Minimization of contact resistance between metal and polymer by surface doping

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Abstract

The technique of surface doping is used to reduce the contact resistance between Au and poly(3-hexylthiophen-2,5-diyl) (P3HT) in Au(bottom)/P3HT/Au(top) sandwich type cells. To implement this technique, dodecyl benzene sulfonic acid (DBSA) is found to be an effective bulky dopant of P3HT as confirmed by four probe conductivity measurements, absorption and photoluminescence spectra. Sandwich cells treated with DBSA showed electrical short due to diffusion of DBSA across P3HT film in Au(bottom)/DBSA/P3HT /DBSA/Au(top) sandwich cells which confirms that DBSA is not immobilized at the surface. To restrict DBSA primarily at the surface, aqueous solution of poly(ethylenedioxy thiophene) stabilized in poly(styrene sulfonic acid) (PEDOT:PSS) is utilized to make an emulsion with DBSA. The application of this emulsion at the top and bottom Au/P3HT interface has resulted into a decrease of contact resistance by nearly four orders of magnitude.

1. Introduction

Since the advent of conjugated polymers, it has been utilized in various kinds of interesting applications because of its ease of processibility and fabrication procedure [1]. Related to this, polymer field effect transistor (PFET), light emitting diodes (PLED) polymer solar cells, electro-chromic devices (PEC), Schottky diodes, etc., [2] has been fabricated and extensively studied by many investigators in the past few decades. Out of these polymer electronic devices, only PLED and PEC has been commercialized [3-4] because of their excellent price-to-performance ratio. However, the other electronic devices suffer from many problems that lead to lower performance, lack of repeatability, etc. with respect to its inorganic counterpart. Although significant efforts have been made by various research groups in the past decade to improve the performance of these polymer based electronic devices, but a considerable improvement is yet to be attained that could parallel the performance of immensely commercialized silicon devices.

The success of silicon devices is mainly due to two reasons: high mobility of charge carriers in the bulk and very low contact resistance between the carrier injecting electrode and semiconductor. To give a feel for the situation, the charge carrier mobility values for amorphous silicon (a:Si) is typically ~ 0.7 cm^2/Vsec [5], as compared to 0.1 cm^2/Vsec or lower in the case of poly(3-hexylthiophene) (P3HT) [6], a widely studied conjugated polymer. Similarly, the value of contact resistance is typically less than 10^{-5} Ω cm^2 for gold/silicon contact [7], whereas it is 10^4 Ω cm^2 for Au/P3HT contact [8]. One could draw a fuzzy line of connection between mobility and contact resistance as it apparently appears that an increase in mobility could bring down the contact resistance. There are many reports on various efforts to increase the carrier-mobility in conjugated polymers but the best obtained values are still lower than those of a:Si. Nevertheless, serious investigation in this front is still in progress.

For obtaining the desired electrical characteristics from conjugated polymer based electronic devices, it is very important to have an ohmic contact between the metal electrode

and the polymer, except those cases where a Schottky contact is the very requirement. The choice of element for the metal electrode is decided by the work function and how close (the difference should be within a few tenth of eV) it is with respect to the HOMO level of the polymer in use. This is because all conjugated polymers are hole-only devices, and therefore holes could only be injected in or taken out from the HOMO level of the polymer. As an example, gold, having a photoelectric work-function of 5.1 eV, is preferably chosen to achieve an ohmic contact with P3HT, which has a HOMO level at around 5.1 eV. More specifically, if $e\phi_m$ is the work function of the metal, $e\chi_s$ is the electron affinity of the p-type semiconductor, and E_g is the band gap, then according to inorganic semiconductor theory [9], an ohmic contact could be fabricated if the following necessary condition is satisfied: $e\phi_m >$ $E_g + e\chi_s$. For P3HT, the values for electron affinity and band gap are 1.4 eV and 2.1 eV, respectively. These values satisfy the above mentioned condition to yield an ohmic contact between gold and P3HT. Hence a low and linear contact resistance is expected, although it is not a necessary condition. On the contrary, a very high contact resistance depicting non-linear nature, of the order of a few tens of mega-ohm, is observed in P3HT based FETs [10]. One probable reason for such an anomaly is that the quoted work-function for gold is in ultra high vacuum (UHV) (10^{-9} mbar), while the apparent work function near the Au/P3HT interface could be lower. This could lead to a formation of potential barrier for the charge carriers. Another probable cause for such a high contact resistance is the presence of impurities [11] at the Au/P3HT interface during the step of vacuum deposition at pressure much higher than that required for UHV. Either way, the presence of potential barrier at the interface leads to very low current values, especially in P3HT based FETs and sandwich cells.

To improve the charge injection across metal/polymer interface, a number of tactics has been tried out by various research groups. Some notable one is the tuning of the metal work function by surface treating it with a polar molecule that it can self assemble and form highly order two dimensional layer having the dipole moment in the desired direction [12-14]. Another method for improving the charge injection between metal and polymer is to

incorporate a *buffer layer* that provides a step between the Fermi level of metal and the HOMO level of the conjugated polymer. Poly(ethylenedioxy thiophene)/poly(styrene sulfonic acid) is the most utilized *buffer layer* in polymeric LEDs [15,16] and solar cells [17]. Other than these methods, doping the conjugated polymer could also increase its conductivity [18]. Although this method improved the field effect mobility by two orders of magnitude along with a decrease of contact resistance by five orders, the on/off ratio suffered because of higher 'off' current than the FET fabricated from the undoped conjugated polymer. This happens due to possible migration of the dopant molecule along the channel.

In the present investigation, we have used Au/P3HT interface as our model system, as it is the most widely studied metal/conjugated polymer interface. Regarding this, sandwich cell of Au/P3HT/Au is fabricated. The work by Chen et al [15] has motivated us to look for dopant molecules that are much bulkier than the common dopants, like $FeCl_3$, I_2, so as to stop its migration across the electrodes. Related to this, dodecyl benzene sulfonic acid (DBSA) is found to dope P3HT and conductivity of the doped film could be varied by three orders of magnitude. Latter, a surface treatment of Au/P3HT interface by DBSA embedded in PEDOT:PSS matrix is found to result to a decrease in contact resistance by about four orders of magnitude with almost no migration of the dopant molecules across the thickness of the sandwich cell.

2. Experiment

Sandwich cells of Au/P3HT/Au are fabricated by first ionically sputtering gold strip-line [width (w) = 1 mm], while using JEOL JFC-1500 Ion Sputtering Device, on a glass substrate (1 cm × 1 cm). Prior to the sputtering the glass substrate was treated with H_2O_2 + NH_4OH solution followed by ultrasonic cleaning in various solvents. The sputtering step is followed by spin coating of P3HT (thickness ≈ 0.25 μm) under ambient atmosphere from a 5% solution (w/v) in chloroform. On top the P3HT layer the top gold electrode was either sputtered or deposited under vacuum in the form of strip (w = 1 mm) but oriented perpendicular to the

bottom gold strip-line. The sputtering and vacuum evaporation was performed at a rate of 1.5 and 0.1 Å/sec approximately and at a pressure of 10^{-3} and 10^{-6} mbar, respectively. The effective cross-sectional area of the device was 1 mm^2.

The fabrication procedure for Au(bottom)/DBSA/P3HT/DBSA/Au(top) sandwich cell is identical to the above, with the only difference that an aqueous solution of DBSA at various concentrations [% (w/w)] was spin coated on the bottom Au electrode or top of P3HT layer at a very high rate (7000 rpm for 30 sec). Similarly, the sandwich cells of Au(bottom)/DBSA-in-PEDOT:PSS/P3HT/DBSA-in-PEDOT:PSS/Au(top) were also fabricated by first preparing an aqueous solution of DBSA in PEDOT:PSS at various concentrations [% (w/w)], and then spin-coated on the bottom gold stip-line and top of P3HT layer at a very high rate. The *I-V* characteristics for all the sandwich cells are measured at room temperature by Keithley 6517 electrometer and at a pressure of 10^{-6} mbar. All the measurements are repeated a number of times on various samples of the same batch to check the reproducibility of results.

Samples for four-probe-conductivity (σ_{4Probe}) are fabricated by vacuum depositing four gold strips, having a width of 1 mm and separated by 50 μm, on a cleaned glass substrate by shadow masking. Aqueous solution of DBSA, prepared at various concentrations, was latter spin coated under ambient atmosphere followed by the spin coating of P3HT. The measurement of conductivity was performed in room temperature and under vacuum (10^{-6} mbar).

3. Results and Discussions

The *V-I* characteristics of Au(bottom)/P3HT/Au(top) sandwich cell is shown in Figure. 1. As can be seen, the current is preferred in one direction (bottom electrode at higher potential than the top one) and it is inhibited in the other (top electrode at higher potential than bottom). The current value increases nonlinearly for both the regimes of positive and negative potential (see inset figure 1). The resistance values at 60 and -60 V are 16 KΩ and 7.7 MΩ, respectively. For the measured room temperature conductivity of P3HT ($\sigma \approx 0.8 \times 10^{-6}$ S/cm),

a resistance of 2.5 KΩ is expected solely from the semiconductor bulk. A comparatively higher resistance in the both the positive and negative regions suggests that the contact resistance (R_c) offered by the Au/P3HT interface is enormous, especially in the case when the top electrode is at higher potential than bottom. More specifically, in the region of positive potential, R_c is 6.5 times higher than the P3HT bulk resistance (R_{P3HT}) at 60 V, whereas in the case of negative potential regime, it is about 3×10^3 times at -60 V. The possible reason for such a difference is analyzed in details, as in our previous report. In this investigation, we try to focus on how to reduce the contact resistance, so as to increase the current output from the device.

Doping the surface of the semiconducting material at the contact region is a technique which is used in silicon technology to yield extremely low contact resistance [9]. This surface treatment causes to increase the conductivity of the surface to a great extent along with the narrowing of band gap. As a result, the conduction (valance) band at the surface gets attuned to the Fermi level of the electron (hole) injecting metal electrode with no energy barrier. A very high contact resistance between metal/polymer-interface could be circumvented by using a similar technique as used in silicon technology. So, to reduce the contact resistance prevailing at Au/P3HT interface, the search and incorporation for the *right* dopant molecule for P3HT is required.

Among the various reported dopants for P3HT, the most well known are Iodine, $FeCl_3$, oxygen etc. It should be noted here that the *right* dopant molecule is the one which is bulky enough to resist any movement inside the polymer on application of external field. However, the size of all the above mentioned dopant molecule are small enough to allow movement inside the polymer network under the influence of applied electric field. Such movements could, not only result in instability, but also lack of reproducibility of *V-I* characteristics of the device. Therefore, the use of such dopants would not be appropriate for surface-doping of the conjugated polymer.

After much trial and error, it is found that the bulky DBSA molecule, a well known surfactant, could dope P3HT. Table 1 shows the room temperature conductivity of P3HT doped with various concentrations of DBSA. The method of doping is described in experimental section. Compared to the pristine P3HT, the conductivity increased by nearly four orders of magnitude as function of the concentration of DBSA. However, for concentrations of DBSA soln. less than 1 %, there is no noticeable increase in conductivity and it stayed more or less constant at concentrations greater than 10 %. The size of DBSA molecule is estimated to be about 10.3 Å, which is several times bigger than the size of any other known dopants for P3HT, and therefore there would be much less probability of migration of dopant molecule across the bulk of the semi-conducting polymer as compared to the other smaller sized dopants. Hence, the use of DBSA in P3HT could provide the intended surface doping at the Au/P3HT interface.

To confirm that DBSA is doping P3HT, the absorption and photoluminescence (PL) spectra are taken. Figure 2 shows the absorption spectra of P3HT doped with DBSA having a concentration of 10 % (w/w). For comparison, the absorption spectra for P3HT is also shown along with it. The appearance of shoulder at around 1.4 eV indicates the formation of polaronic/bipolaronic bands in P3HT. However, the magnitude of absorption is still high between the HOMO-LUMO levels as shown by the relatively higher peak point for energy values around 2.3 eV. PL spectra of P3HT doped DBSA for concentration of 1 % and 10 % is shown in figure 3. For a concentration of 1%, the PL count decreased with respect to a pristine film of P3HT. When the concentration is increased further by 10 times, i.e. 10 %, an absolute quenching of PL count is observed. This phenomenon of PL quenching is usual for any conjugated polymer system having high conductivity due to higher degree of doping [19,20]. This result, along with the absorption spectra and the measured conductivity values (see table 1), affirms that DBSA acts as a dopant to P3HT.

Sandwich cells in which both the top and bottom Au/P3HT contact are treated with DBSA, i.e. Au(bottom)/DBSA/P3HT/DBSA/Au(top), showed a resistance in the range of 10

to 50 Ω, and it was considered as a *short*. These values are far lower than the P3HT bulk

resistance (≈ 2.5 KΩ) and the contact resistance as determined from figure 1, and hence it is a

clear indication that the size of DBSA is not enough to help it anchor at the surface of P3HT.

In fact, DBSA diffuses across the bulk of P3HT sandwich cell, thereby doping the entire

semi-conducting region in the process. Although there is a reduction in contact resistance as

indicated by the *short circuit*, the uncontrolled doping is not of much implication in view of

its application to organic electronic devices.

In order to inhibit the diffusion of DBSA and keep it immobilized at the surface of P3HT,

a aqueous emulsion of DBSA and PEDOT:PSS was prepared. It is assumed that DBSA could

remain attached to the PEDOT chain through electrostatic interaction between the oppositely

charged chain and dopant moiety, just like the chain of PSS. Thus the emulsion of DBSA and

PEDOT:PSS could be visualized as a dangling dopant molecule hanging in all possible

directions from the polymer network, as shown for a small segment of chain in Figure 4. We

will next show that a fine layer of this emulsion between gold and P3HT could effectively

reduce the contact resistance present at the interface while suppressing the diffusion of the

dopant ions into the bulk of semi-conducting polymer.

The *V-I* characteristics of the Au(bottom)/P3HT/Au(top) sandwich cell treated with

PEDOT:PSS/DBSA emulsion for top and bottom interfaces is shown in figure 5. It could be

noticed that the plot is exhibits a great deal of linearity both in the positive and negative

potential regime. The non-linearity and unidirectionality of the *V-I* data for untreated cell (see

figure 1) have been totally eliminated. The inverse of the slope gives the resistance of the cell

and it is about 12 KΩ. Taking the resistance offered by P3HT bulk into consideration, the

total contact resistance could be deduced to be in the range of 10 KΩ. This value indicates a

colossal change in the contact resistance of Au/P3HT interface, a parameter that severely

limits the effective carrier mobility of P3HT based FETs as determined from its transfer

characteristics. If the data shown in figure 1 and 5 are compared, it could be noticed that

there is no substantial increase of current density in the regime of positive potential, but the

current density in the regime of negative potential changes by almost four orders of magnitude. This could be understood in the following manner. It is reported in our previous communication [8] that the hole barrier height at the top P3HT/Au contact is higher than that at bottom. In the negative potential regime, the top gold electrode is the hole injecting electrode and the difference in barrier height leads to unidirectional nature of charge injection. When the sandwich cell are treated with PEDOT:PSS/DBSA for the top and bottom contacts, the *effective* hole-barrier-height is substantially reduced due to surface doping of P3HT, thus resulting into higher current density (8.82×10^{-5} A/cm^2 and 0.3 A/cm^2 for the untreated and treated cell at -40 V, respectively). If the positive potential regime is considered, where the bottom gold contact is the hole-injecting electrode, the increase in current density is from 0.08 A/cm^2 for the untreated sandwich cell to 0.4 A/cm^2 for the treated one at a potential difference of 40 V.

The results reported here have wide implication to the performance organic electronic devices which are limited by severe contact resistance. It should be noted that the method described here could only be applied to sandwich type cells. To implement it to planar type organic devices, such as organic FET, could be rather difficult and may require innovative ideas to exploit this technique.

4. Conclusions

Sandwich cells of Au(bottom)/P3HT/Au(top) are fabricated and it showed non-linear unidirectional *V-I* characteristics. To improve the hole injection at the top and bottom Au/P3HT contacts, the concept of surface doping is implemented and DBSA is found out to be suitable bulky dopant, as was determined by four probe conductivity measurement of DBSA doped P3HT films. Absorption and photoluminescence data also confirmed that DBSA dopes P3HT. Sandwich cells treated with DBSA showed severe shorting problem and straight away confirmed that DBSA diffuses inside the film of P3HT despite its bulky size. To resist the diffusion of DBSA, aqueous emulsion of PEDOT:PSS/DBSA was prepared and

sandwich cells were treated with this emulsion at the top and bottom contacts. It was assumed that the charged chain of PEDOT could hold DBSA through electrostatic interaction. A completely linear *V-I* characteristics was obtained for these sandwich cells with higher current density with respect to the untreated cells and it indicated a drastic reduction in contact resistance by four orders of magnitude.

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Table Caption

Table 1: Four probe conductivity of P3HT doped with DBSA at various concentrations.
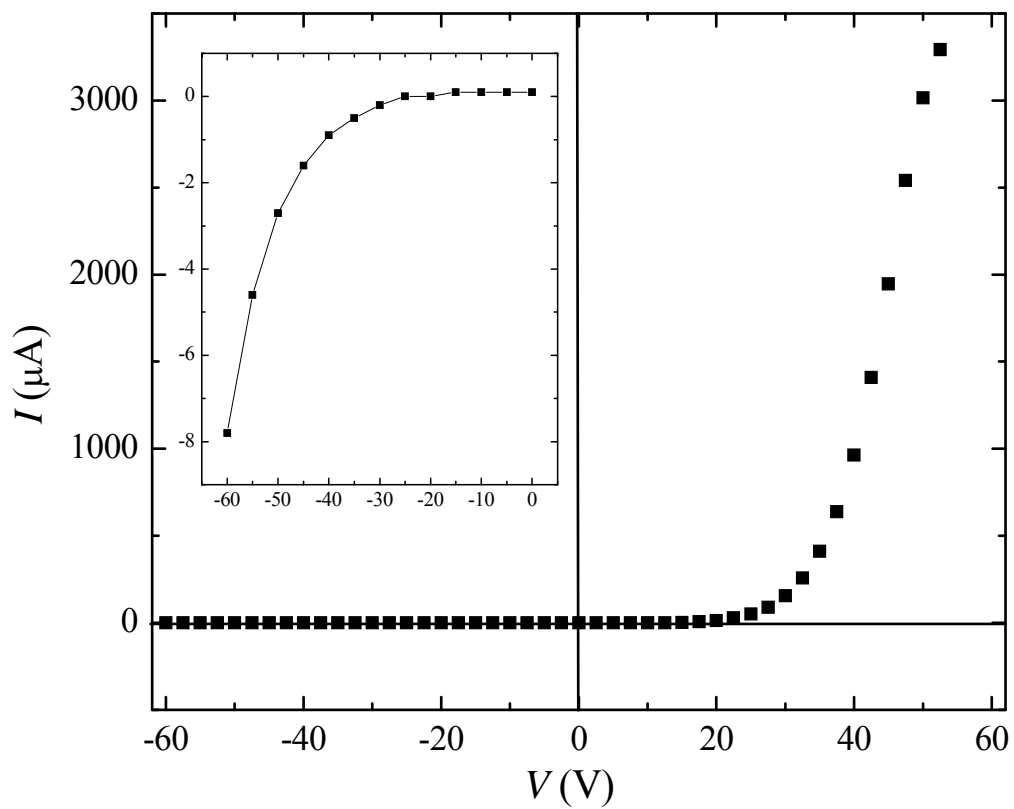

Figure Captions

Figure 1: *V-I* characteristics of Au(bottom)/P3HT/Au(top) sandwich cell. The inset shows the

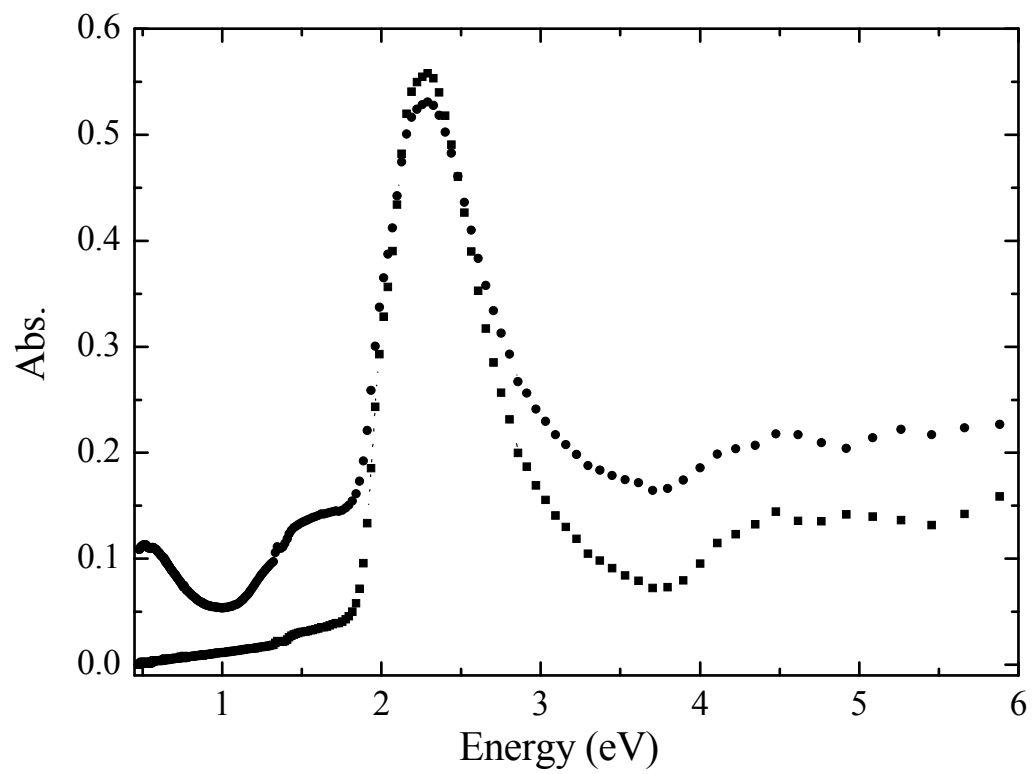negative potential regime data in its appropriate scale.

Figure 2: Absorption Spectra of pristine (■) and DBSA (10 % w/w) doped P3HT (●).
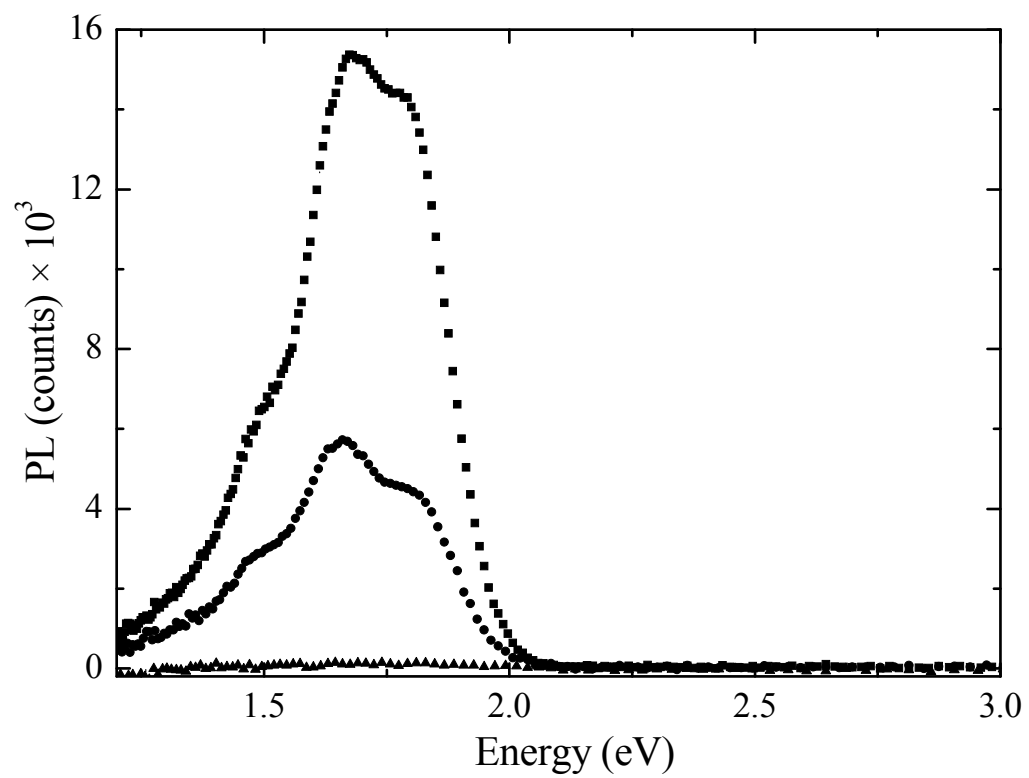

Figure 3: Photoluminescence spectra of pristine (■), 1 % (●) and 10 % (▲) DBSA doped

P3HT.

Figure 4: A schematic showing the picturisation involved in PEDOT:PSS/DBSA emulsion.

Figure 5: *V-I* characteristics of Au(bottom)/P3HT/Au(top) sandwich cell whose top and

bottom Au/P3HT contacts are treated with PEDOT:PSS/DBSA emulsion.

Table 1: Four probe conductivity of P3HT doped with DBSA at various concentrations.

Concentration of DBSA (% w/w)	Room temperature Conductivity (S/cm)
1	1.0×10^{-5}
2.5	3.8×10^{-5}
5	7.1×10^{-4}
7.5	5.0×10^{-3}
10	8.1×10^{-3}

Figure 1: *V-I* characteristics of Au(bottom)/P3HT/Au(top) sandwich cell. The inset shows the negative potential regime data in its appropriate scale.

Figure 2: Absorption Spectra of pristine (■) and DBSA (10 % w/w) doped P3HT (●).

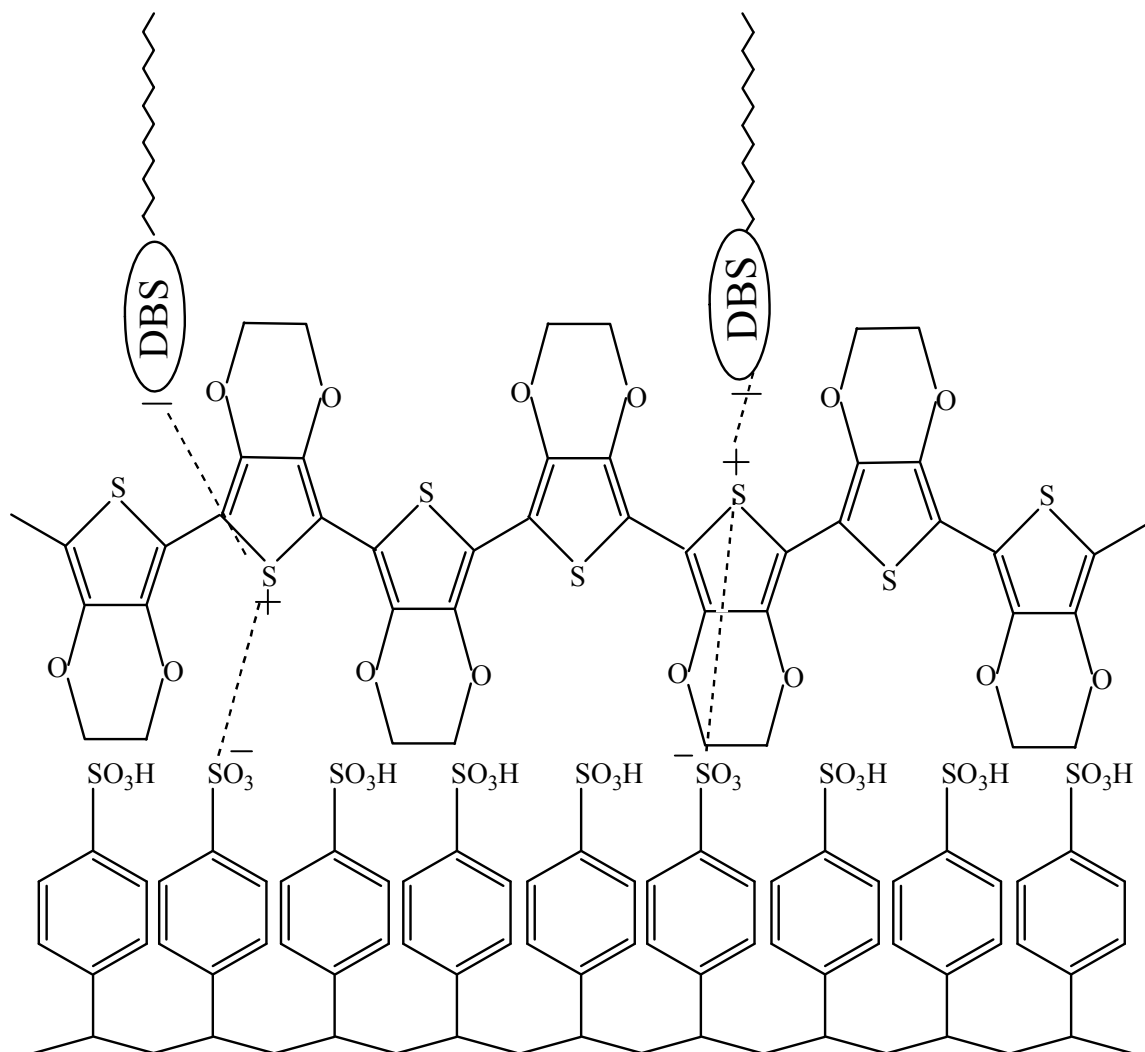Figure 3: Photoluminescence spectra of pristine (■), 1 % (●) and 10 % (▲) DBSA doped P3HT.

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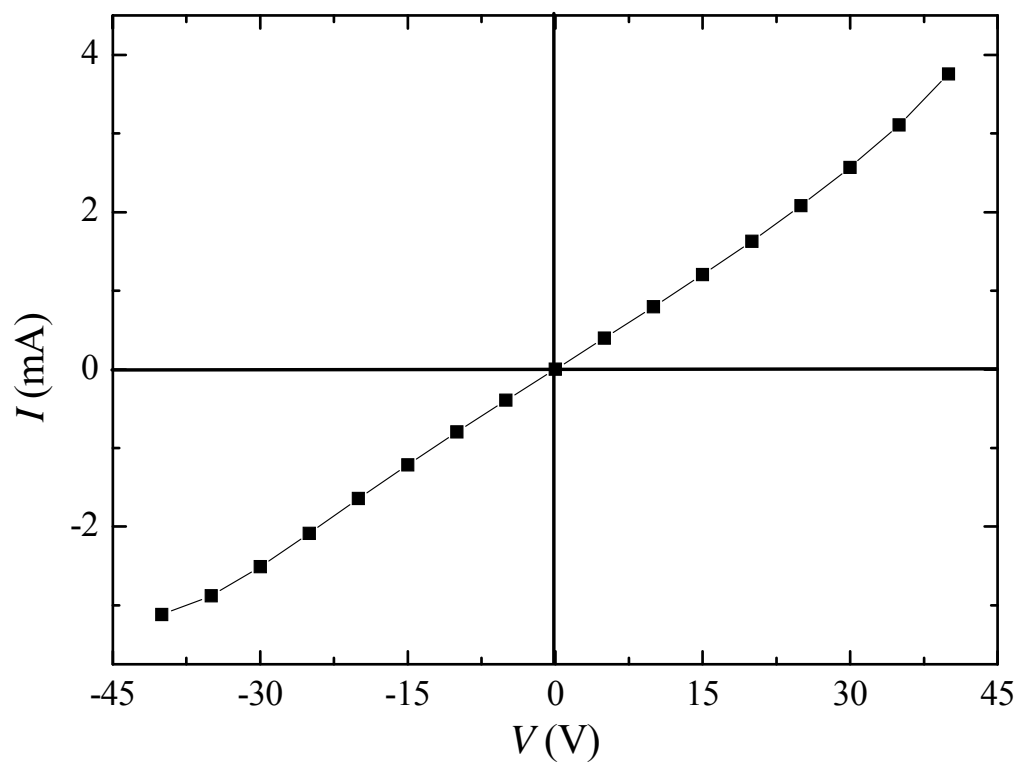
Figure 5: *V-I* characteristics of Au(bottom)/P3HT/Au(top) sandwich cell whose top and bottom Au/P3HT contacts are treated with PEDOT:PSS/DBSA emulsion.