Doping of Conjugated Polythiophenes with Alkyl Silanes

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1. Introduction

Molecular self-assembly is a surface modification technique that can be used in emerging applications in organic and molecular electronics.[1–5] The self-assembly of silanes has recently been observed at the surface of organic semiconductors, which opens new opportunities for fundamental and applied research.[6] Our primary interest stems from the observation of a large increase in conductivity induced by a self-assembled monolayer (SAM) deposited on the surface of organic single crystals. Here, we extended our studies of SAM-functionalized organic semiconductors to a class of solution-processable conjugated polythiophenes,[7–9] and we demonstrate how the interaction of these polymers with hydrolyzed fluoroalkyl trichlorosilane (FTS) resulted in a drastic modification of the electrical and optical properties of these semiconducting polymers. Upon doping with FTS, the electrical conductivity of ultrathin polythiophene films increased by up to six orders of magnitude, reaching $(1.1 \pm 0.1) \times 10^3 \text{ S cm}^{-1}$ for poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) and $50 \pm 20 \text{ S cm}^{-1}$ for poly(3-hexyl)thiophene (P3HT). Interband optical absorption of the polymers in the doped state is drastically reduced, making these highly conductive films transparent in the visible range. The dopants within the porous polymer matrix are partially crosslinked via a silane self-polymerization mechanism that makes the samples very stable in vacuum and nonpolar environments. The mechanism of SAM-induced conductivity is believed to be based on protonic doping by the free silanol groups available within the partially crosslinked SAM network incorporated in the polythiophene structure. The SAM-doped polythiophenes exhibit an intrinsic sensing effect: a drastic and reversible change in conductivity in response to ambient polar molecules, which is believed to be due to the interaction of the silanol groups with polar analytes. The reported electronic effects point to a new attractive route for doping conjugated polymers with potential applications in transparent conductors and molecular sensors.

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molecular components of organic field-effect transistors (OFETs) and other electronic devices (e.g., to improve structural and/or electronic properties of organic thin films).

The recent observation of molecular self-assembly at the surfaces of small-molecule organic crystals broadens the range of materials of interest for SAM research.[6] A dense SAM of silanes can be formed at the surface of p-type molecular crystals, e.g., rubrene or tetracene. In contrast to SAMs on Au or SiO2, those at the surface of organic semiconductors can drastically modify the electrical conductivity of these materials. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (C8H4F13SiCl3), or simply FTS, grown at the surface of rubrene induces a remarkably high conductivity, as high as $\sigma = 2.2 \times 10^{-2}$ S cm$^{-1}$ in a saturated doping state; the corresponding sheet conductivities typically achieved by electrostatic doping in OFETs. The effect is thought to be due to mobile holes induced by the SAM in the top layer of the highly ordered molecules in the organic crystals.

2. Results and Discussion

Conjugated polymers are complementary solution-processable semiconducting materials with intriguing optoelectronic properties.[7,8,16] The electronic state of these materials can be tuned from insulating to conducting by changing the carrier concentration via chemical doping or injection from contacts in an OFET geometry.[17–20] In this work, we performed FTS functionalization of thin films of P3HT and PBTTT, and observed that exposure to FTS introduced mobile carriers into these conjugated polymers, rendering the samples highly conducting. The experiment was performed using spin-coated polymer films prepared on glass according to optimized procedures reported in the literature.[19,20] FTS doping was performed from the vapor phase, following a similar process that was used to grow SAMs on molecular crystals.[8]

For specific details of sample preparation and doping, see the Experimental Section. As shown in Figure 1, when a film of P3HT or PBTTT with a thickness of 20 nm was exposed to FTS vapors, the conductivity rapidly increased and reached $\sigma_{\text{P3HT}} = 30$ S cm$^{-1}$ and $\sigma_{\text{PBTTT}} = 1100$ S cm$^{-1}$ in a saturated doping state; the corresponding sheet conductivities were $\sigma_{\text{P3HT}} = 0.6 \times 10^{-2}$ S cm$^{-1}$ and $\sigma_{\text{PBTTT}} = 2.2 \times 10^{-3}$ S cm$^{-1}$. The effect was stable in high vacuum and under an atmosphere of nonpolar gases, including oxygen. Contrary to densely packed molecular crystals, where the SAM growth is restricted to the surface, FTS molecules penetrate deep into the nanoporous polymeric materials, interact with the surface of individual nanocrystalline domains, and dope the entire film. This behavior could be detected using different methods and was most strikingly observed by a strong suppression of interband optical absorption of the polymer, which made the samples almost completely transparent (Fig. 2).

In order to characterize this “bleaching” effect, we measured optical absorption of FTS-doped samples (Fig. 3). The pristine samples exhibited a broad interband absorption peak at $\lambda = 560$ nm (2.21 eV), as expected (curve 1). Both the P3HT and PBTTT samples exhibited vibronic bands, indicating high structural order in the samples. The vibronic bands are more obvious in the P3HT spectrum, where they are separated by 0.16 ± 0.02 eV, in agreement with the 1450 cm$^{-1}$ Raman stretching mode of the C –– C bond. Once doped with FTS to the maximum conductivity, the interband optical absorption of the samples was almost completely suppressed (curve 2), while another broad long-wavelength band appeared simultaneously at $\lambda > 800$ nm. Interestingly, if the samples were exposed to ambient air, their absorption spectra, the original purple color, and the initial high electrical resistivity recover within days in the dark or within hours under ambient illumination (curves 3, 4, and 5). At the end of this recovery process, the samples reached the initial insulating state with $\sigma$ and $\lambda_{\text{max}}$ similar to the pristine polymers, suggesting that the doping/dedoping cycle did not damage the conjugated backbone of the polymer. As will be shown below, this dedoping was not due to the evaporation of FTS molecules from the sample, but rather it was an electronic effect.

Atomic force (AFM) and scanning electron microscopy (SEM) imaging showed that when FTS was incorporated into the sample there was an increase in roughness resulting in a bumpy surface morphology for the doped films (swelling) due to the possible self-polymerization of FTS in the polymer matrix (Fig. 4). This is consistent with the permeable nanoporous structure of the polymers, confirming the bulk character of the doping in this case. Interestingly, the AFM images of freshly doped and dedoped samples are very similar. This indicates that FTS molecules were likely not physically removed from the samples during dedoping, and the primary role of dedoping was to “switch off” the conducting state. Another indication that FTS molecules did not “escape” from the polymer film was the high stability of the conductivity during long-term storage under high vacuum. SEM images of pristine and dedoped insulating samples could not be obtained due to sample charging.

We observed that highly conductive FTS-doped polythiophenes exhibited interesting sensing properties. Figure 5 shows the dark conductivity response of an FTS-doped P3HT film to vapors of acetone, water, and hexane. An immediate and large (~100%) decrease of conductivity was observed on exposure to saturated...
acetone vapor. The conductivity recovered readily on vapor removal by pumping. A similar, but smaller in magnitude, response was observed with H₂O vapor. Hexane, which is nonpolar, did not have any effect on the conductivity. Interestingly, this behavior is similar to the sensing effect observed in FTS-coated rubrene, which suggests that the sensing mechanisms in these two systems have a common origin likely related to the dipolar interaction of analytes with FTS.[6] In the case of conjugated polymers, however, their solution-processability, availability of large-area samples, and mechanical flexibility make SAM-functionalized polymers especially attractive for applications.

In order to understand the dedoping effect (i.e., the recovery of optical and electrical properties, when FTS-doped polythiophenes are exposed to air), we exposed highly conducting FTS-doped P3HT samples to various ultra-high purity (UHP) gases in the dark and under illumination while monitoring the conductivity (Fig. 6). Illumination was performed using white light with a smooth spectrum in the visible range (a 20 W quartz-tungsten-halogen lamp). Intensities were kept sufficiently low to avoid radiative heating of the sample. We observed that inert gases (e.g., Ar and He) and nonpolar gases present in air (O₂ and N₂) have no effect on the conductivity of FTS-doped polymers: there is only a very slow, gas-independent drift of \( \sigma \) at a very slow rate of \( \frac{1}{C_24} \% h^{-1} \) (the initial portion of the curve in Fig. 6).

However, when saturated water vapor was introduced into the test chamber, an obvious decay of \( \sigma \) occurred. Under illumination, this decay proceeded much faster, with the rate proportional to the illumination intensity (inset in Fig. 6). Instantaneous changes in light intensity resulted in almost instantaneous changes in the decay rate; the inset in Figure 6 shows that reducing the illumination intensity by a factor of 4 caused the decay rate to decrease by a factor of \( \sim 4 \), which produces a kneelike feature in the curve of the time-dependent current. This indicated that dedoping under illumination is a photo-induced e
Overall, this experiment showed that the analyte responsible for dedoping these samples in air is H$_2$O, in agreement with the humidity-related degradation of p-type conductivity observed in polythiophene FETs.[20] The sensing effect shown in Figure 5 can be more generally interpreted as reversible dedoping caused by polar molecules. Full reversibility of this effect indicated that volatile analyte molecules were easily removed from the sample by pumping, while FTS molecules remained in the film. This suggests that the molecules of polar solvents were more weakly absorbed in the sample, while FTS molecules were bound to the polymer much more strongly.

The conductivities that we obtained by doping polythiophenes with fluoroalkyl silanes are among the highest previously obtained in this class of polymers using small-sized dopants, such as I$_2$, PF$_6^-$, and ClO$_4^-$. The saturation conductivities of our optimized samples are $\sigma^{\text{P3HT}} = 70 S \text{ cm}^{-1}$ and $\sigma^{\text{PBTTT}} = 1100 S \text{ cm}^{-1}$ (i.e., $\sigma^{\text{P3HT}} = 1.4 \times 10^{-4} S \text{ sq}^{-1}$ and $\sigma^{\text{PBTTT}} = 2.2 \times 10^{-3} S \text{ sq}^{-1}$). Typically, polymer samples doped with small ions and molecules display relatively poor stability (especially in vacuum), because of the rapid diffusion of small-sized dopants in the polymer matrix. On the contrary, the FTS-doped samples exhibited remarkable stability: the conductivity did not show any decay in high vacuum and only a very minor drift ($\sim 0.5\% \text{ h}^{-1}$) in an atmosphere of nonpolar gases. It is important to emphasize that doping in our experiment was performed at a solid/vapor interface, using highly ordered polythiophene films, which allowed the use of the well-characterized structural, morphological, and transport properties of these polymers as a starting point for data analyses.[20–23] The above values were calculated using the thickness of undoped films ($20 \pm 3 \text{ nm}$).

Despite some degree of swelling that occurred on doping, these estimates are justified because silane molecules are not conducting even in the cross-linked state, and therefore, the total number of conjugated chains in the cross-section of the film (the conducting channels) remained roughly the same as that before doping.

Although the nature of silane–polythiophene chemical interaction is not clear at this stage of investigation, the stability of the doped state in high vacuum points to a relatively strong interaction. Our X-ray photoelectron spectroscopy (XPS) and Rutherford back scattering (RBS) data show that there was virtually no chlorine present in the films after vapor-phase FTS.
doping,[24] which suggests that the FTS has hydrolyzed in situ, either as a result of water trapped in the polymer film or water vapor present in the doping chamber.[23] Such hydrolyzed silanes are known to readily self-condense and polymerize to form partially cross-linked siloxane polymers.[3,26] On silicon dioxide surfaces, these can bind to the free surface hydroxyl groups to form monolayers. In the present case, we believe the FTS was to form into a nonvolatile, partially cross-linked siloxane polymer within the film, accounting for the high stability of the samples under vacuum. In addition, low-concentration oxygen defects known to be present in polythiophenes might serve as anchoring sites for hydrolyzed FTS.[27] The mechanism of the doping of the conjugated polymer by FTS is unclear, but it may be similar to the mechanism of SAM-induced surface conduction in small-molecule organic crystals, where an electronegative SAM molecule induces an electron transfer across the SAM-crystal interface.[6] Additionally, free silanol groups [Si-(OH)] within the partially cross-linked siloxane are known to exhibit relatively high acidities,[28] they may result in protonic (acid) doping of the organic semiconductor.

To fully understand the mechanism of FTS incorporation and functioning, nanoscale structural details of FTS-polythiophene samples should be investigated. For instance, one of the intriguing questions is whether FTS molecules break apart individual $\pi$-$\pi$ stacked crystalline nanofibrils and domains, known to constitute P3HT and PBTTT films,[20,22,29,30] or if they merely bind to the surface of these crystallites. The monolayer character of FTS on molecular crystals and the very high (nearly metallic) conductivity of FTS-doped polythiophenes point to the latter scenario, in which the $\pi$-$\pi$ stacking required for good charge transport is preserved.

Understanding the detailed chemical structure and composition of these functionalized electronic materials is very important. We used ion scattering spectroscopy and XPS to study the elemental composition of FTS-doped polythiophenes point to the high stability of the samples under vacuum. Our preliminary data indicate that fully doped samples contain approximately one FTS molecule per thiophene ring, with an areal density of fluorine atoms of $117 \times 10^{21} \text{ cm}^{-2}$, which corresponds to the 3D density of FTS molecules, $n_{\text{SAM}} = 4.5 \times 10^{13} \text{ cm}^{-2}$, associated with the 13 F atoms per FTS molecule. Using simple conductivity arguments ($\sigma = \epsilon n \mu$), in which $\sigma = 70 \text{ S cm}^{-1}$ is the 3D saturated conductivity of doped P3HT, $\epsilon$ is elementary charge, and $\mu \sim 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ is a typical hole mobility in P3HT,[21,22] the density of FTS-induced holes can be estimated: $n_h = 4.4 \times 10^{11} \text{ cm}^{-3}$, which is comparable to the very high carrier density induced in P3HT by electrolyte gating.[9] Quantitative agreement between the density of FTS molecules and that of charge carriers doped into the system obtained by the two independent techniques (ion scattering and conductivity) suggests that on average, one hole was doped into the polymer per FTS molecule. The very large doping level (approximately one hole per thiophene ring), the very high stability of the conducting state in high vacuum, and the lack of chlorine in the XPS and RBS spectra indicate that the doping effect was due to hydrolyzed FTS.

Our experiment clearly shows that the dedoping of SAM-polythiophene samples in air was caused by water vapor. More generally, this indicates that dedoping can be deliberately induced by exposing the samples to vapors of polar analytes, such as ketones, alcohols or water. In the dark, dedoping is fully reversible, which is beneficial for the development of electrical chemosensors. One explanation for this effect is that it is caused by conformational changes of the polymer backbone induced by a dipolar interaction of fluoroalkyl SAM molecules with polar analytes. Such conformational changes are known to effectively reduce the conjugation length of polymers and affect their physical properties.[8,31] Alternatively, polar analytes would be expected to interact strongly with the free silanol groups within the siloxane backbone formed in situ, which might reverse the protonic doping effect and switch off the conducting state. Understanding the actual mechanism of this effect requires further studies.

It has been shown that due to the nondegenerate ground state of polythiophenes, the lowest-energy excitation in these polymers involves the formation of a bipolaron, that is, two solitons on a conjugated chain attracted to each other and creating a weakly localized pair.[32] Prior studies of optical absorption of P3HT have shown that the interband transition of pristine (undoped) polymer centered at 2.2 eV (560 nm) decreases upon dilute doping with LiClO$_4$ and NPOF$_6$ with a simultaneous appearance of two new broad absorption bands at 0.4 eV (~3 $\mu$m) and 1.6 eV (~800 nm) indicative of bipolaron formation.[32,33] The two new bands correspond to optical transitions from the highest occupied molecular orbital (HOMO) to the new gap states associated with bipolarons. An increase of doping to the highest concentration (saturation doping) leads to a complete “bleaching” (suppression) of the interband transition and transformation of the bipolaronic bands into a very broad low-energy shoulder in the absorption spectrum, which corresponds to delocalized polarons in highly conducting samples. The absorption spectrum approaches that of a metal with free carriers.[32] Similar effects have been observed in doped polyaniline.[34,35] In our case, the spectral range of our apparatus did not allow the observation of the full evolution of bipolaronic bands. Nevertheless, the drastic suppression of the interband absorption at 560 nm (~2.2 eV) and the appearance of the broad long-wavelength peak at $\lambda > 650 \text{ nm}$ (< 1.9 eV) shown in Fig. 3 are both consistent with prior studies and indicate that FTS-doping of P3HT and PBTTT results in a metalliclike state with a high density of mobile polarons. Interestingly, calculations predict that wavefunctions of polarons and bipolarons should significantly overlap at these high carrier densities, which might lead to the formation of “polaron or bipolaron lattices.”[36]

Studies of temperature-dependent conductivity, the Hall effect, IR absorption, and surface analysis are underway in order to elucidate the details of the conduction mechanism and chemical structure of the SAM–polythiophene system. Particularly, IR spectroscopy has been proven to be very useful for the studies of polarons in polythiophene films,[37] polymer OFETs,[38] and small-molecule crystalline OFETs.[39] For instance, the position of the polaronic peak in the mid-IR range is associated with the polaron relaxation energy, and therefore, is indicative of the degree of order in polymer chains.[37]

### 3. Conclusion

To summarize, we have demonstrated that the interaction of ultrathin solid films of polythiophenes with the vapors of hydrolyzed fluoroalkyl trichlorosilanes results in a drastic
increase of the electrical conductivity and a strong suppression of interband optical absorption of these polymers. Upon doping with fluoroalkyl silanes, the electrical conductivity increased by up to six orders of magnitude, reaching $(1.1 \pm 0.1) \times 10^{3} \text{cm}^{-1}$ in poly(thieno-thiophenes) and $50 \pm 20 \text{cm}^{-1}$ in poly(3-hexylthiophene). The effect is tentatively attributed to the protonic doping of the polymer chains by silanol groups of the hydrolyzed trichlorosilanes available within the partially polymerized siloxane network. The doped polymer films exhibited a very good stability in high vacuum and nonpolar gases and showed an interesting electrical response to polar vapors. These effects point to an attractive new route of doping of conjugated polymers that might be interesting for applications in molecular sensors, transparent conductors, and organic electronics.

4. Experimental

Regioregular P3HT from Alfa-Aesar and PBT TT from Merck were dissolved in chloroform and chlorobenzene, respectively. The concentration of P3HT in chloroform was 1.0 mg mL$^{-1}$ (0.07 wt%). The concentration of PBT TT in chlorobenzene was 0.5 wt%. In the case of PBT TT, heat was applied through a water bath to dissolve it thoroughly. Both solutions were spin-coated on glass substrates at 2000 rpm for 40 sec in ambient air. The spin-coated P3HT and PBT TT films were then annealed at 160–180 °C for 10 min in a flow of UHP Ar. The film thickness was 20 ± 3 nm, as determined by AFM. Handling of annealed samples was done in ambient air. An aqueous solution of colloidal graphite (Ted Pella, Redding, CA) was deposited onto the two opposite edges of the annealed samples to form electrical contacts, defining an approximately square film with a width and length of 1 ± 0.1 cm. After the graphite paint was dried, samples were placed on a sample holder for electrical measurements and loaded into an FTS treatment chamber. The chamber was evacuated by a chemically resistive mechanical pump that used Solvay Solexis Fomblin SV inert PFPE fluid (Kurt J. Lesker, K2400 source-meters and K6512 electrometers. SEM and AFM measurements were performed using Keithley (Cleveland, OH) 1700, respectively. Optical absorption spectra were measured with an Ocean Optics transmittance spectrometer (Dunedin, FL).

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