Doping Polythiophene Derivatives with

Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane

by

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ABSTRACT OF THE THESIS

Doping Polythiophene Derivatives with Tridecafluoro-1,1,2,2-

Tetrahydrooctyl Trichlorosilane Vapor

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Thesis director: Eric Garfunkel

A conducting polymer system of derivatives of polythiophene has been achieved by doping with tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (TTT). After doping, conductivities of both polymers, poly(3-hexylthiophene) (P3HT) and poly[2,5-bis(3-decabutylthiophene-2-yl)thieno(2,3-*b*)thiophenes] (PBTTT), increased by over five orders of magnitude. We observed non-homogeneous swelling of the polymer film using atomic force microsopy and other microscopic methods. We also showed that under certain conditions the doping was reversible. Based on an analysis of the UV-Vis spectra and other data, it seems that the dedoping was almost complete. We demonstrated that dedoping could be efficiently facilitated by exposing the films to light. We also observed large protrusions on the surface of some samples that could be explained as a mixture of polymer and organic solvent. These surface features do not contribute to the conductivity.

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ABBREVIATIONS

CP: conjugated polymer

ITO: indium tin oxide

P3AT: Poly(3-alkylthiophene)

P3HT: Poly(3-hexylthiophene)

RR: regioregular

RRa: regiorandom

PBTTT: Poly[2,5-bis(3-alkylthiophene-2-yl)thieno(2,3-*b*)thiophenes]

PBTTT-C14: Poly[2,5-bis(3-Octabuylthiophene-2-yl)thieno(2,3-*b*)thiophenes]

Introduction

Organic Electronics, Conducting Polymers, and Doping

Conductive and semiconductive organic compounds have been studied for several decades, from the first small molecular semiconductor reported by M. Pope in 1963[1] to the first conducting polymer reported by R. McNeill in 1963[2]. Using the field effect to modulate the conduction of organic compounds has been studied for decades as well[3]. In recent years, organic electronics were studied even more intensely due to improvements in material and device fabrication and the growth of various applications. Both small molecular- and polymer- based materials have been applied to transistor and light emitting devices, and in some cases are in production.

In 1963, R. McNeill published several reports on conjugated polymers (CPs), including iodine-doped polypyrrole, with a conductivity as high as 1 $\Omega^{-1}cm^{-1}$[2]. In the next few years, breakthroughs were achieved by several groups[4], and the extension and expansion of research in conducting polymers has lasted for several decades. In 2000, due to their significant contribution to the field, H. Shirakawa, A. G. MacDiarmid, and A. J. Heeger were honored with the Nobel Prize in chemistry.

The interesting topic of charge transport in conducting polymers has been discussed since the birth of the field. Although charge transport in CPs is not yet clearly understood, it has been explained by suggesting that it is due to quasi-particle transport, including solitons, polarons, and bipolarons. In general, the pristine polymers usually display low conductivities while conductivities can be increased several orders of magnitude by doping with electron-receptor or electron-donor species known as dopants. After doping, solitons, polarons, and bipolarons will be created, and they play the main roles in charge transfer in CPs. For CPs that have

degenerate ground states (Fig. 1a) (e.g. *trans*-polyacetylene), solitons are the dominant charge transport species. On the other hand, for CPs that have non-degenerate ground states (Fig. 1b) (e.g. polythiophene), polarons and bipolarons are the dominant species for charge transfer since solitons are not stable in this situation. As a result, soliton states are created and exist as degenerate pairs in the middle of energy gap. On the other hand, the polaron and bipolaron states are split into two states between the valence and conduction bands. After these states are created, electrons can be added or extracted to generate neutral, negatively and positively charged quasi-particles.
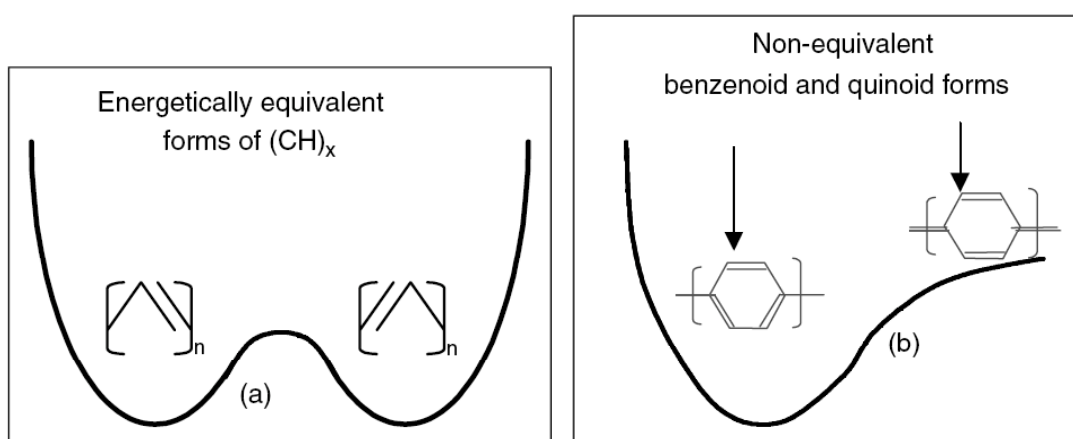
Figure 1. a) Illustration of degenerate energy states in a conducting polymer; b) non-degenerate energy states in a CP. [5]

Due to the low conductivity of pristine CPs, doping has become the primary procedure to achieve high conductivity. In general, there are four methods that can be, and have been, used to dope polymers: chemical doping, electrochemical doping, acid-base doping and photo-doping.

Chemical doping is the first method to be invented for doping highly conductive polymers. Also, since the catalyst in the last step of the polymerization is a

very electronegative molecule, without further purification, the freshly-synthesized polymer is already unintentionally doped. However, in general, the basic idea of chemical doping is to directly expose the polymer films to a dopant that would either be a liquid or a vapor. For p-doping, the dopants could be I_2, Br_2, AsF_5, $NOPF_6$, $FeCl_3$, etc. For example, I_2 is a good material for vapor phase doping (though it can also used in solution); a typical reaction might proceed as follows: polymer + I_2 $\rightarrow$ (polymer$^+$)(I_3^-). On the other hand, for n-doping, the dopant could be an alkaline metal, for example, Na^+.

Electrochemical doping has also been intensely applied to CPs. In this method, the polymer works as one of the electrodes. A typical design is shown in Fig. 2, which is convenient for electrical measuring the real time absorption change of doping.
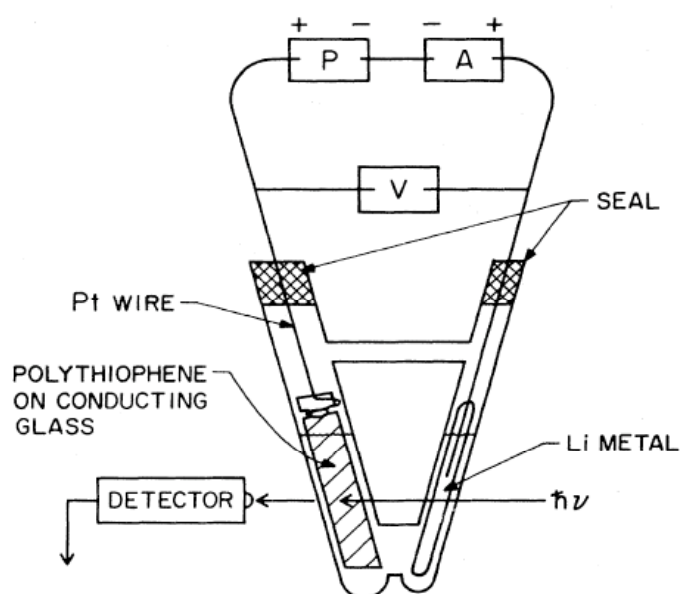

Figure 2. Design of electrochemical experiment device.[6]

In this classic design, the polymer is coated with or grown on an indium tin oxide (ITO) film on glass. By immersing the polymer in an electrolyte and applying a bias voltage, the polymer can be either oxidized or reduced. In most cases, the oxidation

and reduction processes are reversible, i.e. one may shift the doping level back and forth by applying different bias voltages.

Acid-base doping is also a reversible doping process, although it has mainly been applied to polyaniline films. This type of doping leads to a change of chemical structure. The polymer changes between an aromatic and a quinoid structure by changing the pH of the solution. The doping process is shown in Fig.3.
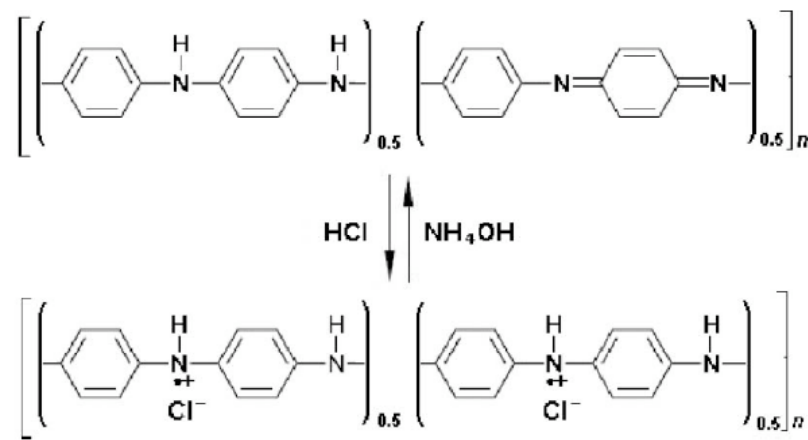

Figure 3. Acid-base dope-dedope processes in the polyaniline system.[7]

Photo-doping effects have been observed when light is exposed to polymer films. Photons excite electrons in a film creating localized electron-hole pairs; these quasi-particle states are generated in $\sim 10^{-13}$ seconds[8][9].

Among these four types of doping processes, our study focuses on chemical doping. It is not the most popular doping method since it is not as reversible as electrochemical doping is found to be. However, due to the rather straightforward experiment process and concept, chemical doping is still be used in studies of basic properties of CPs.

De-doping

Although CPs can be either p-doped or n-doped, most studies have been performed on p-doped systems (by using electronegative dopants). One reason for this preference is that there are more electronegative species in air, e.g. oxygen. P-doped films are more stable in air while the doping effect of n-type films is often quickly compensated in air. However, "de-doping" effects can also be seen by intentionally exposing a p-doped film to an "electron-donor" vapor, e.g. NH_3. In this case, the conductivity goes down due to charge compensation. However, this is not "real" de-doping since the original dopant is still inside the polymer film although the initial charged species have been over-compensated; this is different from the normal regeneration of gas chemosensors (in which the dopant itself is removed from the film). One example was demonstrated by N. Suzuki et. al. in which they treated a AsF_5-doped polyacetylene with NH_3[10]. The absorption spectra are shown in Fig.4. In these spectra, it can be seen that after exposing to NH_3, although the soliton peak intensity decreases, the original peak intensity didn't increase as expected.
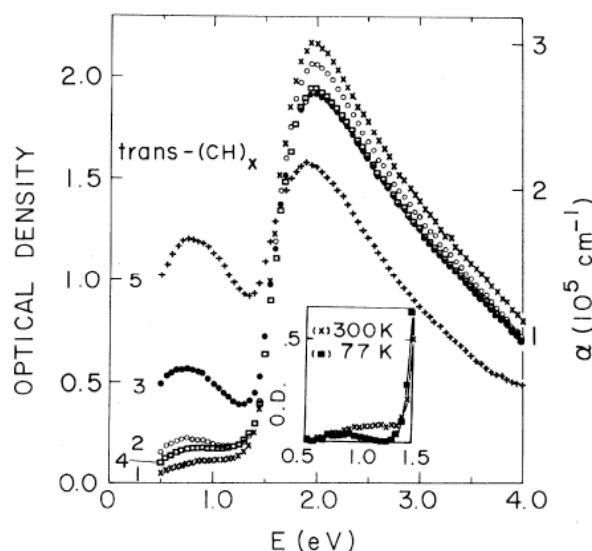

Figure 4. Absorption spectra of *trans*-polyacetylene. 1:undoped; 2:~0.01% AsF_5; 3:~0.1% AsF_5; 4:compensated with NH_3; and 5:~0.5% AsF_5. [10]

The term "de-dope" is now mostly used to refer to the process in which one "removes the unintentionally air-doped O_2 from the polymer" instead of de-doping the "real dopant." For CPs, oxygen is recognized as the most active species in air and will dope CPs very quickly, especially when concurrently illuminating the sample. It is a problem especially for CPs used as semiconducting materials in organic transistors. Because once the CPs are doped with O_2, the conductivity (or the off-current in a transistor structure) will increase, which will reduced the on/off ratio of a device because the on-current will not increase as well. Also, the active oxygen inside the film may potentially damage the film in the future, thus, dedoping of oxygen of CPs films is an important issue in organic electronics. A common way to dedope oxygen is to anneal the film in vacuum, which is also called "thermal dedoping."

As noted above, another important "dedoping" process is to remove the catalyst from the film that is present during the last step of polymerization, mostly $FeCl_3$, as it is a good dopant for p-doped conducting polymers. The common way to dedope $FeCl_3$ is using an NH_3 solution to neutralize it. However, this problem only happened on those who synthesize the polymers by themselves. For the commercially available CPs, e.g. P3HT, they usually have been properly purified and sealed in a bottle in an N_2 or Ar ambient.

Poly(3-hexylthiophene)

Since 1986, poly(3-alkylthiophene) (P3AT) has attracted much attention due to its relatively high solubility in organic solvents. Among P3AH derivatives, poly(3-hexylthiophene) (P3HT) has been the most widely-studied because of its high charge carrier mobility (>0.1 cm^2/Vs), chemical and thermal stability and is ease of fabrication. There are two isomers of P3AT: regioregular (RR) and regiorandom (RRa)

(Fig.5). The regioregularity can significantly affect the crystallinity and electrical performance.
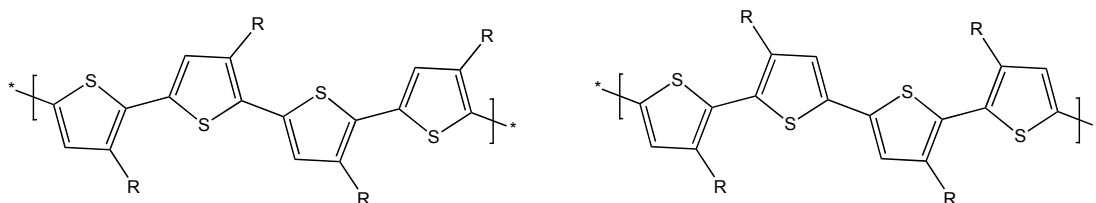

Figure 5. Structure of P3HT. Left: RR-P3HT; Right: RRa-P3HT.

Poly[2,5-bis(3-alkylthiophene-2-yl)thieno(2,3-*b*)thiophenes]

PBTTTs have attracted much attention recently and the basic structure of PBTTT is shown in Fig.6 [11]. Among this series of compounds, PBTTT-C14 is the most notable one because it holds the record of highest mobility of all semiconducting polymers (>0.6 cm^2/Vs); PBTTT-C14 is one of the conjugated polymers used in this thesis.
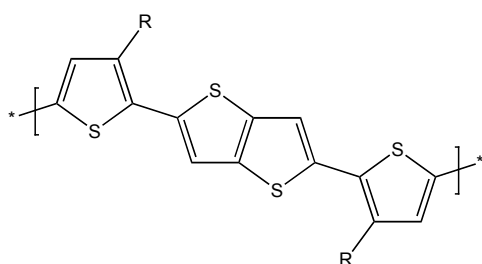

Figure 6. Structure of PBTTT. For PBTTT - C14, R=octabutyl group

Experiment Set-ups and Chemicals

In this work, the structure of our *doping chamber* is shown in Fig 7.
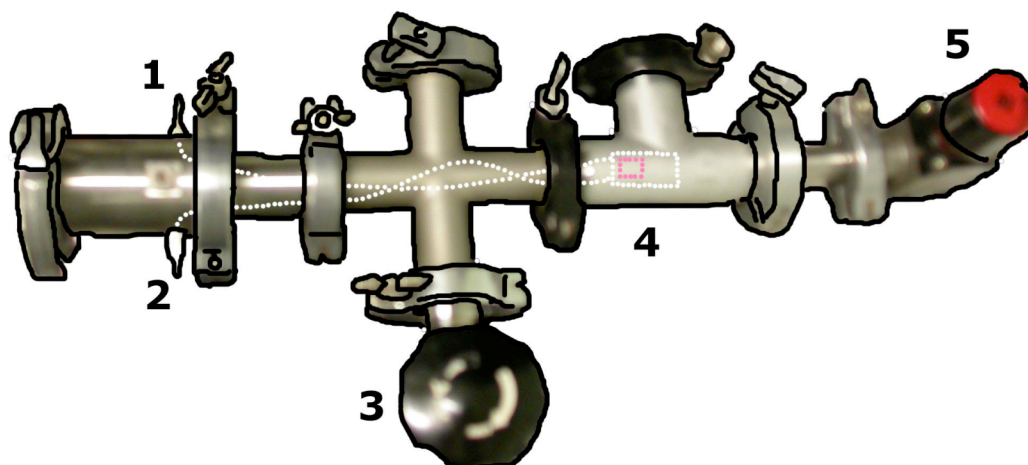

Figure 7. Structure of doping chamber. 1 & 2: junctions connected to source-meter and electrometer; 3: angle valve connected to pump; 4: sample holder inside chamber; 5: valve and dopant container. (white dots indicate the wiring and placing of sample)

Electrical measurement was done on Keithley K2400 source-meters and a K6512 electrometer.

UV-Vis spectrometer is PC2000 – ISA of Ocean Optics, Inc.

AFM is NanoR AFM of Pacific Nanotechnology.

The chemicals and substrate are:

The dopant used in this study is Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane

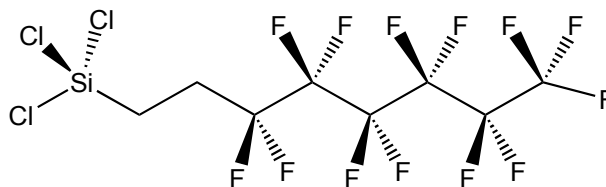(TTT) bought from Gelest, Inc. The structure is shown in Fig.8.

Figure 8. Structure of Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (TTT).

The conjugated polymers we used in this work are P3HT and PBTTT while the

structures have shown in introduction already. The P3HT we used is RR-P3HT, and it

was bought from Alfa Aesar. PBTTT-C14 was from Dr. McCulloch of Merck.

Experimental Methods and Results

In this study, studies of the doping effect have been examined for two polymers: P3HT and PBTTT-C14. For electrical measurements, the glass substrates were first cut into squares, followed by cleaning with deionized-water, acetone, and isopropanol and then blown with dry nitrogen. After cleaning, silver contacts were thermally deposited on the substrates to a thickness of ~30 nm. For samples made for purposes other than electrical measurements, the substrates were prepared in the same way but without depositing silver contacts. P3HT was spin-coated on the substrate from a cold chloroform solution (~0.1 wt%) at 2000 rpm for 40 seconds. PBTTT-C14 was spin-coated onto a substrate from a warm chlorobenzene solution (0.5 wt%) in 2000 rpm for 40 seconds. By following the conditions above, the film thickness of P3HT was found to be about 16 nm, while that of PBTTT-C14 was about 12 nm. The structure is shown in following figure (Fig.9).
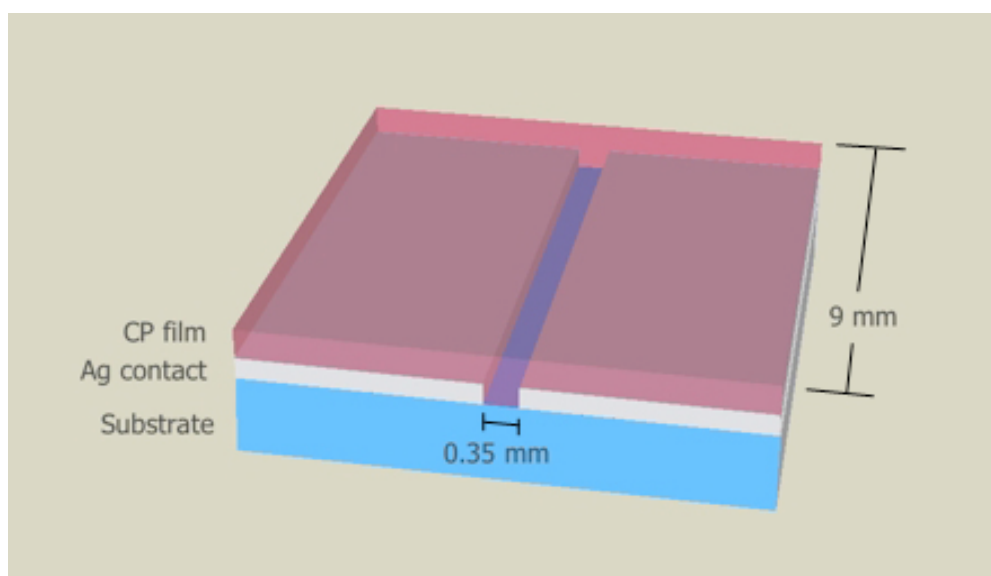

Figure 9. Structure of samples for electrical measurement.

After spin-coating, for those samples made for electrical measurements, the polymer films were partially removed such that probes could making contact to the Ag electrodes. Acetone was used for removing P3HT, and chlorobenzene was used for removing PBTTT-C14. After making contacts, the sample was put in a chamber and pumped for 30 minutes; pumping had the dual effect of decreasing the solvent content in the samples and it also created a vacuum environment for doping. One minute before the end of pumping, the valve to the TTT container was opened to fill the chamber with a TTT vapor. After this procedure, the pump was turned off with the TTT valve opened for the rest of the treatment.

For the restoring (dedoping) experiments, treated samples were put in air either in the dark or with a light placed above the sample.

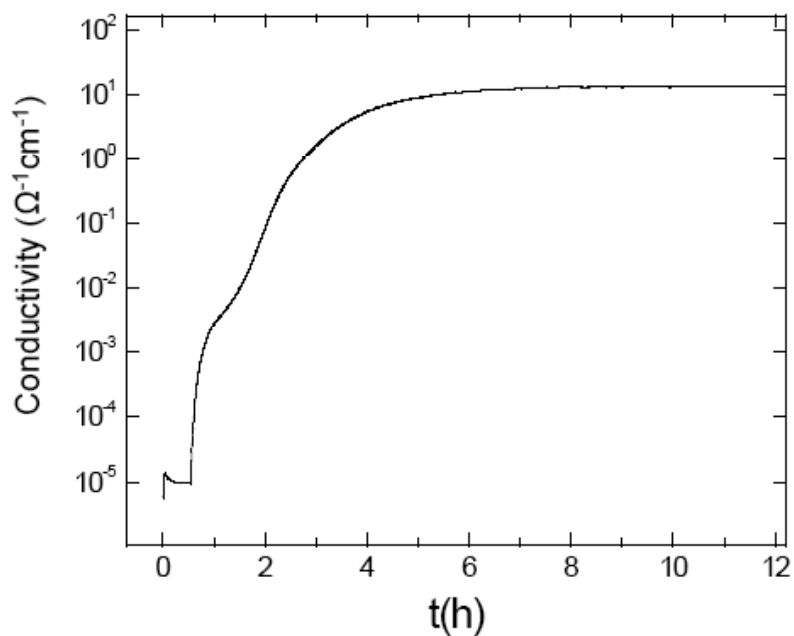The electrical data taken to monitor the process is shown in Fig 10.

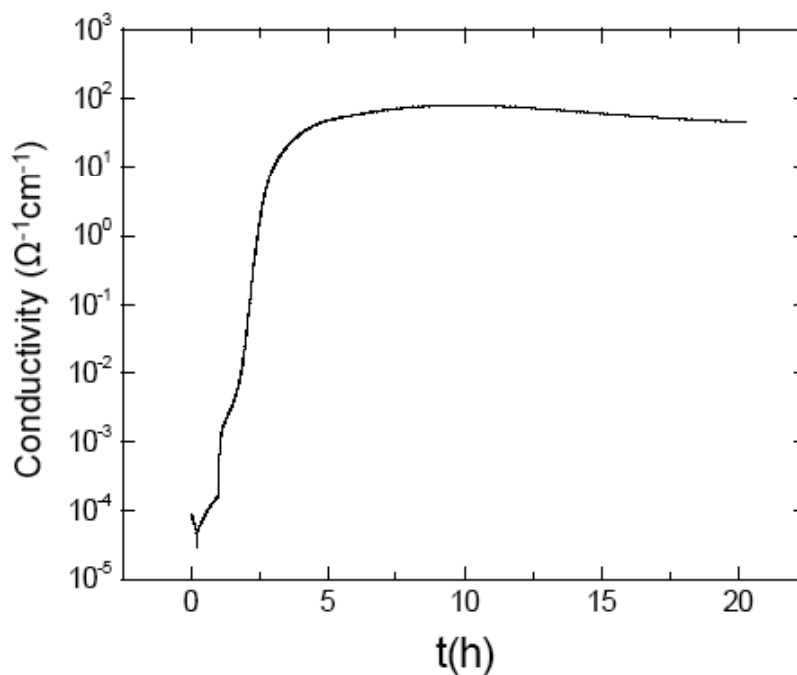**Figure 10.** Conductivity as a function of time during TTT treatment of the P3HT film.

Figure 11. Conductivity as a function of time during TTT treatment of the

PBTTT-C14 film.

AFM images were also taken before and after the doping treatment. Due to our

concern that exposing to light might result in sample changes while taking AFM

images, each AFM image was taken from a different individual sample. The AFM

images of P3HT and PBTTT-C14 are shown in Figs. 12 and 13 respectively.

Figure 12. AFM images of P3HT films. Top left: as-spun film (10x10μm) top right:

as-spun film (0.5x0.5μm); bottom left: TTT treated film (10x10μm); bottom right:

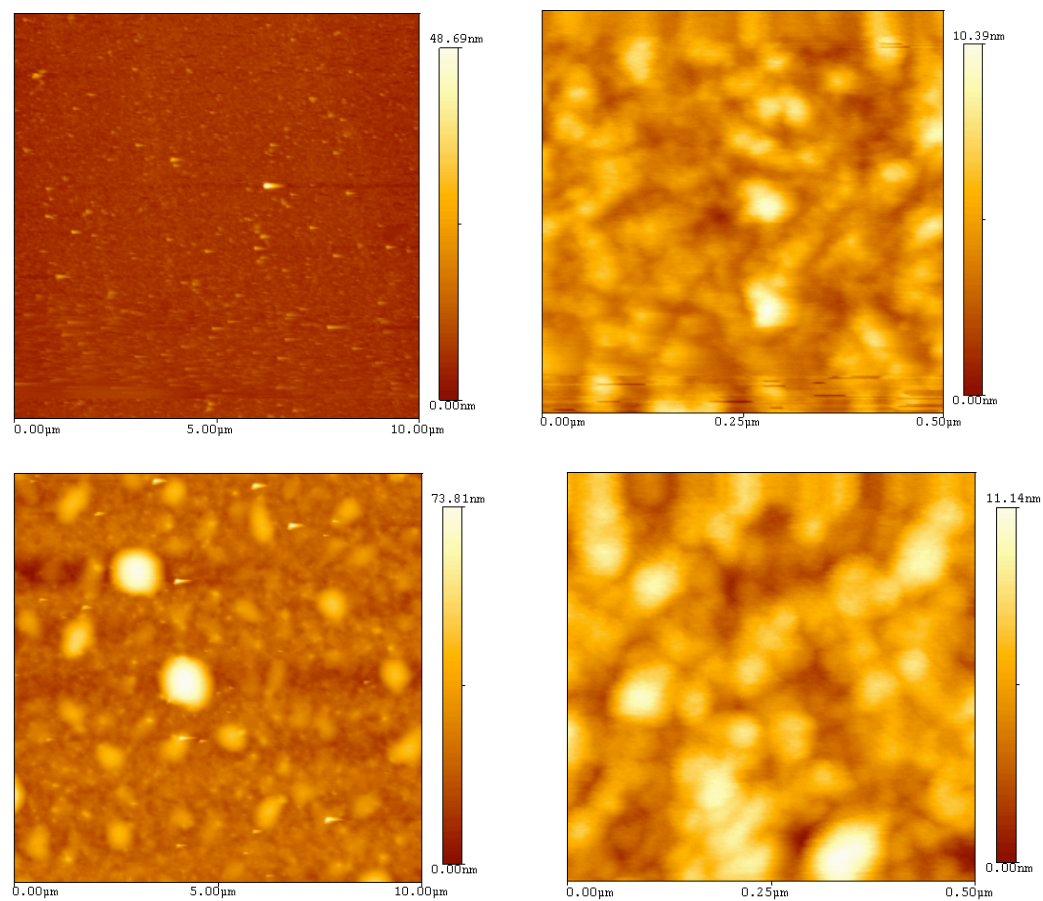flat area between bumps of TTT treated film (0.5x0.5μm)

Figure 13. AFM images of PBTTT-C14 films. Top left: as-spun film (10x10μm) top right: as-spun film (0.5x0.5μm); bottom left: TTT treated film (10x10μm); bottom right: flat area between bumps of TTT treated film (0.5x0.5μm)
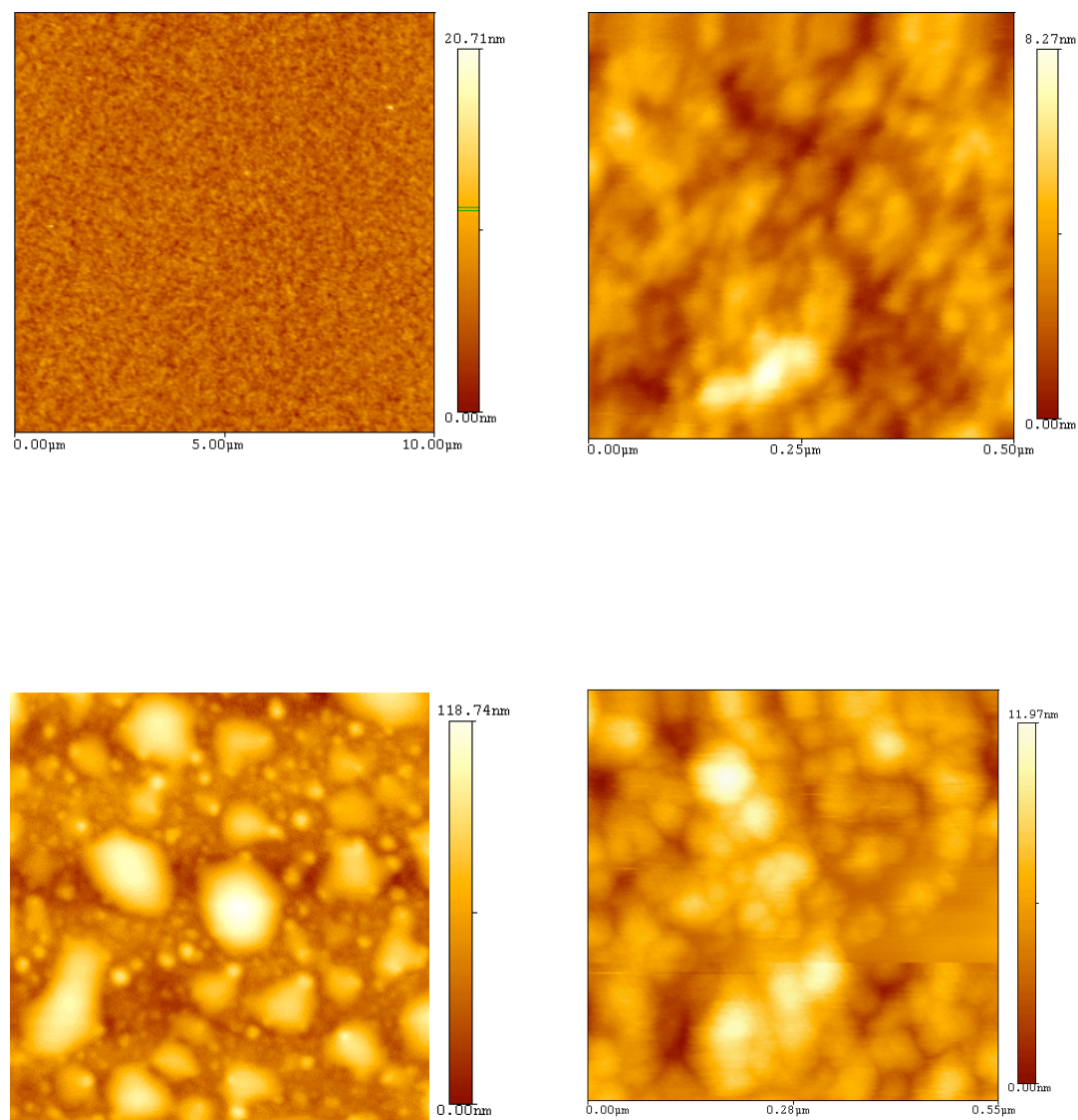
UV-Vis spectra were taken before and after doping, and during restoration (dedoping). The spectra are shown as following:
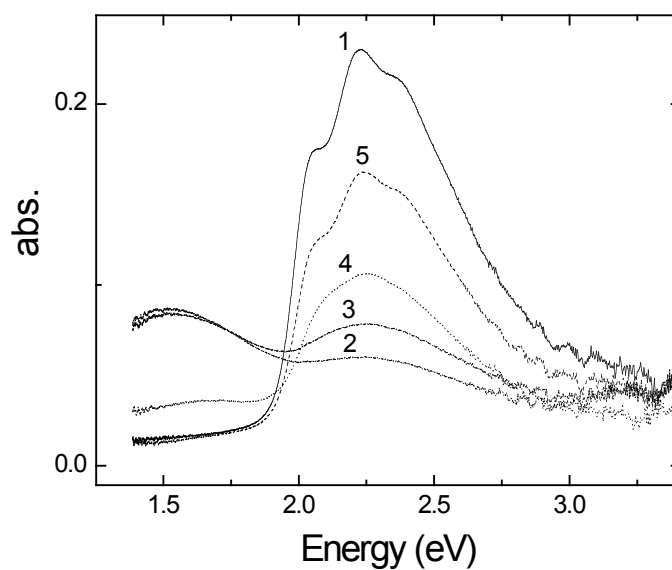

Figure 14. Absorption spectra of P3HT. Curve 1: as-spun; curve 2: just treated; curve 3: in dark and air for 23 hours; curve 4: in dark and air for 95 hours; curve 5: followed by under illumination in air for 16 hours.
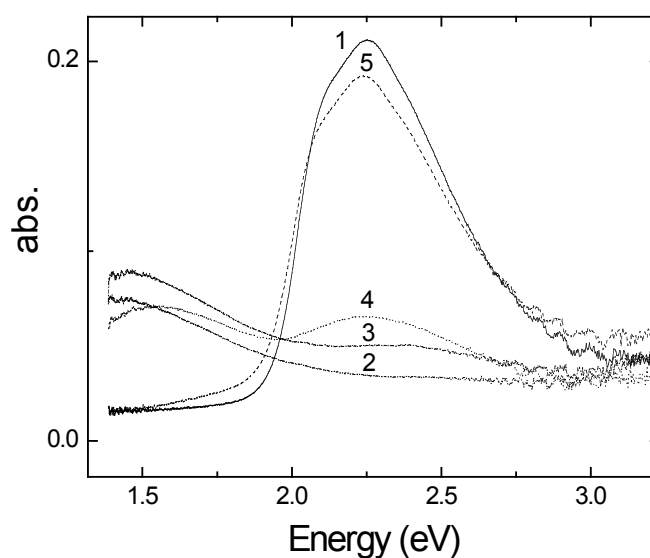
Figure 15. Absorption spectra of PBTTT-C14. The relation between the curve number and the sample condition is the same with Figure 14.
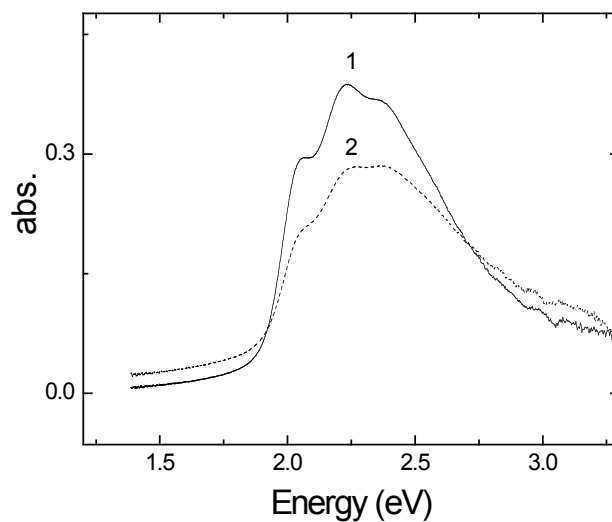
Figure 16. Absorption spectra of P3HT. Curve 1: as-spun; curve 2: under illumination in air for 16 hours.

Images taken from an optical microscope are shown in Figs. 17 and 18. Since the features are more substantial in the PBTTT-C14 film, this observation was mainly done on PBTTT-C14 samples although the P3HT images are also included.
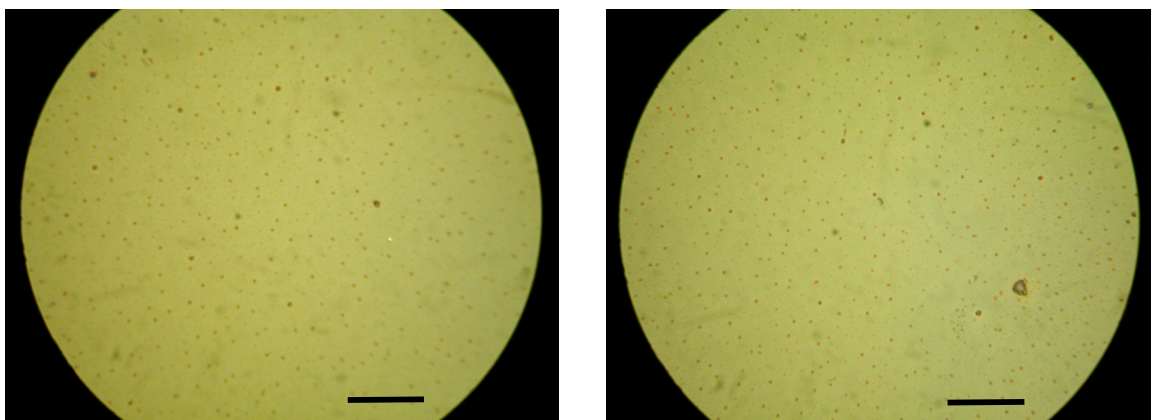
Figure 17. Images of P3HT films taken by an optical microscope. Left: 23 hours in light and air after treatment; right: 66 hours in light and air after treatment. (scale bar is 25 μm)
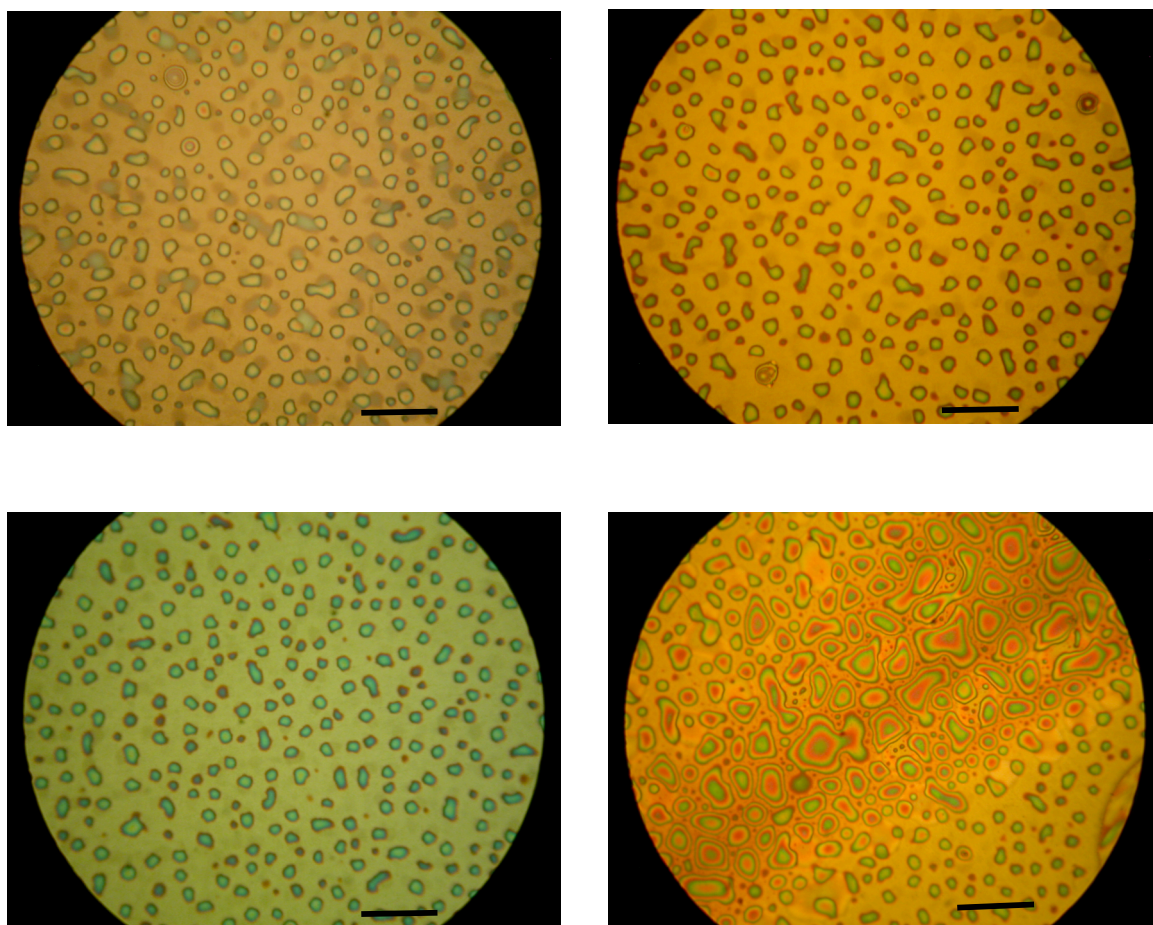
Figure 18. Images of PBTTT-C14 films taken by an optical microscope. Top left: just after treatment; top right: in air and light for 23 hours after treatment; bottom left: in air and light for 66 hours after treatment; bottom right: close to edge of this sample. (scale bar is 25 µm)

SEM images have also been taken before and after treatment are shown as following:
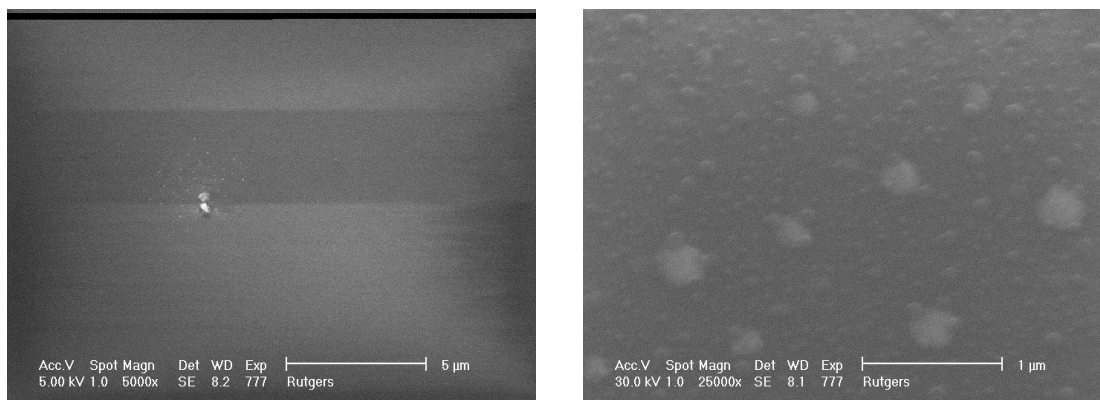
Figure 19. SEM images of P3HT films. Left: as-spun; right: treated with TTT.
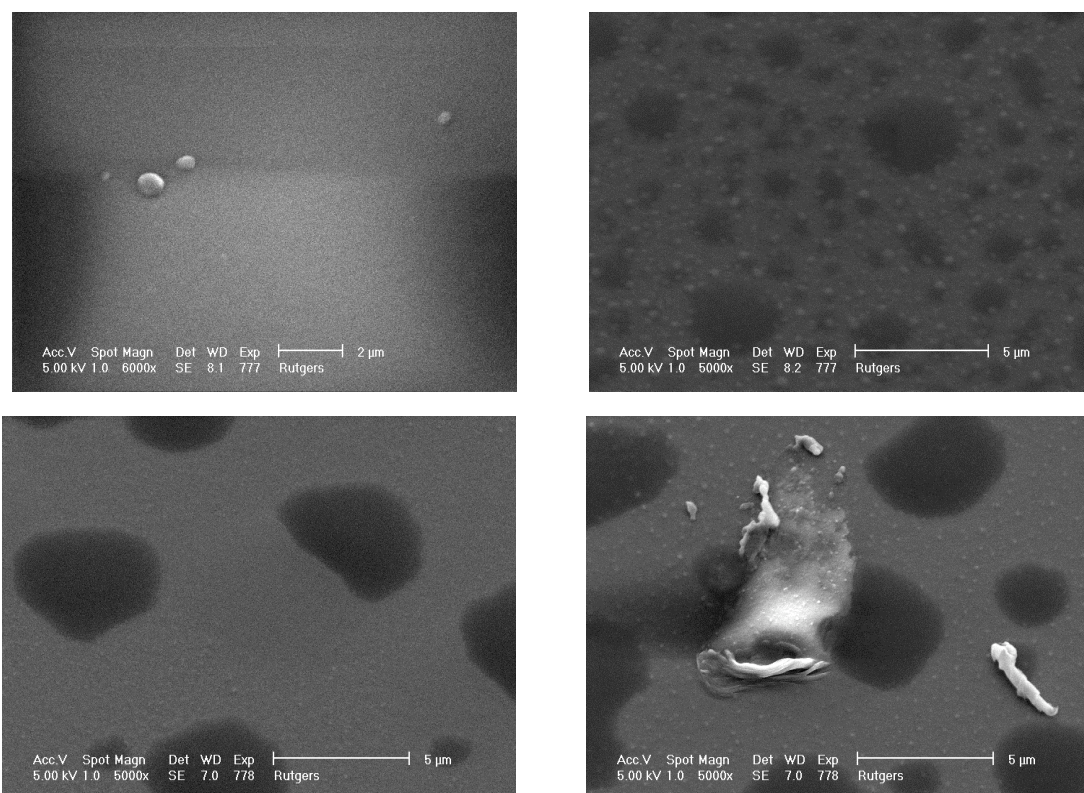
Figure 20. SEM images of BPTTT-C14 films. Top left: as-spun; top right: treated

with TTT; bottom left: a restored film; bottom right: torn part of a restored film.

Discussion

Doping Effects

The doping of P3HT and PBTTT-C14 with TTT can be seen in Figs. 10 & 11. The 5 to 6 orders of magnitude increase in conductivity was observed in both compounds.

In UV-Vis spectra (Figs. 14 & 15), a decrease of absorption intensity of the original absorption band (500-600nm) can be observed after doping. On the other hand, a new band at a lower energy can be observed. The large increase of conductivities can be attributed to the presence of polarons and bipolarons (as noted in the introduction).

AFM images were taken before and after doping. In previous studies, AFM has been used to investigate surface morphology of polymer films. However, not many of the prior studies focused on doped films[12][13][14]. In our study, we used AFM to show the vapor doping induced swelling phenomenon in polymer grains. An expansion in the grain size can be seen in the 0.5x0.5µm AFM images (Fig. 12 & 13). In previous studies, it had been shown that dopant molecules stick to polymer chains and stay in them; an increase in the chain-chain distance was demonstrated by XRD study, although it was with different dopants [15][16].

Discussion of surface topography

In AFM images, some very large protrusions are also observed after treatment, especially on PBTTT-C14 samples. Although they are unlikely responsible for the high conductivity, the features are still of some interest to us and may affect other

properties of these systems. Images by optical microscopy and SEM were taken on these films; all the images are discussed together. From AFM, we can find that the bumps are very high (>100nm for PBTTT-C14). Comparing with the film thickness (~12nm) it is too big for a normal doped swollen polymer[16]. From optical microscopy imaging (Figs. 17 & 18) we can found that the size of the features doesn't change much with time, which also means that they are independent of conductivity. (It is worth mentioning that although the sizes for just-treated and restored samples look different, they are virtually different samples. However, the sample used in an optical microscope is the same one.) Thus, by knowing their dramatic height and their independence of restoring time, it is unlikely that they are just "fully-doped" polymer clusters. By SEM imaging, we can also see that they are not "stand alone" or empty bumps, instead, they are part of the film. In addition, by knowing their sizes are related to film thickness (Fig. 18 bottom-right), there are no bumps observed on annealed (PBTTT-C14) samples (data not shown), and it can be suggested that these bumps features may be due to aggregation of residue solvent in the polymer film during pumping. The solvent for PBTTT-C14 is chlorobenzene while chloroform was used for P3HT. There might be more residue solvent in the PBTTT-C14 film than chloroform in P3HT film, because chloroform is more volatile than chlorobenzene. This may explain the reason why there are only very small bumps on P3HT films.

Discussion on Dedoping

Interestingly, by exposing the sample to air, a current decrease and a color recovery were observed. It is likely that this is a result of dedoping instead of just charge compensation. In the UV-Vis spectra of P3HT, shoulders are observed in the original peak, they are due to the chain-chain interaction that imply a crystalline

structure for the polymer. For high doping concentrations, not only does the original peak decrease in intensity, but the shoulders also disappeared. This can be understood as the result of the insertion of TTT molecules between the P3HT chains, thus there will be much less inter-chain response. However, after dedoping, the shoulders are able to be observed again. This indicates the absence of TTT molecules in these polymer films.

A sensitivity to light was also observed in this system. From Figs. 14 and 15, we can see that the presence of light significantly facilitates the recovery of the absorption spectrum. The recovery rate is several times higher in light than in dark. In both figures, although the absorption didn't recover completely to the initial state, the partial recovery can be attributed to the intrinsic degradation of polymers, especially P3HT, since P3HT is known to not be stable in an environment of both light and ambient air. Also, the difference between these two spectra (Fig. 14, curves 1 & 5) is quite similar to the degradation of P3HT under the same conditions but without doping (Fig. 16). In this point of view, we can tell from Figs. 14 & 15 curve 1 & 5 that PBTTT-C14 displays a better stability and reversibility than P3HT although the instability of PBTTT-C14 had already been reported[17].

We do note yet know with 100% confidence the actual reason for the light-dependent dedoping phenomenon. However, it might be due to the formation of hydroxysilane as a result of the reaction of water with the trichlorosilane part of TTT. Water is one of the few species that TTT can react with in this polymer under these conditions. Also, after forming hydroxysilane from chlorosilane, the partial charge on Si will be reduced because Cl- groups are more electronegative than OH- groups. It will be easier for a hydroxysilane to be released from the polymer film since it is common for a molecule with –OH group, e.g. methanol, performing reversible

response on a chemosensor[18]. As for the light-dependent effect, it might due to the compensation of the retardation of the reaction (chlorosilane to hydroxysilane) caused by electron donation from the polymer to the Si atoms. It might also possibly be related to an oxygen radical-related reaction, because oxygen is more active under light illumination. However, the real mechanism is still an open issue and needs to be examined with more detailed experiments and data.

Conclusion

In this study, we have successfully applied a novel compound TTT to create a doped system of P3HT and PBTTT-C14 films. This system shows a typical response for a doped polythiophene: high conductivity and polaron/bipolaron characteristics in absorption spectra. We also demonstrated swelling phenomena in vapor-doped films by AFM, which, to our knowledge, has not been previously observed. After successfully doping of the films, we showed that they can be either dedoped almost completely (for PBTTT-C14) or potentially could be dedoped completely (for P3HT, if one considers the intrinsic degradation in a dedoping environment). The inter-chain absorption of P3HT was seen again after dedoping. Interestingly, we also observed that this dedoping process could be facilitated by illumination. Upon modifying the nature of this system, this photo-induced dedoping might allow us to create a "selective-area dedoped" device, and further achieve a low schottky barrier device or system on a chip (SoC).

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