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Treating Poly(3-hexylthiophene) with Dimethylsulfate Improves Its Photoelectrical Properties

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Organic semiconductors, OSCs, are attracting recent interest for use in organic photovoltaic (OPV) cells and other devices.[1−3] Because they are flexible, inexpensive, synthetically adjustable, and easily processible, OSCs may ultimately displace inorganic semiconductors in electrically simple, large-area applications such as converting sunlight into electricity. A similar transition has already occurred in the field of electrophotography[4] and is now occurring in some display and integrated circuit applications.[3] Nevertheless, much remains to be learned about OSCs, especially about their doping processes as well as the nature and influence of their defects. Here we introduce a type of defect engineering that beneficially modifies defects in regioregular poly(3-hexylthiophene), P3HT.

There is a surprisingly high defect concentration in thin films of most OSCs which produces a much greater number of free charge carriers than would be present in an intrinsic material. The intrinsic charge density expected in a semiconductor of 2 eV bandgap is $\sim 10^4$ cm^{-3}. However, the measured free hole density in P3HT and similar polymers is $p_f \approx 10^{15}-10^{17}$ cm^{-3}, with the lower range approachable only in extensively purified material.[5] Similar to the hydrogenation of amorphous silicon to passivate its dangling bonds, we reason that some of these defect states in π-conjugated polymers might be modified or eliminated via chemical addition reactions. We report here preliminary results of this study involving the treatment of P3HT, one of the best studied π-conjugated polymers, with the powerful methyl cation donor dimethylsulfate, Me_2SO_4. Solutions of P3HT (Riecke Metals) in chlorobenzene were reacted with Me_2SO_4 for 1 h at room temperature before films were prepared from this solution via spin-coating or drop casting. The unreacted Me_2SO_4 was allowed to evaporate. Films were then annealed at 120 °C for 30 min in a glovebox and kept in vacuum for at least 90 min before characterizing. Although the exact mechanism of the chemical reaction has not yet been determined, we show that this treatment increases the chemical stability of the polymer toward photo-oxidation and increases the hole mobility and exciton diffusion length. Further experimental details are provided in the Supporting Information.

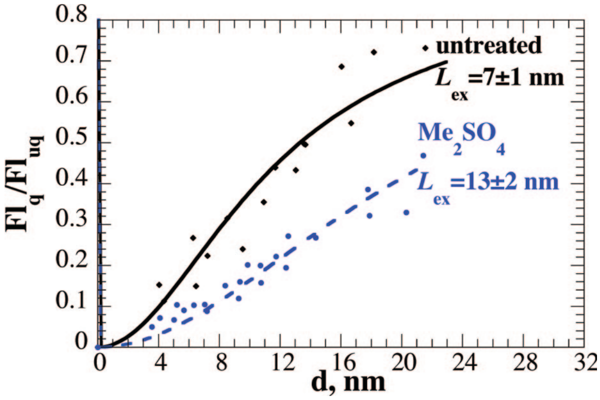

Figure 1. Quenched divided by unquenched fluorescence intensity versus thickness in untreated and treated P3HT films. The solid lines are fits to eq 1.

Optical absorption spectra of P3HT solutions and thin films showed no change upon treatment with Me_2SO_4. Furthermore, XRD spectra of the films showed clearly the (100), (200), and (300) peaks[6] and were unchanged by treatment. This indicates that the treatment caused no gross changes in film structure or morphology while substantial changes in photoelectrical properties are observed.

The exciton diffusion length, L_{ex}, determines the distance over which light can be successfully harvested in the film. Fluorescence quenching experiments to determine L_{ex} employed a two-part substrate made of a glass slide with a piece of highly oriented pyrolytic graphite on one-half as the quencher. By measuring the fluorescence intensity ratio of quenched (Fl_q) to unquenched (Fl_{uq}) parts on the same film, variations in lamp intensity, substrate orientation, and other experimental artifacts are minimized. Data from a large number of films of various thicknesses are shown in Figure 1 and are fit to an approximate model of exciton dissociation at a kinetically fast interface in optically thin films, eq 1,[7]

$$Fl_q/Fl_{uq} = 1 - (L_{ex}/d)\tanh(d/L_{ex}) \qquad (1)$$

where d is the film thickness. Remarkably, treatment with Me_2SO_4 almost doubled L_{ex}, increasing it from 7 to 13 nm, possibly by removing some of the charged defects that

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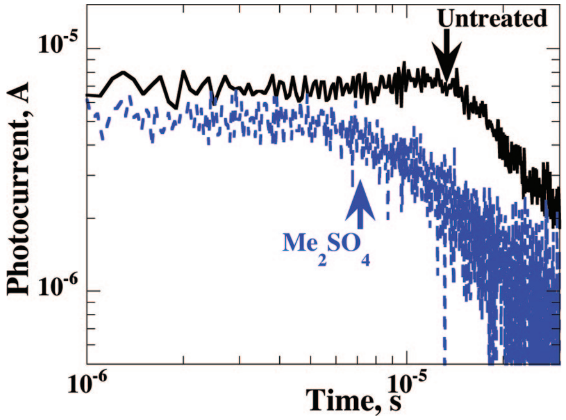

Figure 2. Time-of-flight transients for an untreated and Me_2SO_4 treated samples. Curves are offset for clarity. The arrows indicate the hole transit times.

quench excitons. We are not aware of such a substantial improvement in L_{ex} caused by any other treatment.

Assuming that only one carrier (holes) contributes substantially, the dark conductivity is given by $\sigma = qp_f\mu_p$, where q is the electronic charge and μ_p the hole mobility. Employing interdigitated electrodes, we estimate σ from the slope of the current density versus applied field, $J-F$, curve as it passes through $F = 0$ V/cm. The electrode spacing of 10 μm ensures that bulk properties are being measured rather than interfacial effects. Me_2SO_4 treatment increased σ by a factor of 4−5 from its original value of $\sim 1 \times 10^{-6}$ S/cm.

Hole mobilities were measured by the time-of-flight (TOF) technique commonly employed in studies of P3HT and similar polymers. It has recently been suggested, however, that TOF underestimates the true mobility in samples of relatively high conductivity.[8] Thus, there is some uncertainty in the mobilities and we employ TOF primarily as a relative measure to compare treated and untreated polymer films and to compare our results to those of the literature. Typical data for 3 μm thick films are shown in Figure 2. The transit time, t_{tr}, was estimated from the change in slope of the decay on the log−log plot. The mobility was calculated from $\mu_p = d^2/t_{tr}V$, where V is the applied voltage. The hole mobility in an untreated film was 1.2×10^{-4} cm^2/(Vs), in good agreement with previous work,[9] while in a Me_2SO_4-treated film it increased to 4.2×10^{-4} cm^2/(Vs). The mobilities were weakly dependent on the applied electric field at higher fields for all samples, and the results were reproduced in several different films. The mobility and conductivity results show that the calculated free hole density, $p_f \approx 7 \times 10^{16}$ cm^{-3}, is not greatly changed by treatment with Me_2SO_4. The increase in conductivity results mainly from the increase in hole mobility.

Organic PV cells employing P3HT are generally made in the bulk heterojunction[2] configuration. In these devices a solution containing P3HT and PCBM (a soluble C_{60} derivative) is spin-coated onto a tin doped indium oxide (ITO) electrode coated with a hole conductor (Pedot-PSS). The film is then annealed to effect a nanoscale phase separation between the hole conducting P3HT and the electron conducting PCBM. An aluminum top electrode completes the device. We made such OPV cells with the Me_2SO_4-treated and the untreated P3HT in the standard configuration: ITO/Pedot-PSS/P3HT-PCBM/Al.[10] On average, there was little difference in photovoltaic effect between treated and untreated P3HT cells. This may be explained because such devices are already optimized for untreated P3HT and are not limited by either of the parameters improved by the treatment, L_{ex} and μ_p. There was, however, a dramatic improvement in the stability of devices made with the treated polymer when processed in air (Figure 3). Under these conditions, the untreated polymer cell is strongly degraded. This is significant since the stability of OPV cells is a major concern.

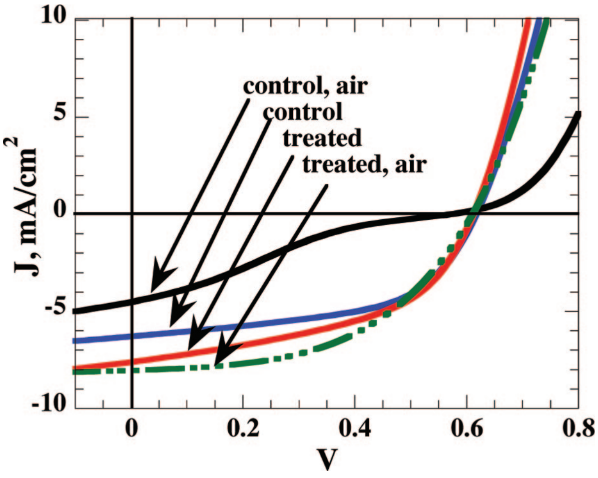

Figure 3. $J-V$ curves of four bulk heterojunction OPV cells under 1 sun illumination: two controls with untreated P3HT and two with Me_2SO_4-treated P3HT. One of each was prepared entirely in the glovebox while the other two were prepared in air.

To further investigate this effect, the bleach times of the polymer films in air under constant low intensity illumination were measured: the half-time to bleach increased from 160 h for the untreated P3HT to 250 h after Me_2SO_4 treatment.

The extent of reaction with Me_2SO_4 is unknown. However, it must be quite small since it does not alter the absorption spectra of solutions or films, and it does not affect the structure of the films as observed by XRD. When reacting P3HT with sodium methoxide (to be reported later), in which a measurable fraction of free holes is removed, apparently only one thiophene in $\sim 10^5$ reacts. Partly because of the limited extent of reaction, we cannot provide a specific reaction mechanism and, in fact, several different mechanisms may be operating simultaneously. Nevertheless, the reactivity of Me_2SO_4 is well understood:[11] it transfers a methyl cation to chemical sites having excess electron density. Pristine P3HT would have no such sites; therefore,

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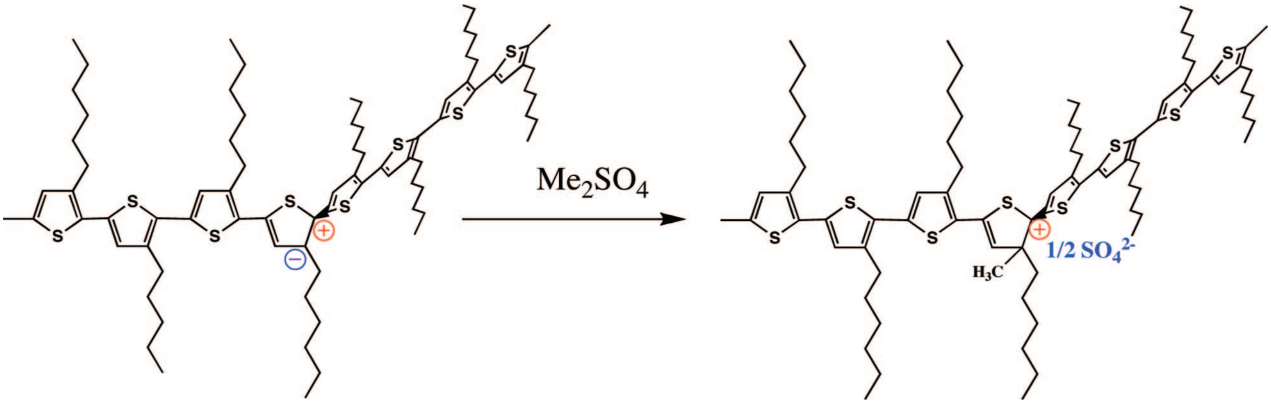

Figure 4. One possible, but speculative, mechanism for the reaction of Me_2SO_4 with defects. A charged morphological defect in P3HT before reaction (left) reacts with Me_2SO_4 via addition of a methyl cation to one of the distorted sp^2 carbons. This substitutes a bound electron on the polymer chain for an electroinactive sulfate anion adjacent to the chain.

Me_2SO_4 is expected to react only at defects which possess a partial or whole negative charge. This suggests a class of likely reactions, one example of which is shown in Figure 4. This reaction will be employed as an illustration to discuss our results.

To be defect-free, every one of the sp^2-hybridized carbons that make up the backbone of the π-conjugated polymer must be planar and trigonal. This ideal structure can occur only in a perfect single crystal and is unlikely to be realized, except in nanoscopic domains, in any real film. Deviations from the ideal sp^2 carbon bond angles and lengths perturb covalent bonds and thus generate electronic states in the bandgap, some of which will be charged. A possible example is shown in Figure 4. Other charged defects may result from chemical impurities in the polymer. Approximately equal numbers of positive and negative charges must be created, although negative charges are often more deeply trapped than positive. That fraction of charges that are not strongly bound or trapped are responsible for the measured zero field conductivity. The total charge density (both mobile and trapped) may be substantially higher than the value of p_f estimated from the conductivity and mobility measurements. Although the measured value of $p_f \approx 7 \times 10^{16}$ cm^{-3} may dominate the photoelectrical properties of the semiconductor, it still represents only a few defects per hundred thousand thiophenes, making exact chemical analysis very difficult. Similar to the experience with inorganic semiconductors, it may take years of research to prove the chemical identity of charged defects in P3HT, but their presence is obvious from their profound influence on the electrical properties.

The methyl groups of Me_2SO_4 are highly reactive because of their very weak ester bonds; thus, methyl cations are readily donated to acceptors such as the postulated anionic site shown in Figure 4. The addition of a methyl cation to the polymer backbone would eliminate an anion (bound electron) and replace it with a sulfate counterion near, but not attached to, the polymer. The electroinactive sulfate ion should have a less detrimental effect on the hole mobility and the exciton transport than would an electron on the chain. This may explain the increases in μ_p and L_{ex} upon reaction. Moreover, the bound electron sites may be especially susceptible to attack by oxygen when the polymer is exposed to light and air. Thus, elimination of some of these sites via reaction with Me_2SO_4 would stabilize the polymer against photodecomposition. Finally, by eliminating bound electrons while leaving holes, the reaction with Me_2SO_4 is equivalent to a classical p-type doping process, aside from the fact that the remaining anion (SO_4^{2-}) is somewhat mobile.

In summary, treating P3HT with dimethylsulfate increases the hole mobility, the exciton diffusion length, and the stability of the polymer against photodecomposition. This is consistent with removal of a bound electron by addition of a methyl cation to the polymer backbone leaving an unbound sulfate as the electroinactive counterion. This work illustrates the potential for defect engineering via chemical modification of π-conjugated polymers and may ultimately lead toward improved organic materials for photovoltaic and other electrical applications.

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Supporting Information Available: Two pages of experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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