Effect of excited states and applied magnetic fields on the measured hole mobility in an organic semiconductor

J. Y. Song,[1] N. Stingelin,[2] A. J. Drew,[1] T. Kreouzis,[1] and W. P. Gillin[1]
[1]*Department of Physics, Centre for Materials Research, Queen Mary University of London, London E1 4NS, United Kingdom*
[2]*Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom*
(Received 24 May 2010; published 20 August 2010)

The hole mobility in thin films of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine has been measured using the dark injection transient method. These measurements were performed in the presence of a small, variable offset bias in unipolar and ambipolar samples, with and without an applied magnetic field. A reduction in mobility is observed in ambipolar samples at offset values above the turn-on voltage and is consistent with site blocking by triplet excitons. This is directly linked to the presence of electrically generated excited states by measuring the current-voltage-luminescence characteristics of such devices. The application of a ~500 mT magnetic field has the effect of increasing the measured mobility; an effect that is enhanced by the presence of excited states in ambipolar samples (from ~3.2% below turn-on to ~6.5% above), as opposed to the unipolar samples, where it remains constant independent of offset voltage. We thus conclude that the observed mobility enhancement with magnetic field in ambipolar structures is a result of a decrease in the concentration of site-blocking triplet states and provides direct measurement of a microscopic mechanism accounting for the phenomenon of organic magnetoresistance.

DOI: 10.1103/PhysRevB.82.085205 PACS number(s): 72.80.Le, 72.10.−d, 72.20.Dp, 75.47.−m

I. INTRODUCTION

Charge-carrier transport in organic materials is of considerable interest due to the recent development of organic electronics. For example, organic light emitting diodes (OLEDs) were first demonstrated in 1987 (Ref. 1) and since then improvements have resulted in a number of commercially available devices. Despite this there are still gaps in our knowledge of the charge transport mechanisms that operate in these devices. For example, very little attention has been paid experimentally to the role of excited states on charge transport despite the knowledge that, by definition, OLEDs have extremely high excited-state populations. Some work has been done however on a theoretical level. Agranovich *et al.*[2] studied the possibility of charged excitons in 2001 and their work showed that not only could such sites exist but that they should act as shallow traps with energies on the order of 10–100 meV.

It is well known that magnetic fields can play a role in a number of excitonic processes in organic semiconductors[3] and in 2003 it was observed that magnetic fields can have dramatic effects on the current through OLEDs;[4] this effect has been named organic magnetoresistance (OMR) and it has been attracting increasing interest,[5–11] partly because it is surprisingly universal. A number of models have been proposed to account for OMR, which can be divided into two main groups. The first class, which are in the majority, are exciton-based models,[4,9–11] although there are notable differences within this group. Some suggest that the OMR is due, at least in part, to increased dissociation of either singlets[4,9,10] or triplets;[11] one model suggests that interactions between triplets and polarons is the predominant effect.[11–16] In addition to these excitonic models there is also a bipolaron model,[17] which suggests that organic magnetoresistance can be observed in unipolar devices. However, pure unipolar devices are very hard to achieve in thin laminar device structures due to the very large electric fields in the devices. This can even result in electron injection from high work function cathodes such as gold with relatively modest applied voltages.[14] Many of the excitonic models also explain the changes in light output or efficiency that are normally observed along with the changes in current. They all assume that the magnetic field introduces a level of intermixing between the singlet and triplet states, either at the level of the pair state[4] or at the excitonic level.[11] This mixing is generally claimed to result in higher singlet concentrations, hence the improved light output. The model of Kalinowski *et al.*,[4] as well as some of the others,[9,10] then assume that the exciton dissociation is higher for the singlet state and it is this effect that increases the current.

In contrast, the triplet-polaron interaction (TPI) model[11,17] suggests that while the magnetic field alters the singlet-triplet ratio, thus giving the increased efficiency, the dominant mechanism behind the change in current is the effect of the triplets on the mobility of carriers (polarons). Under this model the triplets act as a shallow trap[2] for the polaron and can additionally act as a transport blocking site or interaction center for polarons, which may result in triplet quenching, depending on the relative spin state of the polaron and triplet. Therefore, if the triplet concentration is reduced the mobility will increase. This contrasts with dissociation-based excitonic models, which all predict no change in mobility for carriers with increasing exciton concentration and consequently no change in mobility with either drive voltage or an applied magnetic field.

Recently, we reported preliminary dark injection (DI) measurements on poly-(3-hexylthiophene) (P3HT) and found that we can correlate a decrease in mobility with the onset of ambipolar current injection.[18] These proof of principle measurements showed that it is possible to perform DI measurements with a dc bias applied prior to the DI pulse. They demonstrated the effect of sample preconditioning (e.g., prior

hole injection or hole *and* electron injection) on the measured mobility and showed that in the P3HT system there is a reduction in mobility for ambipolar devices that is coincident with the device turn on. In this paper we report a study of the mobility of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) layers, using DI with a dc bias and the effect of a magnetic field on these measurements.

II. EXPERIMENTAL METHOD

The samples comprised plasma treated indium tin oxide (ITO) coated substrates covered by a vacuum deposited (~600-nm-thick) layer of TPD followed by either an aluminum or gold vacuum deposited cathode (~80 nm thick). The ITO substrate was patterned using photolithography and cleaned by sequential ultrasonication in detergent solution, water, acetone, and chloroform. Following this, the ITO was treated in an oxygen plasma for 5 min at 30 W and 2.5 mbar pressure using a Diener electronic femtoplasma system. The plasma-treated substrate was immediately transferred to the deposition chamber for device fabrication. The deposition of the organic layers and metal electrodes were performed using a Kurt J. Lesker SPECTROS evaporation system with a base pressure during evaporation of $\sim 10^{-7}$ mbar. The rate of deposition of organic materials was about 0.2 nm/s while that of the aluminum was varied from ~0.1 to 0.5 nm/s. A calibrated oscillating quartz crystal monitor was used to determine the rate and thickness of the deposited layer. The whole device fabrication was performed without breaking vacuum. The resulting diode structures were measured in forward bias. 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 analyzed by fitting a cubic function to the region around the peak and differentiating to find the maximum value. The sample current response to a voltage step displayed the characteristic peak whose position determines the DI time, t_{DI}, used to calculate the carrier mobility (see Fig. 1, inset a). The mobility, μ, at a given bias, V, was calculated using t_{DI} and the sample thickness, d using the relationship[19]

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

Current-voltage (*I*-*V*) measurements were also carried out on the same samples using a Keithley 236 source measure unit. Voltage-luminescence measurements were made using a square wave from a pulse generator and detected using a photomultiplier and SignalRecovery 7265 lock-in amplifier. All sample measurements (*I*-*V*-*L* and DI) were carried out in vacuum ($\sim 10^{-5}$ mbar) to reduce device degradation.

III. RESULTS AND DISCUSSION

The measured hole mobility was found to show a slight field dependence, over the range of fields studied, and varied from sample to sample between 2.5×10^{-4} and 6×10^{-4} cm^2 V^{-1} s^{-1} in agreement with literature values.[20] A typical plot of hole drift velocity versus electric field is shown in Fig. 1, inset b and more detail is given in the supplementary information.[21] A plot of the mobility ratio, defined as $\mu_{(\text{offset}\neq 0)}/\mu_{(\text{offset}=0)}$, versus dc offset is shown in the main plot of Fig. 1. For offset voltages exceeding ~2 V there is a significant drop in the measured hole mobility for the ambipolar devices, compared to the unipolar structures. In Ref. 18, where this drop was attributed to the site-blocking effect of triplet excitons formed when ambipolar injection is achieved, the presence of excitons was only inferred by the onset of electron injection corresponding to the superlinear transition in the *I*-*V* characteristic. In this paper, we are able to unequivocally link the drop in hole mobility to the presence of excited states, as it is not only consistent with the rapid increase in the current observed in the *I*-*V* curve of the ambipolar structure but more importantly it is associated with a significant light output from the device, as shown in Fig. 2. This is further confirmed by results from the unipolar device, where no drop in the hole mobility is found up to bias voltages of 4.5 V (Fig. 1), consistent with the lack of luminescence shown in Fig. 2.

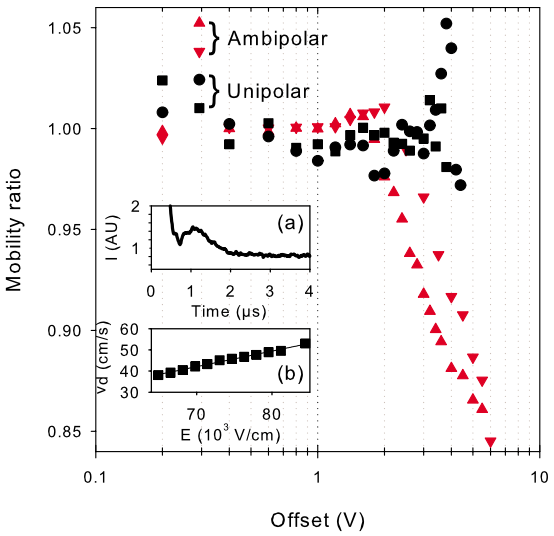

FIG. 1. (Color online) Hole mobility ratio, $\mu(\text{offset} \neq 0)/\mu(\text{offset}=0)$, versus offset, measured in four, 600-nm-thick TPD devices with either Au (unipolar) or Al (ambipolar) cathodes (measured at 1.1×10^5 V cm^{-1}, room temperature). There are two samples of each type. Inset (a) Typical DI current transient in an ambipolar (Al cathode) sample (zero offset, 7.5×10^4 V cm^{-1}). Inset (b) Calculated hole drift velocity versus electric field in an ambipolar (Al cathode) sample.

It is also worth noting that the measured mobility reduction due to the presence of excited states is independent of the material studied, as it is observed in molecular systems as different as P3HT and TPD. This provides strong evidence that it is a general feature of organic semiconductors where predominantly hopping transport applies. This is exactly as would be expected from the triplet site-blocking mechanism. It could be argued that the reduction in mobility is actually correlated with the injection of electrons and hence columbic trapping may be the cause rather than interactions with triplets. The role of trapped charge on current transport has been

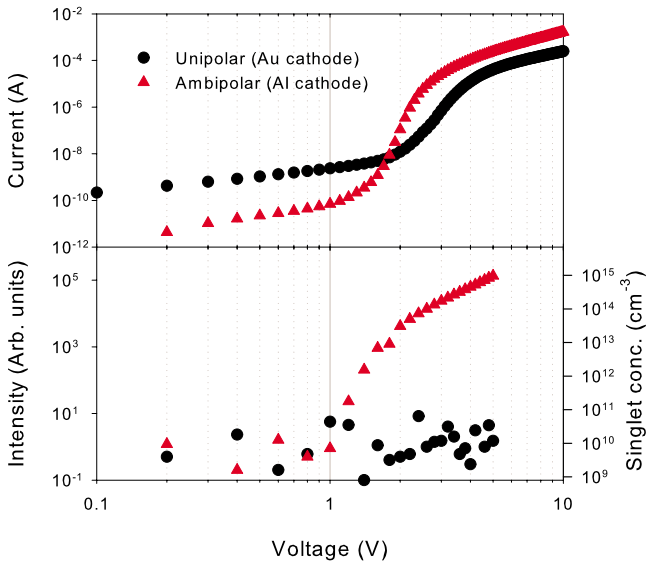

FIG. 2. (Color online) Current-voltage characteristics of unipolar (Au cathode) and ambipolar (Al cathode) samples and luminescence-voltage characteristic of the same samples. The estimated singlet concentration is shown on the right hand axis.

studied theoretically by (e.g., by Rackovsky and Scher[22]). they demonstrated that trapped charge levels above $\sim 10^{13}$ cm^{-3} would affect carrier mobility if the trapped charge was acting as shallow traps. In our system we have directly measured the electron mobility in the TPD using time of flight and have found that it is virtually identical to that for holes. From this the electron concentration in the layers can be estimated to be at least 10^6 times lower than the level needed to affect the dark injection pulse and any trapping of holes with free electrons would be likely to produce the excitons that we are considering. This calculation assumes that only 1 electron in a 1000 undergoes recombination with holes which is probably an underestimate given the huge mismatch between electron and hole injection in this device.

The microscopic mechanism for OMR, proposed by our group, states that the primary action of a magnetic field on an OLED is to increase the singlet concentration within the organic layer[11] which results in the improved efficiency; at the same time it also reduces the triplet concentration. By reducing the triplet concentration their effect on the mobility is also reduced. We have proposed that there are three primary mechanisms through which triplets can affect mobility[11,18] depending on the relative spin states of the polaron and triplet. If a polaron encounters an exciton in the triplet state, and its spin state is the same as the corresponding electron or hole of the triplet, then the site is blocked (see Fig. 3) and the mobility is decreased as the polaron has to find an alternative route. The polaron may also be weakly trapped through the formation of a charged Frenkel exciton as proposed be Agranovich *et al.*[2] However, if the polaron has the opposite spin state, then it can interact with the triplet molecule and here there are a number of possible outcomes, again depending on the spin conditions (see Fig. 3). The polaron can depart the molecule leaving a triplet behind, although both polaron and triplet may exchange their spin to result in different spin

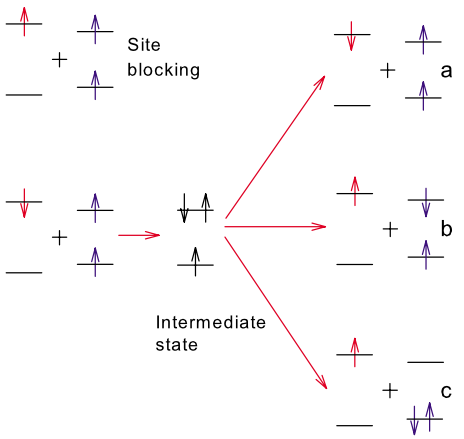

FIG. 3. (Color online) A schematic of the interaction of an electron polaron with a triplet exciton. The particle in the highest occupied molecular orbital represents the hole. Where the spin of the electron is the same as the electron spin in the exciton the electron cannot hop onto that site and site blocking occurs. In the second case an intermediate state can form and there are a number of possible outcomes. In (a) the intermediate state is returned to the initial configuration. In (b) there has been spin exchange and although a polaron and triplet remain their spin states are different. In (c) the polaron has quenched the triplet but leaving a polaron behind. These three interactions will take some time and will hence affect the mobility of the polaron.

states, or the polaron can quench the triplet leaving just the polaron.[11] Both of these processes will change the mobility of the polaron and in addition they would likely have some magnetic field dependence, which would be convolved with the magnetic field dependence of the triplet population (caused by the change in the intersystem crossing mentioned earlier). This probably accounts for the observed difference between the magnetic field dependence of the device efficiency and current seen in OMR experiments and the experimentally observed variation in OMR line shape with drive current.[11–15] It is not clear from our work whether the interaction between a polaron and a triplet results in a charged exciton, as we have schematically shown in Fig. 3, or a close pair state (charged Frenkel exciton). Both of these possibilities were considered by Agranovich *et al.*[2] and would depend on the energetics of the particular combination. If the system favored only the formation of the bound pair state then the site-blocking mechanism would not occur. Rather the exciton would only act as a trapping center. However, the fate of this pair state would still depend on the spins of the polaron and triplet as outlined by Ern and Merrifield.[23]

For this mechanism to operate effectively we must consider what the likely triplet concentration in our device is. Although we needed to use a lock-in amplifier to measure the light emission at very low voltages we were able to directly measure the light output in an integrating sphere at higher voltages. From this we found that at 10 V the light intensity was $\sim$0.1 nW. Assuming the emitted photons are monochromatic with an energy of 2.9 eV ($\sim$420 nm) and the singlet lifetime is 10 ns we can estimate the singlet concentration in our device as $\sim 10^{16}$ cm^{-3} at 10 V and approximately one order of magnitude lower at the voltages used for

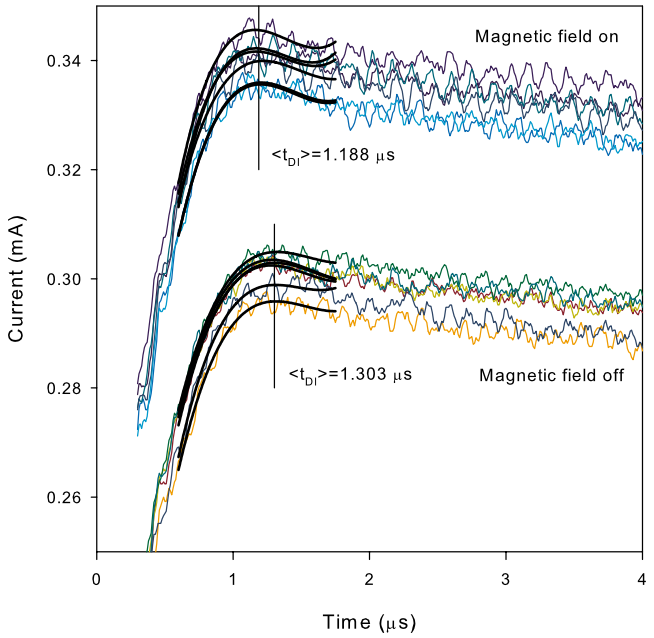

FIG. 4. (Color online) A set of DI curves and fits for the ambipolar device with an offset voltage above turn on (3.5 V) both with and without a magnetic field to show that the effect of the *B* field can be reliably measured.

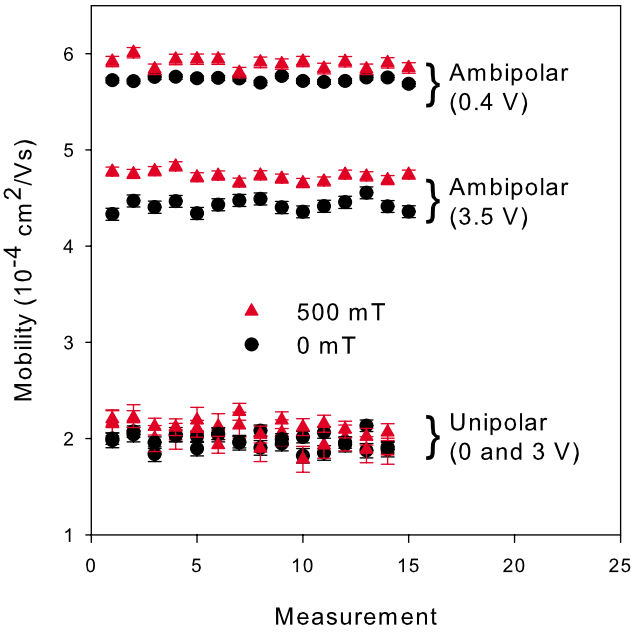

FIG. 5. (Color online) Repeat measurements of hole mobility, using unipolar (Au cathode) and ambipolar (Al cathode) samples, in the presence (triangles) and absence (circles) of a magnetic field. The two offset values, 0.4 V (top) and 3.5 V (bottom), have been chosen to correspond to regions below and above device turn-on, respectively, in the ambipolar sample. The two offset voltages for the unipolar sample, 0 and 3 V, are virtually indistinguishable.

our measurements (5 V). Assuming a triplet lifetime of only 10 μs this would still give a triplet concentration of $\sim 10^{18}$ cm^{-3}. It should be stressed that one of the possible outcomes of polaron interaction with triplets is quenching of the triplet state[23] and hence this may go some way toward controlling triplet concentration in real devices.

In order to probe changes in charge transport due to magnetic fields, we also performed DI measurements on the diode structures in the presence and absence of a magnetic field (typically 500 mT) by repeatedly placing and removing a small neodymium iron boron magnet directly above the sample. These were carried out on both unipolar and ambipolar devices, at different dc offset values. Figure 4 shows a set of dark injection curves, and the fits, for an ambipolar device with an offset voltage above turn-on both with and without an applied magnetic field. Fifteen repeat measurements were taken with the field first applied and then removed and each measurement took approximately 2 min. From Fig. 4 it can be seen that over the hour or so that it took to perform this experiment the sample remained highly consistent and there was a reproducible and measurable difference in arrival time between the field on and off. Note only six repeats are shown for clarity. Figure 5 shows the measured hole mobility in two samples at different offset values in the presence or absence of a magnetic field for 15 repeat measurements. The ambipolar structures results show a drop in the zero magnetic field mobility of $\sim$15% between the 0.6 and 3.5 V offset results, consistent with Fig. 1 whereas for the unipolar sample there is no effect due to the offset voltage. From Fig. 4 it can be seen that while the unipolar sample does show some improvement in mobility with applied magnetic field the effect is small and independent of the dc offset voltage. This is in contrast to the improvement measured in the ambipolar sample which more than doubles, from (3.2 ± 0.8)% below device turn on (offset 0.4 V) to (6.5 ± 0.8)% above device turn on (offset 3.5 V). The increase in mobility enhancement due to a magnetic field in the presence of excited states provides the most striking confirmation of the role of excited states in OMR. The offset-independent enhancement in mobility with magnetic field displayed by the unipolar sample may be due to the small number of excited states generated by the DI measurement pulse itself (6 V). We have shown in previous work[12] that an ITO/TPD/Au structure can display magnetoresistance at high driving voltages ($\sim$7 V) and that luminescence can be seen from it at drive voltages $>$12 V. However, because the gold is such a poor electron injector the power efficiency for such devices was only $\sim 10^{-11}$% at 15 V. It is therefore quite possible that the 6 V dark injection pulse might produce small numbers of excited states. We note however that this unipolar result is also consistent with OMR theories that do not require ambipolar injection (e.g., Bobbert *et al.*[17]). The same mechanisms can also explain the small magnetic field mobility enhancement seen in the Al electrode sample below turn on.

Models of OMR that rely on changes in the recombination rate of electron hole pairs or changes in dissociation probability for excitons due to a change in the balance of singlets and triplets[4,9,10] predict that the increase in current seen in our results is due to an increase in the number of free carriers present rather than a change in mobility. As we stated earlier, Rackovsky and Scher[22] showed that trapped charge could act to reduce mobility and hence with these models of OMR one would expect to see a decrease in mo-

bility with applied magnetic field rather than the increase we observe here.

The changes in mobility with magnetic field measured in TPD can be compared with the change in the steady state current after the DI pulse. For the aluminum cathode the OMR measured in the steady state region was $8.7 \pm 3.0\%$. This value is the same as the mobility changes measured $(6.5 \pm 0.8)\%$, within experimental error, and support the view that the change in current can be attributed to the change in mobility.

IV. CONCLUSIONS

In conclusion, we show that for a unipolar device we see no change in mobility with dc bias, whereas for the ambipolar device, we obtain a reduction in mobility that can be perfectly correlated with light emission, which strongly suggests that excitons have a critical role in reducing the mobility in organic semiconductors. This is strongly supported by the fact that when measuring the effect of a magnetic field on the mobility of the TPD under different bias conditions, the magnetic field results in a significant increase in mobility for the ambipolar sample. TPD is a sufficiently different molecular system to the previously reported P3HT to confirm the site-blocking mechanism as a general feature of long-lived excited states in organic semiconductors. These results therefore strengthen the view that excitons have a significant effect on carrier mobility, thus providing support for the TPI model of organic magnetoresistance. Furthermore, our results may have more far-reaching implications, for instance in device modeling, where the role of excitons on current transport in OLEDs has been overlooked up to now. Indeed, if even the very low exciton concentrations present in our structures (due to the considerably smaller electron injection compared to holes) can reduce mobilities by 15% then the level of excitons present in functional OLEDs should cause significant changes in mobility.

ACKNOWLEDGMENT

This work was supported by the Leverhulme Trust (A.J.D.).

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] V. M. Agranovich, D. M. Basko, K. Schmidt, G. C. LaRocca, F. Bassani, S. Forrest, K. Leo, and D. Lidzey, Chem. Phys. **272**, 159 (2001).
[3] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, New York, 1999).
[4] J. Kalinowski, M. Cocchi, D. Virgili, P. Di Marco, and V. Fattori, Chem. Phys. Lett. **380**, 710 (2003).
[5] A. H. Davis and K. Bussmann, J. Vac. Sci. Technol. A **22**, 1885 (2004).
[6] T. L. Francis, O. Mermer, G. Veeraraghavan, and M. Wohlgenannt, New J. Phys. **6**, 185 (2004).
[7] O. Mermer, G. Veeraraghavan, T. L. Francis, and M. Wohlgenannt, Solid State Commun. **134**, 631 (2005).
[8] O. Mermer, G. Veeraraghavan, T. L. Francis, Y. Sheng, D. T. Nguyen, M. Wohlgenannt, A. Kohler, M. K. Al-Suti, and M. S. Khan, Phys. Rev. B **72**, 205202 (2005).
[9] B. Hu and Y. Wu, Nature Mater. **6**, 985 (2007).
[10] V. N. Prigodin, J. D. Bergeson, D. M. Lincoln, and A. J. Epstein, Synth. Met. **156**, 757 (2006).
[11] P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, N. A. Morley, and M. R. J. Gibbs, Phys. Rev. B **75**, 094423 (2007).
[12] P. Desai, P. Shakya, T. Kreouzis, and W. P. Gillin, J. Appl. Phys. **102**, 073710 (2007).
[13] P. Desai, P. Shakya, T. Kreouzis, and W. P. Gillin, Phys. Rev. B **76**, 235202 (2007).
[14] P. Shakya, P. Desai, T. Kreouzis, and W. P. Gillin, J. Appl. Phys. **103**, 043706 (2008).
[15] P. Shakya, P. Desai, M. Somerton, G. Gannaway, T. Kreouzis, and W. P. Gillin, J. Appl. Phys. **103**, 103715 (2008).
[16] N. Rolfe, P. Desai, P. Shakya, T. Kreouzis, and W. P. Gillin, J. Appl. Phys. **104**, 083703 (2008).
[17] P. A. Bobbert, T. D. Nguyen, F. W. A. van Oost, B. Koopmans, and M. Wohlgenannt, Phys. Rev. Lett. **99**, 216801 (2007).
[18] J. Y. Song, N. Stingelin, W. P. Gillin, and T. Kreouzis, Appl. Phys. Lett. **93**, 233306 (2008).
[19] M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970).
[20] T. Mori, E. Sugimura, and T. Mizutani, J. Phys. D **26**, 452 (1993).
[21] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.82.085205 for sample DI curves for the ambipolar device (with and without offset voltage) and drift velocity against electric field and a Poole-Frenkle plot for the ambipolar device.
[22] S. Rackovsky and H. Scher, J. Chem. Phys. **111**, 3668 (1999).
[23] V. Ern and R. E. Merrifield, Phys. Rev. Lett. **21**, 609 (1968).