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Abstract

We have used the introduction of shallow hole traps in poly(3-hexyl-thiophene) (P3HT) to test one of the predictions of the bipolaron theory of magnetoconductance. The results show that the introduction of shallow traps effectively increases the degree of energetic disorder in the transport states whilst not affecting the position of the Fermi level and that this results in an increase in the MC response. These results are demonstrated to be in qualitative agreement with the theory and suggest one mechanism through which trap states may affect the MC response of organic semiconductors. This work presents a controllable way of chemical doping to engineer a change in absolute current at a given bias depending on the choice of anodes. It also allows for tuning the magnitude of negative MC response and EL efficiency under different driving conditions.

Introduction

Charge transport and magnetoconductance (MC) response in organic semiconductor diodes can be affected by introducing trap states through different routes, both in small molecule and polymer based devices.[1-5] Three major models: Electron-Hole Pair model, [6] Bipolaron model [7] and Triplet-Polaron Interaction model [8] were reported to describe the MC or magnetoresistance (MR) effect. However, no single model can explain all the experimental results and the origin of MC is still under discussion (e.g. changes of sign and magnitude in nominally identical systems). [9-11]

In 2008, Niedermeier *et al*. [2] enhanced the MC in poly(paraphenylene vinylene) (PPV) through electrical stressing. They later attributed the increased MC to charge trapping effects. [3] In 2012 Wohlgenannt *et al*. [4] introduced charge trap states through X-ray irradiation of aluminium tris(8-hydroxyquinolate) (Alq_3) and obtained a similar increase in the magnitude of the MC. Neither of these groups, however, could clearly explain the nature of these traps (electron traps, hole traps or exciton traps) or the mechanism by which they enhance the MC. In 2013, Cox *et al*. [5] developed a chemical doping method using 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) as an electron trap centre in poly(p-phenylene vinylene) (PPV), and 4-(dicyanomethylene)-2-methyl-6-(dimethylaminostyryl)-4H-pyrane (DCM) as an electron trap filling material. Their results showed that the MC response decreased through electron trap filling by DCM, but kept constant with the F4-TCNQ doping. This suggested that electron trapping centres were the origin of at least some of the MC in PPV, and filling the electron trap states would suppress the MC response.

Within the bipolaron model it is predicted that the MC response will increase as the energetic disorder in the conduction levels increase (providing the Fermi level remains constant). If shallow trap states are introduced into the gap of an organic semiconductor they have the effect of broadening the energetic disorder. Therefore this may provide a possible explanation for one mechanism by which trap states could enhance the MC response. Pentacene, due to its elevated highest occupied molecular orbital (HOMO), can act as a hole-trap centre in (P3HT). Using literature values, [12-13] we take 5.0 eV as the average ionisation potential (HOMO position) of pentacene and 3.0 eV as the electron affinity (LUMO position). Similarly, we have used literature values [14] for the HOMO and LUMO positions in P3HT, namely 5.2 eV and 3.0 eV respectively. This system therefore provides a simple test where we can control the concentration of shallow trap centres in P3HT and investigate their role on current transport and MC.

Experimental Details

All measurements were performed on "unipolar" device structures consisting of ITO/P3HT(X% Pentacene doped)/Au. The P3HT was dissolved in 1,2-dicholobenzene (30 mg/ml) and pentacene added in different amounts (0%, 2%, 5% and 10% by weight). 300 nm thick P3HT layers were formed by successively spin coating the polymer solution 5 times at 1000 rpm for 1 minute resulting in a smooth 300nm thickness film on the ITO coated

substrate. After annealing at 120 °C under nitrogen for 15 minutes, a 50 nm Au counter

electrode was evaporated (typically at ~10^{-6} mbar and ~5 A.s^{-1}). All polymer thicknesses were measured using a Dektak surface profilometer. Immediately after growth, the devices were placed in a light-tight, evacuated (~10^{-5} mbar) sample holder.

For the dark injection transient current measurements (DI) [15] a step voltage was applied to the device whilst the current through the device as a function of time. A pulse generator (TTi TG1010A) provided the bias and the resulting current transient was detected as a voltage drop across a load resistor (typically 50 Ω) connected to the input of an Agilent Infinium digitizing oscilloscope. The dark injection transients were analysed by fitting a cubic function to the region around the peak and differentiating to find the maximum value. At large electric fields, where the RC displacement current decay interferes with the DI peak, a differential amplifier and sample matched capacitance are used to subtract the RC decay from the signal. Details of this method are given by Helfrish and Mark [16] and also J.C. Scott [17].

MC measurements were taken with the device operated in constant voltage mode. Magnetic field measurements were made from 0 to 300 mT for positive fields only (earlier tests had shown that the direction of the field did not affect the results [8]). Immediately before and after each field measurement, a measurement at null field was taken. The two null-field measurements were then averaged and used to calculate the change in current and intensity with applied magnetic field. A Keithley 236 source-measure unit was used to average the current measurements over 16 readings and the drive voltage was applied to the device only when it was in a stable field.

Results and Discussion

Figure 1 shows the measured current density versus nominal electric field for a number of Au/P3HT/ITO devices in forward and reverse bias with different pentacene doping concentrations. We define forward bias where the Au acts as the anode, and reverse bias where the ITO acts as the anode. Pure P3HT unipolar devices show very different current densities in forward and reverse bias. This is probably due to the higher Au work function (5.0 eV), compared to ITO (4.9 eV), (using literature values [18-19]) resulting in improved hole injection from the Au.

As the pentacene concentration increases, the forward bias current is initially reduced at a given bias), whereas the reverse bias current increases. The decrease in current density in forward bias can be attributed to the hole trapping effect of pentacene and subsequently reduced mobility. Any improved hole injection from the Au, due to the presence of pentacene, is more than offset by the trapping effect. When the pentacene concentration reaches 10%, there is a significant increase in current density. This may be due to holes hopping through the HOMO levels of the pentacene at such high concentrations and/or significantly increased hole injection from Au directly into the pentacene HOMO. Both these effects will lead to a recovery in current density.

In contrast to the forward bias results, the effect of increasing pentacene doping in reverse bias is one of a steady increase in current density. This is because in reverse bias, holes can be injected from the ITO into the pentacene HOMO with a reduced barrier (0.1 eV) compared to P3HT (0.3 eV). The increase in pentacene doping concentration can therefore lead to an increase in the hole injection efficiency which dominates over the reduced mobility caused by the shallow hole trapping effect of the pentacene.

In order to investigate the effect of shallow trapping due to pentacene doping, we measured the mobility in Au/P3HT/ITO devices using DI. Figure 2(a) shows typical DI current transient results, with and without the use of a differential amplifier to remove the RC contribution to the transient current. The dark injection peak time, t_{DI}, scales correctly with bias (decreasing with increasing bias) and is unaffected by the differential amplifier. The dark injection time, t_{DI}, is related to the transit time, t_{trans}, by $t_{DI} \approx 0.786 t_{trans.}$ [20]

We note that DI transients displaying clear peaks were only obtained using Au as the anode, due to the comparatively poor hole injection from ITO compared to Au and the sensitivity of the technique to the presence of any injection barrier. In figure 2(b), the reciprocal of the transit time is plotted against the nominal electric field (E). The gradient of such a plot is equal to the charge mobility divided by the thickness (μ/d) and the plot also highlights any trapping effects which may manifest themselves as a noticeable y-axis intercept. In the pure P3HT sample the intercept in figure 2(b) is zero indicating that there is no trapping and that the mobility obtained by the gradient corresponds to the mobility, μ, commonly calculated at a given field using equation 1:

$$\mu = \frac{v_d}{E} = \frac{d^2}{V t_{trans}} = \frac{0.786 d^2}{V t_{DI}} \tag{1}$$

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Where, μ is the mobility, v_d is the drift velocity of the carriers, E is the applied electric field, V is the applied bias voltage, d is the thickness of P3HT, t_{DI} is DI transit time.

However, as the pentacene concentration in the system is increased, the intercept becomes larger which suggests an increasing trap concentration. We therefore introduce the parameter $t_{trapping}$ to describe the trapping effect. Of course for shallow traps, there is a de-trapping process which is affected by the temperature. Thus the parameter $t_{trapping}$ includes at least two effects, trapping and de-trapping. Here we just describe that the parameter $t_{trapping}$ decreases as the concentration of the trap states increases, because the trapping effect will block the charge transport. When the carriers are being depleted by these two effects the overall rate is the sum of the individual rates as per equation 2:

$$\frac{1}{t_{trans}} = \frac{1}{t_{extraction}} + \frac{1}{t_{trapping}} = \mu \frac{V}{d^2} + \frac{1}{t_{trapping}} \tag{2}$$

Here, the parameter $t_{extraction}$ is the charge transport time without the trapping effect.

The inset in figure 3(b) shows the average hole mobility, calculated from the gradient, versus pentacene concentration. The mobility first decreases and then increases when the concentration reaches 10%. We attribute the decrease to the hole-trapping effect and the increase to transport through the pentacene electronic states which no longer act as traps due to their high concentration. At the same time, the intercept in figure 2(b), which corresponds to the trapping rate, keeps increasing as the concentration of pentacene increases. This confirms that pentacene acts as a hole-trap centre when introduced into P3HT.

From the bipolaron model it is predicted that as the absolute value of $|E_F/\sigma|$ decreases, where E_F is the Fermi level and σ is the density of state (DoS) distribution, assuming a Gaussian disorder model, the magnitude of the MC response will increase. We can model the effect of pentacene doping on E_F and σ for P3HT by taking the literature values for each material [21-22] and adding the corresponding Gaussians in the ratio of their concentrations in the doped layers. If we then fit the resulting distribution with a simple Gaussian we can obtain the effective E_F and σ for the doped layer. This procedure was carried out numerically on a desktop computer by adding two DOS states, one centered at -5.2 eV with a width of 70meV representing the P3HT and one centered at -5 eV also with a width of 70 meV, representing the Pentacene, whose integrals were chosen to be in the ratio of 9:1 respectively.

The mean and standard deviation of the resulting distribution yielded HOMO and σ for the

doped sample. An example of this is given in table I for the 10% doped sample.

From Table I it can be seen that the Fermi level shift is negligible with doping, but the change in σ is significant. This therefore results in a change of $|E_F/\sigma|$ of ~6.8% for the 10% doped layer. Simulations based on the bipolaron theory [23] show that the MC response will increase as the absolute value of $|E_F/\sigma|$ decreases.

We therefore investigated the MC response for the doped P3HT layers in both the forward and reverse bias regions as a function of the pentacene doping concentration. Although we have utilised a "unipolar" device structure for these measurements it is still vital to keep the operating voltage low in order to stop any electron injection which would complicate the analysis. We observed that in our devices the MC response was always negative and could be well fitted with a single non-Lorentzian curve provided the operating voltage was kept between -1V and 1V. Above these voltages we began to see a positive spike at low magnetic fields which evolved into a positive MC response at higher drive voltages. We believe that this is evidence that other processes were being introduced which were correlated with the onset of some electron injection. Figure 3 shows the MC response of the P3HT layers at operating voltages from 0.6 to 1.0V as a function of operating voltage. The solid lines on the graphs are fits using the non-Lorentzian model but should only be taken as a guide to the eye as the experimental scatter in the data makes accurate fitting difficult. However, it can be clearly seen that at each voltage the effect of the pentacene doping is to increase the magnitude of the MC response by an order of magnitude. It has been reported in the literature, [24] that pentacene shows a negative MC response as high as ~-0.3% under room temperature and there is a transition from negative MC ~-0.4% (low bias <5 V) to positive MC ~+0.4% (high bias >5 V) in P3HT. [25-26] However, the increase of negative MC response under low bias in our system cannot be explained by a combination of P3HT and pentacene MC response as the maximum concentration of pentacene is 10% and we see a factor of 3 to 5 increase in the MC response even at pentacene concentrations as low as 2 to 5%. We therefore conclude that the increase of negative MC under low bias is mainly due to the pentacene-doping which effectively broadens the DoS for the P3HT whilst having no effect on the Fermi energy level. This data supports the view that at low bias voltages in unipolar samples of P3HT the MC response can be fully explained by the bipolaron theory. [23]

Conclusion

Our results show that pentacene acts as a hole-trap centre in P3HT and always causes a decrease in hole mobility under low concentration in unipolar devices. At the same time, it improves the hole-injection for ITO anodes. It is thus possible to engineer both an increase or decrease in device current depending on choice of anode. We have proved that it is the hole trap states that lead to an enhancement of negative MC under low bias probably due to the density of states (DoS) broadening compared to pure P3HT which coincides with the simulation results based on Bipolaron theory. [7] These results provide one possible explanation for the observation by Niedermeier [2-3] and Wohlgenannt [4] that the enhanced MC results from the presence of traps and suggest one mechanism through which this observation could be explained.

Acknowledgements

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Table I Summary of modelled parameters for P3HT, pentacene and 10% doped sample.

	P3HT (eV)	Pentacene (eV)	Doped sample (eV)
HOMO(μ)	-5.200	-5.000	-5.197
σ	0.070	0.070	0.075
E_F	-4.100	-4.000	-4.098
$|E_F/\sigma|$	59	57	55

Figure captions

Figure 1: Current density as a function of nominal electric field for Au/P3HT/ITO based devices under different pentacene doping concentrations.

Figure 2: (a) Typical DI current transients obtained in an Au/2% pentacene doped P3HT/ITO sample with and without the differential amplifier circuit under different bias. The sample was biased in the forward direction (Au positive). The use of the differential amplifier does not affect the t_{DI} obtained (arrowed). (b) $1/t_{trans}$ versus electric field for unipolar devices (Au/P3HT/ITO) under different pentacene doping concentration. The inset shows the hole mobility obtained from the slope of the main graph versus pentacene doping.
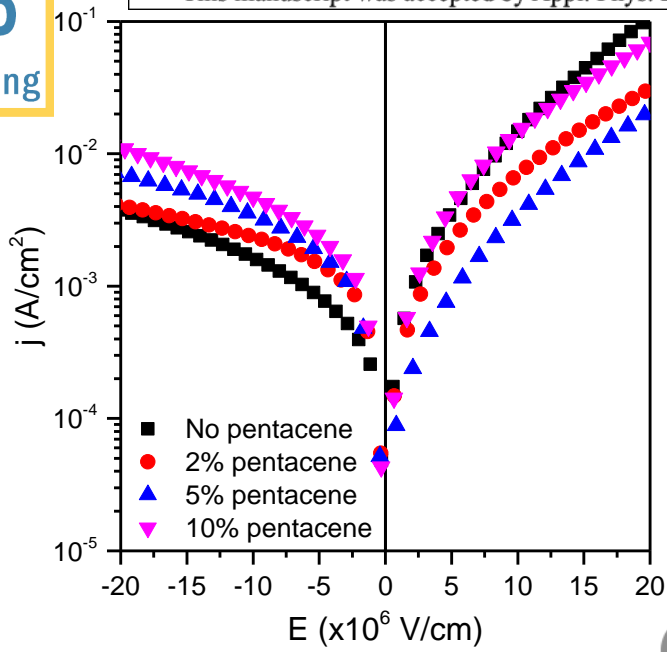
Figure 3: (a) Differential current data as a function of magnetic field for the unipolar devices (Au/P3HT/ITO) with different pentacene content. All MC data measured under 1V, (a) 0.6V, (b) 0.8V, (c) 1.0V.

Figure 1

Figure 2

Figure 3

Figure legend:
- ■ No pentacene
- ● 2% pentacene
- ▲ 5% pentacene
- ▼ 10% pentacene

Axis labels: j (A/cm^2) versus E ($\times 10^6$ V/cm)

(a)

Bias10V No Differential Amplifier
Bias10V With Differential Amplifier
Bias 5V No Differential Amplifier
Bias 5V With Differential Amplifier

(b)

Pure P3HT
2% pentacene
5% pentacene
10% pentacene

(a) Au/P3HT/ITO Bias 0.6V

$\Delta I/I(\%)$
B (mT)

- pure P3HT
- 2% pentacene
- 5% pentacene
- 10% pentacene

(b) Au/P3HT/ITO Bias 0.8V

$\Delta I/I(\%)$
B (mT)

(c) Au/P3HT/ITO Bias 1.0V

$\Delta I/I(\%)$
B (mT)