



Reduced hole mobility due to the presence of excited states in poly-(3-hexylthiophene)

Song, JY; Stingelin, N; Gillin, WP; Kreouzis, T

For additional information about this publication click this link.

<http://qmro.qmul.ac.uk/jspui/handle/123456789/4063>

Information about this research object was correct at the time of download; we occasionally make corrections to records, please therefore check the published record when citing. For more information contact scholarlycommunications@qmul.ac.uk

Reduced hole mobility due to the presence of excited states in poly-(3-hexylthiophene)

J. Y. Song, N. Stingelin, W. P. Gillin,^{a)} and T. Kreouzis

Department of Physics, Centre for Materials Research, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

(Received 18 September 2008; accepted 24 November 2008; published online 12 December 2008)

The hole mobility in poly-(3-hexylthiophene) samples is measured by the dark injection transient technique in both hole only and ambipolar devices. By applying a small offset bias prior to the voltage step, electronic excited states are generated in the ambipolar but not in the hole only devices. The presence of excited states reduces the room temperature hole mobility (typically $5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by as much as 15% compared to that measured without offset, in contrast to the hole only devices where no significant mobility reduction is seen at the same, or indeed higher, current densities. We attribute the lower mobility to interactions between the charge carriers and the long lived triplet states and to an effective reduction in the number of transport sites available.

© 2008 American Institute of Physics. [DOI: 10.1063/1.3049129]

Organic semiconductors are of increasing technological interest in applications such as light emitting diodes, field effect transistors, and photovoltaic devices.¹⁻³ Charge transport in these materials is believed to occur by hopping between available sites and has been extensively studied theoretically, experimentally, and by simulation (for an excellent review on this topic, see Ref. 4). Many factors affect hopping transport, such as wave function overlap between neighboring sites, general morphological considerations (e.g., material phase), and the often quoted energetic and positional disorders in the transport site distribution. Although excitons are known to react with free charges,⁵ the effect that excited states may have on the charge transport is not generally considered in the field of organic electronics. This occurs even though organic light emitting diodes (OLEDs) are known to contain large numbers of triplet states during operation⁶ and hence the role of excited states on carrier mobility could mean that the actual mobility in working devices is considerably different from those measured in idealize time-of-flight measurements. Indeed it is quite possible that the mobility in working devices may well be a function of drive current as the excited state population will change with operating conditions. This work is thus motivated by both technological and fundamental scientific interest.

Poly-(3-hexylthiophene) (P3HT) thin films of typically $1 \mu\text{m}$ thickness were solution cast from chloroform ($\sim 7 \text{ wt } \%$) onto Au covered glass substrates, which was followed by thermal evaporation of 100 nm Au or Al counter electrodes, for the fabrication of hole only and ambipolar devices, respectively. The polymer thickness was measured using a Dektak surface profilometer. The device area was 15 mm^2 .

For both the dark injection (DI) and current-voltage (I - V), measurements devices were housed in a vacuum chamber ($\sim 10^{-5} \text{ mbar}$ pressure). A Berkley nucleonics (model 6040) pulse generator supplied the voltage step required to carry out the DI experiment; this was either connected directly to the substrate electrode (in the case of no

offset) or fed into one of the inputs of a summing amplifier, with the other input connected to a dc supply (in the case of measurements with offset) and the amplifier output then connected to the substrate electrode. Before carrying out the DI measurements, the amplifier output was monitored using a Tektronix TDS2002 oscilloscope and the size of the offset and absolute value of the voltage step was recorded and if necessary adjusted. The DI current transient was observed as a voltage drop across a load resistor (typically 479Ω) connected to the input of a buffer amplifier whose output was digitized using a Tektronix TDS2002 oscilloscope. Signal averaging over several pulses was carried out to reduce white noise at a frequency of 5 Hz .

Figures 1(a)–1(d) show the DI transients obtained under different biases both with and without offset in an ambipolar (Au–Al) sample. The peak time t_{DI} scales correctly with applied bias [Figs. 1(a), 1(c), and 1(d)] and is clearly detectable when an offset is applied [Fig. 1(b)]. The mobilities are calculated using the expression

$$\mu = \frac{d^2 \times 0.786}{V t_{\text{DI}}}, \quad (1)$$

where d is the sample thickness, V is the voltage pulse amplitude, and t_{DI} is the time at which the DI current peak occurs. The numerical factor 0.786 relates the DI time to the transit time.⁷ The calculated hole mobilities are shown as a Poole–Frenkel plot in Fig. 2 showing a slight electric field dependence, both with and without offset, and are comparable to those reported in the literature for P3HT.^{8,9} We note that although the sample is ambipolar, hole DI transients show a clear space-charge cusp. This suggests that the electron injection and transport within these devices is not balanced to that of the holes, as observed in some cases for P3HT.⁹ Indeed, we prepared our devices in air, which is likely to result in strong electron trapping, limiting electron transport in a more pronounced fashion compared to the hole transport. We also note that the average zero offset P3HT hole mobilities for the two types of sample (unipolar and ambipolar) are in agreement, given sample to sample variation, being $\mu_{\text{Au–Au}} = (5.1 \pm 0.9) \times 10^{-5} \text{ cm}^2/\text{V s}$ and $\mu_{\text{Au–Al}} = (4.8 \pm 1.8) \times 10^{-5} \text{ cm}^2/\text{V s}$. This shows that there is no dif-

^{a)}Electronic mail: w.gillin@qmul.ac.uk.

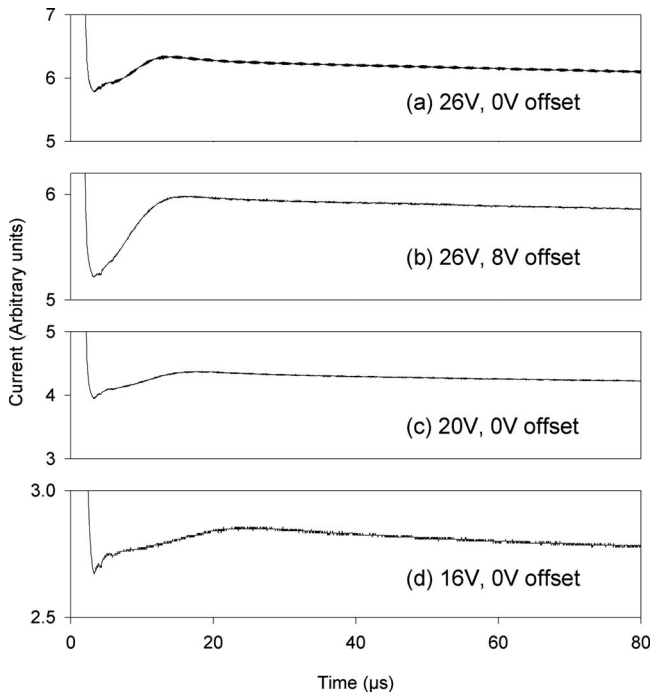


FIG. 1. Typical DI currents obtained in a 1.1 μm thick ambipolar sample. (a) 26 V bias, zero offset. (b) 26 V bias, 8 V offset. (c) 20 V bias, zero offset. (d) 16 V bias, zero offset. The approximate position of peak time t_{DI} used to calculate the mobility is shown as a guide for the eyes.

ference in the samples due to the use of gold or aluminum as the top contact such as from metal diffusion into the devices.

Figure 3 shows the mobility ratio, defined as the calculated mobility with nonzero offset, divided by the mobility at zero offset, i.e., $\mu(\text{offset} \neq 0) / \mu(\text{offset} = 0)$, plotted versus the offset for three hole only (Au–Au) and three ambipolar (Au–Al) architectures. The hole only devices show virtually no change in hole mobility irrespective of the offset, up to 8 V, strongly suggesting that at the experimental carrier concentrations, all hole traps are filled (if there were unfilled hole traps, then an increase in measured mobility would result from the increased offset). For offset voltages below ~ 0.6 V, the data obtained for ambipolar structures are simi-

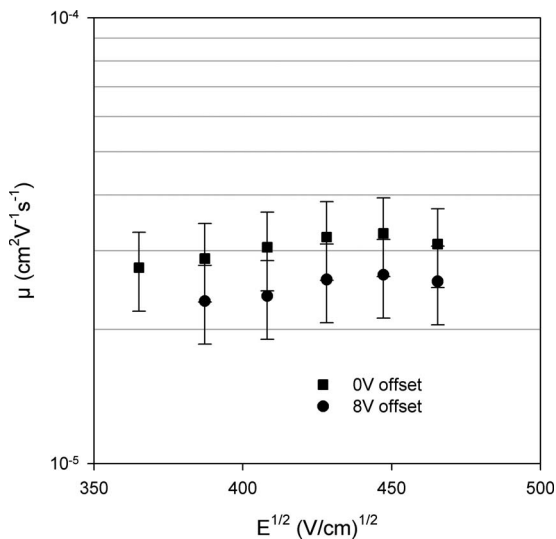


FIG. 2. Pool-Frenkel plot of the hole mobilities calculated for a 1.1 μm thick ambipolar sample with and without an offset.

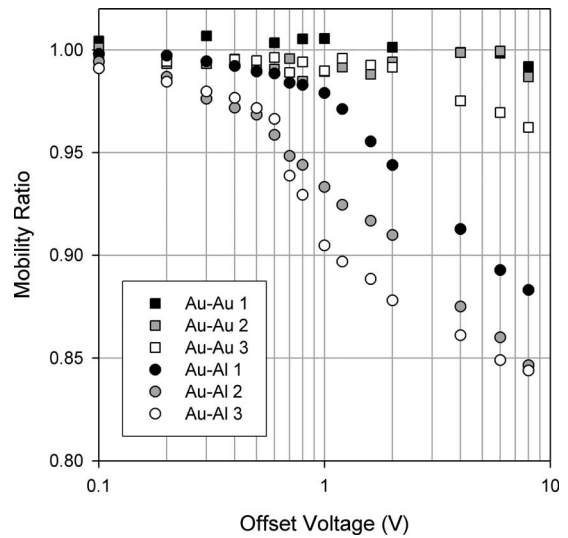


FIG. 3. The mobility ratio vs offset for hole only (Au–Au) and ambipolar devices (Au–Al). All measurements were carried out at 26 V bias and the device thicknesses ranged from 1.0 to 1.3 μm .

lar to those observed for hole-only devices insofar as the mobility is unaffected. At voltages $> \sim 0.6$ V, however, we observe a marked decrease in mobility with offset in the case of ambipolar device architectures.

Figure 4 shows the current-voltage characteristics of the two types of device investigated here. We note that the hole-only characteristic displays no sharp transitions and tends to space-charge limited ($I \propto V^2$) at high voltages. It also shows much higher current densities at low voltage compared to the ambipolar device. The latter can be due to a combination of factors, such as interpenetration of the evaporated gold within the organic layer (effectively reducing the device thickness) and the efficient hole injection and extraction by gold. The ambipolar structures show typical diode device behavior consisting of a hole only current at low voltages, a sharp increase in current at ~ 0.8 V (the turn on, associated with the onset of electron injection), and a space-charge limited ($I \propto V^2$) regime developing at high voltages. Note that the onset of electron injection in Fig. 4 (~ 0.8 V), corre-

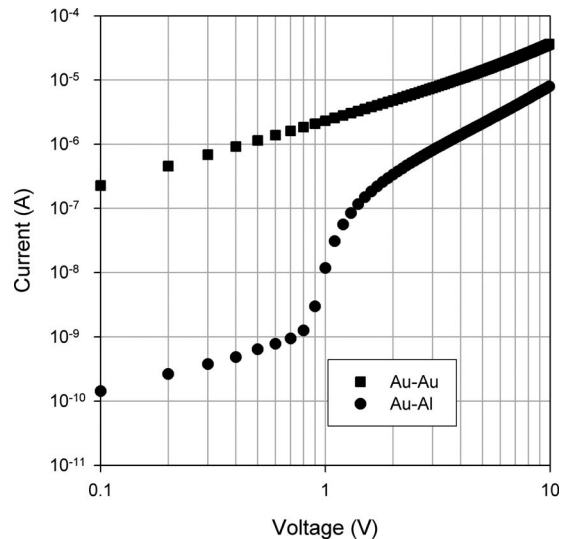


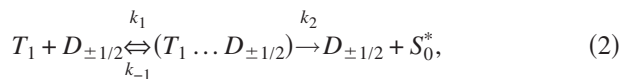
FIG. 4. Current-voltage characteristics for ambipolar (Au–Al) and hole only (Au–Au) devices.

sponds to the onset of mobility reduction (~ 0.6 to 1 V) seen in Fig. 3.

We attribute the reduction in hole mobility (Fig. 3) to interactions of the holes with excited states present in the P3HT. This is for the following reasons. If the lengthening of the DI arrival time were solely due to the injection of electrons into P3HT and the corresponding electrostatic screening effect of these electrons, then the arrival time would not be affected by the offset.

Clearly, electrons will be readily trapped in our devices and as a consequence will directly interact (electrostatically) with injected holes. We observe an offset hole current, however, prior to the application of the DI step, therefore, it is reasonable to assume that all trapped electrons will have formed a bound electron-hole pair before the DI measurement is carried out. Given the long time (~ 200 ms) for which the offset is applied before the DI experiment is carried out, it might be argued that most bound pairs would be in the form of triplet excitons. Triplet excitons, however, are long lived, thus, can be expected to diffuse throughout the bulk of the P3HT film prior to the DI pulse being applied.⁶

Several microscopic mechanisms for the interaction between transiting holes and excited states may be considered. If the transiting hole has the same spin state as the hole on the triplet, then the exciton acts as a blocked site for the transiting hole and will reduce the mobility. We note that the electron in the exciton cannot easily bind with the transiting hole (releasing its own hole for transport) as the triplet binding energy prevents this. It is possible that this interaction could occur but there would be some energetic barrier to overcome and hence at the very least there will be some degree of site blocking or transport delay. If the transiting hole has a different spin state to that on the exciton then there are two possibilities. The triplet can be quenched by the free carrier or can interact with it, but leaving a hole and triplet, resulting in an effective scattering interaction. These two processes are summarized in Eq. (2).⁵



where $D_{\pm 1/2}$ is the hole, and k_1 and k_{-1} denote the rate of formation and backscattering from a pair state ($T_1 \dots D_{\pm 1/2}$), k_2 is the rate for triplet quenching. Both of these processes will take some time and reduce the hole mobility. The net effect is that, on average, half of the triplet exciton sites are disallowed as transport sites, as far as the transiting holes are concerned, and the others would still cause interactions with the hole, which would be expected to reduce the mobility.

In conclusion, we have measured a reproducible and significant reduction in hole mobility in conditions where the P3HT contains excited states and have shown that this is exactly what would be expected from the known interactions between free carriers and excitons, resulting in site blocking. In the device structures used in this work, the triplet concentrations should be much less than those obtained in operating OLED devices and yet mobility reductions of 15% are easily obtained. This suggests that much larger changes in mobility may be observed in OLED type device structures. Future work planned involves measuring the increased positional disorder, which is expected to result from such site blocking, as well as correlating the reduction in mobility due to electrically pumped excited states with light output in emissive systems.

The authors wish to thank Professor Jenny Nelson (Imperial) for fruitful discussions and Merck Chemicals for providing the P3HT.

¹R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Longlund, and W. R. Salaneck, *Nature (London)* **397**, 121 (1999).

²H. Sirringhaus, *Adv. Mater. (Weinheim, Ger.)* **17**, 2411 (2005).

³J. Nelson, *Curr. Opin. Solid State Mater. Sci.* **6**, 87 (2002).

⁴D. Hertel and H. Bassler, *ChemPhysChem* **9**, 666 (2008).

⁵V. Ern and R. E. Merrifield, *Phys. Rev. Lett.* **21**, 609 (1968).

⁶M. A. Baldo and S. Forrest, *Phys. Rev. B* **62**, 10967 (2000).

⁷M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970).

⁸A. J. Mozer, N. S. Sariciftci, A. Pivrikas, R. Osterbacka, G. Juska, L. Brassat, and H. Bassler, *Phys. Rev. B* **71**, 035214 (2005).

⁹S. A. Choulis, Y. Kim, J. Nelson, D. D. C. Bradley, M. Giles, M. Shkunov, and I. McCulloch, *Appl. Phys. Lett.* **85**, 3890 (2004).