Kremer, K.; Mullen, K. *Nat. Mater.* **2009**, *8*, 421–426.

(21) (a) Chen, S.-G.; Stradins, P.; Gregg, B. A. *J. Phys. Chem. B* **2005**, *109*, 13451–13460. (b) Gregg, B. A. *J. Phys. Chem. B* **2004**, *108*, 17285–17289.

Table 1. Dark Conductivity (σ), Hole Mobility (μ_p), Free Hole Density (p_f), Zero-Field Activation Energy for Current (E_{aJ0}), Approximate *p*-type Defect Density (P_{def}), and Exciton Diffusion Length (L_{ex})

parameter	Value		
	P3HT	P3HT_Me$_2$SO$_4$	P3HT_LAH
dark conductivity, σ (S/cm)	1.2×10^{-6}	6.3×10^{-6}	1.5×10^{-6}
hole mobility, μ_p (cm^2/(V s))	1.4×10^{-4}	2.9×10^{-4}	2.4×10^{-3}
free hole density, p_f (cm^{-3})	5.3×10^{16}	1.4×10^{17}	3.9×10^{15}
zero-field activation energy for current, E_{aJ0} (meV)	142	52	53
approximate *p*-type defect density, P_{def} (cm^{-3})	1×10^{19}	1×10^{18}	3×10^{16}
exciton diffusion length, L_{ex} (nm)	7 ± 1	13 ± 1	14 ± 2

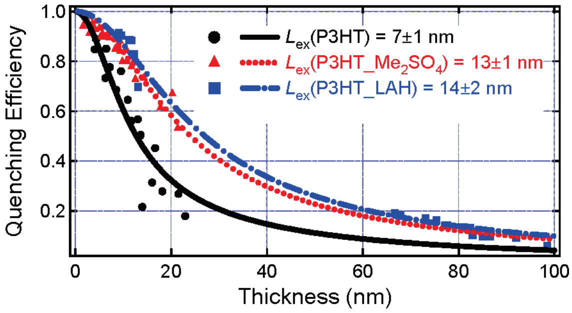

Figure 5. Fluorescence quenching data to determine L_{ex}. Data are fit to eq 4.

P3HT was $\sigma = 1.2 \times 10^{-6}$ S/cm, comparable to the values obtained from other studies.[13,14] Treatment with LAH increased σ only slightly while in P3HT_Me$_2$SO$_4$; σ is ~5-fold higher than in P3HT. The free hole density (see Table 1) calculated from these measurements and eq 2 is $p_f = 5.3 \times 10^{16}$ cm^{-3} for P3HT, similar to values obtained previously by us[8,22] and by others.[13,14] Treatment with Me$_2$SO$_4$ more than doubles p_f, while treatment with LAH decreases it by ~12-fold. This is consistent with the interpretation that the methyl cation addition eliminates bound electron (anionic) sites, whereas hydride anion addition eliminates bound hole (cationic) sites.

Defect Density. In doped OSCs at room temperature, most carriers remain electrostatically bound near a dopant (or defect) counterion.[7,8,23] Only a small, thermally activated fraction will be free to contribute to the conductivity. Identical behavior is observed in doped silicon at lower temperatures.[24] Thus, we estimate a value of the *p*-type defect density, P_{def}, via

$$p_f \approx P_{def} \exp\left(\frac{-E_{aJ0}}{kT}\right) \qquad (3)$$

where E_{aJ0} is the activation energy of the dark current near zero field. A more exact expression would replace E_{aJ0} with the activation energy for free hole production, but this value is difficult to obtain in the absence of Hall effect measurements.[24] Values of E_{aJ0} were measured over the temperature range of 120−298 K for the three polymers and collected in Table 1. E_{aJ0} decreased from 142 meV in P3HT to ~52 meV in both treated polymers. Together with the values of p_f calculated previously, this leads to $P_{def} \approx 1 \times 10^{19}$ cm^{-3} in the untreated P3HT. Treatment with LAH decreases P_{def} by ~400 fold (Table 1), which is consistent with the removal of cationic sites and possibly also the removal of anion/cation pairs to form a neutral single bond. Treatment with Me$_2$SO$_4$ decreases P_{def} by 1 order of magnitude. Because methyl cation addition alone probably cannot account for a decrease in P_{def}, this result may indicate that, during workup, some neighboring cationic sites are also eliminated, resulting in loss of a charge pair.

Exciton Diffusion Length. The exciton diffusion length (L_{ex}) determines the fraction of light absorbed close enough to an interface to contribute to the photocurrent. When L_{ex} is much shorter than the optical absorption length, a nanostructured geometry (bulk heterojunction) is required to usefully employ most of the incident light. Therefore, increasing L_{ex} would relax one of the most severe constraints on the use of π-conjugated polymers in OPV applications. Charges are known to quench excitons,[25] thus limiting L_{ex}. We measured the L_{ex} value in P3HT and P3HT-Me$_2$SO$_4$ previously,[8] and here measure L_{ex} in P3HT_LAH using the same method (see Figure 5). Results are collected in Table 1. Because some of the films were optically thick, we used the full form of the quenching equation[3] to fit the data in Figure 5:

$$Q = \frac{\alpha^2 L_{ex}{}^2 + \alpha L_{ex} \tanh(d/L_{ex}) \exp(-\alpha L) - \alpha^2 L_{ex}{}^2 [\cosh(d/L_{ex})]^{-1}}{(1 - \alpha^2 L_{ex}{}^2)[1 - \exp(-\alpha L_{ex})]} \qquad (4)$$

where Q is the quenching ratio, d the film thickness, and α the absorption coefficient. Treatment with Me$_2$SO$_4$ almost doubles the value of L_{ex}, from 7 nm to 13 nm, as reported previously.[8] Treatment with LAH increases the value of L_{ex} slightly more, to 14 nm. Consistent with the other measurements reported here, decreasing the defect density in P3HT also improves exciton transport.

---

(22) Gregg, B. A.; Gledhill, S. E.; Scott, B. *J. Appl. Phys.* **2006**, *99*, 116104.

(23) Gregg, B. A.; Chen, S.-G.; Cormier, R. A. *Chem. Mater.* **2004**, *16*, 4586–4599.

(24) Pearson, G. L.; Bardeen, J. *Phys. Rev.* **1949**, *75*, 865–883.

(25) (a) Ferguson, A. J.; Kopidakis, N.; Shaheen, S. E.; Rumbles, G. *J. Phys. Chem. C* **2008**, *112*, 9865–9871. (b) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, 2nd Edition; Oxford University Press: New York, 1999.

Defect Doping. Although P3HT is not purposely doped, it is, in fact, strongly doped by its defects. For chemical reasons that are not yet understood, defects in films of P3HT render it *p*-type (see Figure 3). That is, a thermally activated fraction of holes are free[7,21] while their negative countercharges are deeply trapped. The total number of holes and cations must equal the number of anions to preserve charge neutrality. Although there may also be *n*-type defects, free holes will annhilate free electrons, leaving only one dominant charge carrier. Our results suggest that these dopant-like defects have a mostly deleterious effect on the photoelectrical properties of the polymer. However, similar to the defects in aSi, they are more reactive than their neighbors and, therefore, are amenable to modification or removal via chemical reactions.

Solution Reactions for Solid Defects. Because our chemical treatments of P3HT must be done in solution, the results do not address the relative reactivity of defects in the solid state. Instead, the reactions may remove some of the transient defects that occur in solution before the films are cast. The fact that these treatments, which presumably transform sp^2 carbons to sp^3 carbons, have such a powerful and beneficial influence on the solid-state properties of the semiconductor suggests that, perhaps, π-conjugation in the polymer backbone is not always a good thing. Deformations of the planar, trigonal sp^2 backbone of the polymer can generate electronic states in the bandgap that are mostly, but not always,[10] harmful. Providing a few flexible, electro-inactive sp^3 sites that may accommodate some of the inevitable stresses of film formation without creating electronic defects may be a promising new approach to improving the electrical properties of π-conjugated polymers.

Summary and Conclusions

Simple treatments of poly(3-hexylthiophene) (P3HT) with a hydride ion donor or a methyl cation donor greatly improve the hole mobility, the exciton diffusion length, and the photostability of the polymer. Using these treatments, the free carrier density, the defect density, and the Fermi level can be adjusted over a wide range. The results are consistent with reaction of the electrophile and the nucleophile with defects in P3HT and they highlight the ability of defect engineering to tune a polymer's semiconducting properties over a wide range.

Acknowledgment. This work was funded by U.S. Department of Energy, Office of Science, Basic Energy Science, Division of Chemical Sciences, Geosciences and Biosciences (under Contract No. DE-AC36-08GO28308) to NREL. Z.L. particularly thanks Edwin Widjonarko for assistance in Kelvin probe measurement.