Characterization and Optimization of the Electrical Conductivity of a Semi-crystalline Conjugated Polymer PBTTT upon Doping

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Abstract—Semiconducting polymers have been investigated intensively in recent years due to its unique electronic properties and mechanical flexibility that could enable them to be used in a broad range of electronic applications. The electrical properties can be tuned and optimized via chemical doping which enable charge transfer between dopant molecules and organic materials. For each material, how processing conditions impact their electronic properties needs to be understood. Here, we use a representative semi-crystalline conjugated polymer poly(2,5-bis(3-teradecylthiophen-2-yl)thieno[3,2-b]thiophene)(PBTTT) to investigate how doping methods used, different dopant species and different thickness of polymers affect its electrical conductivity. We demonstrate that a combination of processing parameter could lead to the improved electrical conductivity of PBTTT thin film and point directions for future development of polymers with better electrical conductivity.

1. INTRODUCTION
During the five-decade development of organic semi-conducting materials, these materials have been widely used in many fields such as making OLED (Organic Light Emitting Diode)[1,2]. Organic materials show much better flexibility than inorganic materials, which enables them to be used as flexible touch pads screens[2]. With its capacity to be processed in large scale, organic semiconductors are suitable for future development of electronic skin and monitoring devices for human-body wearing[2,3]. The requirements of the electronic properties/ electrical conductivities of organic materials depend on their applications. Chemical doping has been proved to be an efficient and basic method to modulate electronic properties such as the charge carrier density, Fermi level, and, most directly, electrical conductivity [4,5].

Doping efficiency need to be improved further to promote the future development of organic electronics. To achieve this, factors that determine the efficiency of doping need to be well understood and materials behave with different doping methods required to be characterized as well. Hence, here we use a benchmark semi-crystalline semiconducting conjugated polymer, PBTTT to study how dopants types, doping methods, temperature stability, thickness and doping exposure time affect the chemical doping efficiency. Electrical conductivities of PBTTT samples can be sufficiently increased when a good combination of doping conditions are met including reaction time of 60 seconds, polymer thickness of nearly 50 nm, the evaporation method and \( F_4TCNQ \) as the dopant.
2. EXPERIMENTAL METHODS

The molecular structure of dopant molecules as well as the doping methods used are summarized in Fig.1. Active material (neat PBTTT with a concentration of 10 mg/ml) was spun coated at 1500 rpm for 30 seconds from a hot glass pipette (90°C). Sample were annealed at 180°C for 20 minutes and subsequently cooled to room temperature naturally. Doping of polymers was done by either the solution or evaporation method. For solution doping, $F_4TCNQ$ in ACN solution (1mg/ml) was dropped on the top of samples and hold for 2-3 minutes before spin coating. Alternatively, the 20nm thick $F_4TCNQ$ film was deposited on sample via evaporation at a base pressure of $2 \times 10^{-7}$ mbar with a rate of 0.5 s$^{-1}$. Right after the dopant deposition, films were annealed at 80 °C in the glove box for 20 minutes.

Electrical conductivities of prepared samples were measured on customized four point probe microelectronic devices that prepared by photolithograph. An ultra-high vacuum thermal evaporator was used to deposit Ti layer electrodes with a 3 nm thick Ti layer as an adhesion layer followed by a 10 nm thick layer of Au. The electrical conductivity was measured in a low noise four-point-probe station under nitrogen. The electrical conductivities were measured by sweeping the voltage from -1V to 1V and calculated by the following equation:

$$\sigma = \frac{I}{V} \frac{w}{Ld}$$

where I is the drain current, w is the distance between inner probes, l is the length of device, dV is the voltage and h is the thickness of samples. Thickness are determined by AFM scans.

Optical absorptions spectrums were performed by a UV-Vis spectrometer Agilent technology Cary 70000 within the wavelength window of 250nm to 2000nm. The AFM scans were obtained from a Bruker Icon AFM in Peakforce tapping mode.

3. RESULTS AND DISCUSSION

3.1 Thickness dependent electrical conductivity upon doping with $F_4TCNQ$

The thickness dependent electrical conductivities of the PBTTT films is investigated in this experiment. The thickness of PBTTT films were controlled by the spin coating rate as shown in Fig.2a, and the electrical conductivities of films with different thicknesses were shown in Fig.2b. Until 50 nm, the electrical conductivity increases as the thickness of polymer increases. However, as the thickness continues to increase, the electrical conductivity decreases. The first positively related step is because addition layer of polymer provides additional conductivity layer to allow charge carriers to transport which is analogy to the parallel electrical circuit. However, if the thickness is over a threshold value, it is difficult for dopants to penetrate/diffuse throughout the whole thickness of the film due to limited
diffusion rate of dopant molecules, resulting in some of the polymer undoped and a lower electrical conductivity than the maxima. Hence, to maximise the electrical conductivity for a given dopant and polymer system, the thickness of polymer films needs to be optimised.

Figure 2. The thickness dependent electrical conductivity of spin coated PBTTT thin film. a) thicknesses of films as a function of spin coating rates; b) measured electrical conductivities as a function of film thickness.

4. ELECTRICAL CONDUCTIVITIES WITH DIFFERENT DOPANTS AND EXPOSURE TIME

The electrical conductivity of PBTTT doped by F$_4$TCNQ, F$_6$TCNNQ and Mo(tfd)$_3$ are investigated by the time PBTTT films were immersed with dopants solutions prior to spin coating dopant solutions. Samples’ electrical conductivities increase significantly from 0.001 S/cm to an order of 100 S/cm when dopants are introduced within 10 seconds. The F$_6$TCNNQ is the most powerful dopant improving the electrical conductivity to 139.8 S/cm, while the values for PBTTT doped by Mo(tfd)$_3$ and F$_4$TCNQ are 117.6 and 121.4 S/cm respectively. For both the F$_4$TCNQ and F$_6$TCNNQ doped PBTTT films, electrical conductivities increase as the increasing dopant exposure time while the change is less significant than the improvement in the initial 10 seconds. Differently the electrical conductivity of the film doped with Mo(tfd)$_3$ saturates after the initial 10 seconds. The electrical conductivity of F$_4$TCNQ doped polymer is increasing at a constant rate during the increase of exposure time, in the opposite, F$_4$ – TCNQ doped polymer’s electrical conductivity merely increases during the increasing exposure time from 10 s to 60 s. One possible explanation is that the charge transfer process between F$_4$TCNQ and PBTTT has been completed within the first 10 s as evidenced from Fig.3b that the neutral absorption peak bleached[6,7,8,9]. It clearly shows that F$_4$TCNQ doped polymer has an advantage of quick reaction and is relatively more suitable. The other possible explanation is that the F$_4$TCNQ dopants have lost their reaction ability when the exposure time reaches 10 s, which means the charge transfer process stopped after 10s due to the degradation of dopant molecules. [8,10] It is unlikely but beyond the scope of this study.

Fig.3b reveals the optical transition of PBTTT changes with doping time. As doping time increases, the height of PBTTT neutral absorption peak at 2.26 ev decreases monotonically while the polaron absorption peak at 1.46 ev rises. This is a clear signature of increasing charge carriers in PBTTT with increasing doping time. This suggests that a sufficient reaction time is required to fully dope PBTTT due to the finite diffusion rate of dopant molecules within PBTTT as well as reaction time of charge transfer process.
5. THERMAL STABILITY OF PBTTT DOPED BY DIFFERENT DOPANTS

Electrical conductivities of PBTTT films doped by $F_4$TCNQ, $F_6$TCNNQ and $Mo(tfd)_3$ are 120 S/cm, 140 S/cm and 118 S/cm respectively, which are comparable to previous reports[9,10]. For these three doped films, the electrical conductivities of polymers decrease monotonically with increasing the annealing time at 400K. This phenomenon shows that inside each PBTTT, the number of charge carrier decreases and dedoping is taking place. Heat provides dopants sufficient energy to overcome its columbic force between PBTTT and dopants. Dopants can hence diffuse to leave the PBTTT, resulting in a reverse charge transfer process which holes are transferred back to PBTTT. The degradation rate under thermal annealing is different among these dopants. After been heated for two hour, $F_6$TCNNQ doped polymer is relatively more stable while $F_4$TCNQ doped polymer has the fastest degradation rate. Although the electrical conductivity has dropped significantly from fully doped state, PBTTT films still exhibit a electrical conductivity of more than 1 S/cm after thermal annealing at 400K, which is a decent performance in some electronic applications. It is desired that the doping thermal stability can be improved further in future.

Figure 3. Characterization of the level of doping of PBTTT film upon doping with $F_4$TCNQ, $F_6$TCNNQ and $Mo(tfd)_3$. a) the electrical conductivity as a function of exposure time of doping solution prior to spin coating; b) the optical absorption signal with increasing the doping time of $F_4$TCNQ.

Figure 4. Electrical conductivities of doped PBTTT films that are thermally annealed at 400K under Ar atmosphere. Thermal stability of three dopants were studied, $F_4TCNQ$, $F_6TCNNQ$ and $Mo(tfd)_3$. 
6. TEMPERATURE DEPENDENT ELECTRICAL CONDUCTIVITY

Temperature dependent electrical conductivities of neat PBTTT and PBTTT upon solution doping and evaporation doping are investigated to understand the impact of doping process on the charge transport of PBTTT film with F4TCNQ as shown in Fig.5. For all samples, electrical conductivities increase monotonically with increasing temperature, revealing a 'hopping-like' charge transport and charges need to overcome energetic barrier to transport (Fig.5a), consistent with previous reports. The temperature dependent electrical conductivities are normalized to the value at 300K to compare the slope of these PBTTT film as shown in Fig. 5b.

![Graphs showing temperature dependent electrical conductivity](image)

Figure5. Understanding of the charge transport thermal activated barrier and impact of doping methods on charge transport by the temperature dependent electrical conductivity of neat and doped PBTTT thin films. a) temperature dependent electrical conductivity of neat and doped PBTTT thin films; b) temperature dependent electrical conductivity normalized to values at 300K; c) data is fitted with an Arrhenius-like mobility edge model to extract the thermal activation energy, consistent with previous observations[3,10,11]; d) comparison of the height of the energetic barriers of each sample.

The temperature dependent electrical conductivity of all samples fit well with the Mobility Edge model proposed by Mott (Fig. 5c), which charge carriers are localized and not mobile below the transport edge[3,11]. Charges become mobile when they are thermally activated by thermal fluctuation to energetic states higher than the transport edge. \( E_A \) is represented as the slope which is the energy barrier that the electron must overcome. \( \sigma_0 \) is the intrinsic electrical conductivity of the material. Higher intrinsic electrical conductivity means the larger charge mobility within the material[10]. As summarized in Fig.5d that doped polymers have a lower energy barrier than the undoped polymers regardless of its doping methods. Charges in PBTTT propagate along its backbone via pi-pi electron cloud. While PBTTT is semi crystalline with ordered and disordered regions, charges cannot transport ballistically. In disordered regions, the overlapping of wavefunction of nearby chains is weak that charges are localized which means that they cannot move freely from one chain to the other, limiting
the charge transport. Thermal fluctuation energy (kT) could activate these localized charges to a higher energetic state that the overlapping of wavefunction become larger, resulting in a larger charge transfer integral and electrical conductivity\[1,2,10\]. As sample is doped, the charge carrier densities increase filling the low energy tail states of PBTTT. The enhanced wavefunction overlapping induce a larger population of delocalized charges and hence the activation energy is smaller when samples are doped. In addition, trapped state induced by water molecules or other defect exist in PBTTT film impeding the charge transport. Charge carriers hence need to overcome an energetic barrier to travel to the next delocalized state. The height of this energetic barrier is determined by the nature of defects as well as the level of disorder within the microstructure\[11\]. It has been reported that dopants induced via evaporation doping tend to locate between the alkali chain of PBTTT without disrupting its microstructure significantly\[12\]. As the crystallinity of evaporation-doped PBTTT is higher than the solution-doped PBTTT, less charge carriers are trapped and PBTTT doped by evaporation method is less temperature dependent\[13\].

7. CONCLUSION
We have demonstrated that various optimizations steps are required including a. optimization of the thickness of films; b. the choice of dopant, which in our study, F$_6$TCNNQ is the best; c. the reaction time of the dopant and thin films to achieve a high electrical conductivities of PBTTT films; d. doping method. Smaller dopants like F$_5$TCNQ saturate quickly as about 10 second, while larger dopants like F$_6$TCNNQ and Mo(tfd)$_3$ requires more time to diffuse and hence a longer reaction is needed to maximise the electrical conductivity. Doping method is also a key factor as we have shown that evaporation doping is more effective than solution doping due to the reduced thermally activation transport barriers for charge transport. For a given dopant and polymer system, optimization is required. The complexity of the doping efficiency requires more in-depth investigation\[14,15\]. For better use of the organic semi-conducting material, how to measure and improve the strength of the doped polymer while maintaining the electrical conductivity should be further investigated, such as ion-exchange and double-doping strategy. Also, the methods of increasing thermal stability of doped polymers should be studied\[13\].

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