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## Time-of-flight measurements and vertical transport in a high electron-mobility polymer

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We investigate charge transport in a high-electron mobility polymer, poly(*N,N*-bis 2-octyldodecyl-naphthalene-1,4,5,8-bis dicarboximide-2,6-diyl-alt-5,5-2,2-bithiophene) [P(NDI2OD-T2), Polyera ActivInk™ N2200]. Time-of-flight measurements reveal electron mobilities approaching those measured in field-effect transistors, the highest ever recorded in a conjugated polymer using this technique. The modest temperature dependence and weak dispersion of the transients indicate low energetic disorder in this material. Steady-state electron-only current measurements reveal a barrier to injection of about 300 meV. We propose that this barrier is located within the P(NDI2OD-T2) film and arises from molecular orientation effects. © 2011 American Institute of Physics. [doi:10.1063/1.3657827]

While several conjugated polymers exhibit hole-mobilities approaching that of rival technologies like amorphous silicon, very few of them have demonstrated equally high electron mobilities. Recently a breakthrough was achieved with poly(*N,N*-bis 2-octyldodecyl-naphthalene-1,4,5,8-bis dicarboximide-2,6-diyl-alt-5,5-2,2-bithiophene) [P(NDI2OD-T2), Polyera ActivInk™ N2200], which enabled electron mobilities of  $>0.1$  cm<sup>2</sup>/Vs in field-effect transistors (FETs).<sup>1</sup> However, some unanswered questions remain about this material, such as why it does not perform well as an electron acceptor in polymer solar cells<sup>2</sup> and why electron transport perpendicular to the substrate (vertical transport) in a sandwich-type architecture is much slower than expected.<sup>3</sup> In a previous study, we showed that sandwich-type electron-only devices were injection limited irrespective of the choice of electrode. However, contact resistance was found to be low even with high work-function contacts for in-plane transport in a transistor architecture.<sup>4</sup> In this letter, we combine temperature-dependent time of flight (TOF) mobility and steady-state current measurements to calculate the energetic barrier to injection for vertical transport. From the electric field dependence of the barrier energy, we conclude that the barrier must be located within the P(NDI2OD-T2) film. We propose a model, based on molecular orientation effects, that describes the observed data well.

TOF electron mobility measurements were performed on sandwich-type devices comprising: glass/indium tin oxide (ITO)/50 nm poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/P(NDI2OD-T2)/40 nm Al, with an active area of 0.16 cm<sup>2</sup>. The P(NDI2OD-T2) was spin-coated from a 100 g/l chlorobenzene solution in an N<sub>2</sub>-filled glovebox. Devices were measured in vacuum in a cold-finger He cryostat at temperatures from 100 to 295 K. They were excited with 412 nm laser pulses of 6 ns width and 500 Hz repeat rate through the negatively biased transparent bottom electrode. The resulting transients were recorded by an oscilloscope connected to a current preamplifier.

Two types of devices were measured, having a P(NDI2OD-T2) layer thicknesses of 2.1 and 3.2 μm. Both yielded the same room-temperature mobility of  $0.06 \pm 0.01$  cm<sup>2</sup>/Vs, the highest TOF electron mobility ever recorded in a conjugated polymer. This value is  $\sim 10\times$  higher than previously reported,<sup>3</sup> which we attribute to the lower disorder of this particular batch of polymer. Note that polymerization synthesis has been optimized for P(NDI2OD-T2) since the first report<sup>1</sup> to ensure a greater control of the polymer architecture parameters. The transients recorded here showed little dispersion (see inset, Figure 1). We found no significant mobility dependence on the electric field up to  $5 \times 10^7$  V/m.<sup>5</sup> The temperature dependence of the mobility for the 3.2 μm P(NDI2OD-T2)-thick device is shown in Figure 1. The mobility,  $\mu$ , fits to Arrhenius behavior,  $\mu \propto \exp(-E_a/k_B T)$ , where  $E_a$  is the activation energy,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature, with  $E_a = 95 \pm 5$  meV. Alternatively, the mobility fits in the range  $T > 125$  K to the Bässler model<sup>6</sup> for a Gaussian-broadened density of states (DOS):  $\mu \propto \exp[-(2\sigma/3k_B T)^2]$ , with  $\sigma = 40 \pm 5$  meV. The temperature dependence is weak compared to the majority of undoped electron-transporting polymers, which typically show temperature dependencies at least twice as much,<sup>7,8</sup> which were attributed to the presence

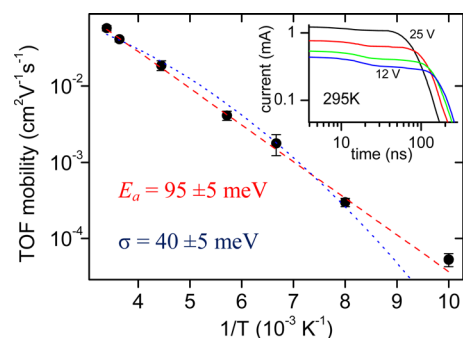


FIG. 1. (Color online) TOF mobility in 3.2 μm film of P(NDI2OD-T2) (circles). Arrhenius (red dashed line) and Bässler model (blue dotted line) fits. Inset: TOF transients at 295 K at 12, 14, 18, and 25 V.

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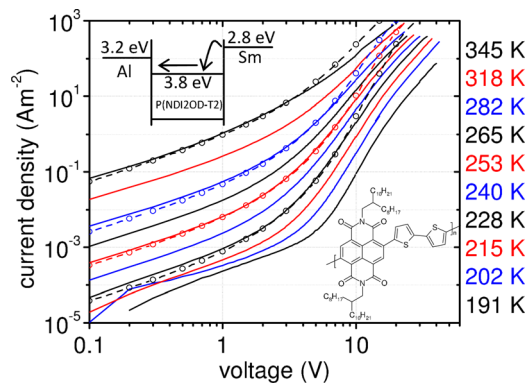


FIG. 2. (Color online) Current-voltage characteristics of 2.8  $\mu\text{m}$ -thick electron-only device parameterized by temperature (solid lines) and simulated device at 228, 253, 282, and 345 K (circles and dashed lines). Inset: approximate energy-level diagram showing direction of electron flow.

of electron traps or energetic disorder. The results from our TOF measurements are indicative of very little disorder in this polymer. This is consistent with recent experiments revealing an exceptionally narrow distribution of tail states.<sup>9</sup>

Recently, we demonstrated that the current density in P(NDI2OD-T2) electron-only devices was limited more by charge injection than by bulk charge transport for film thicknesses up to several micrometers, despite the use of low work-function contacts.<sup>3</sup> The current density depended only on the electric field independent of the device thickness. To investigate this aspect in more details, we measured the current-voltage characteristics of a new P(NDI2OD-T2) 2.8  $\mu\text{m}$ -thick electron-only device comprising: glass/ITO/PEDOT:PSS/Al/P(NDI2OD-T2)/Sm/Al, with the active layer prepared as for the TOF samples. The PEDOT:PSS layer was included to reduce the roughness of the Al bottom contact, as described in Ref. 8. The results are shown in Figure 2 for electron injection from the Sm contact. Using the TOF mobility, the space-charge limited current can be predicted by the Mott-Gurney law

$$J_{SCLC} = \mu\epsilon \frac{8V^2}{9d^3} = \mu\epsilon \frac{8F^2}{9d}, \quad (1)$$

where  $\epsilon$  is the permittivity,  $V$  is the applied voltage,  $d$  is the film thickness, and  $F = V/d$  is the mean electric field. The measured current was far below this limit, indicating injection-limited behavior. The injection efficiency (ratio of actual current density to the theoretical  $J_{SCLC}$ ) was  $\sim 5\%$  at 345 K and only  $\sim 0.05\%$  at 228 K at low fields and reached  $\sim 20\%$  and  $10\%$ , respectively, at high voltages. The current followed Arrhenius-type temperature dependence at all voltages. The activation energy is shown in Figure 3. At low voltages, it is about four times the activation energy of mobility. However, the activation energy of the electron current approaches that of the mobility at higher voltages as the injection efficiency increases. This indicates a transition from injection-limited towards bulk-limited or quasi bulk-limited<sup>10</sup> conduction as the electric field is increased. In the latter regime, the injected current depends on the electric field at the injecting contact, which is reduced by the build up of bulk space-charge.

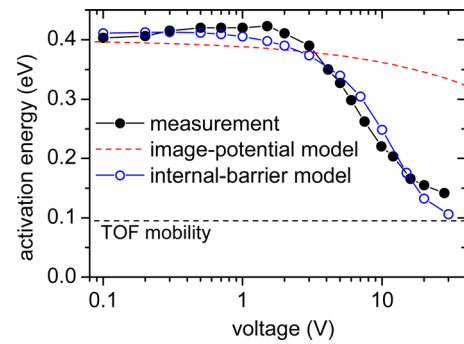


FIG. 3. (Color online) Activation energy of current versus applied voltage in a P(NDI2OD-T2) 2.8  $\mu\text{m}$ -thick electron-only device.

There are a number of conventional explanations for this behavior. However, none of them seem adequate here. First, the low-voltage regime could correspond to the filling of trap-states or the low-energy tail of a broad DOS. Such behavior would lead to a slope greater than two in Figure 2 for the trap-filling regime. This explanation is inappropriate since it would cause an even stronger dependence of current density on the polymer thickness than predicted by Eq. (1),<sup>7,8,11</sup> contrary to our previous findings.<sup>3</sup> A second explanation is that an oxide or other spatial barrier forms between the injecting contact and the polymer film, limiting the injection current. In such a case, the injection current would be determined by tunneling through the barrier. Tunnel currents have no temperature dependence, and hence, we would expect the activation energy to be close to zero at low voltage and to increase towards the bulk transport limit at higher voltages. Thus, this can also be excluded. The third possible explanation is that an energetic barrier is present at the interface between the Sm contact and the polymer. According to the Schottky model, this injection barrier will be reduced as electric field is increased due to injected carriers' image-charge potential by an amount<sup>12,13</sup>

$$\Delta\phi = \sqrt{\frac{e^3 F}{4\pi\epsilon}}, \quad (2)$$

where  $e$  is the elementary charge. The predicted temperature dependence is shown by the dashed line in Figure 3 assuming a dielectric constant of 3.5 and a 300 meV injection barrier. The electric field is not high enough to induce barrier-lowering of the magnitude required to explain our data. Furthermore, the work function of (environmentally contaminated) Sm is about 2.8 eV,<sup>9</sup> compared to the onset of conduction states (lowest occupied molecular orbital, LUMO) at about 3.8 eV in P(NDI2OD-T2),<sup>1,9</sup> suggesting that there should be no energetic barrier to electron injection at the interface. Kelvin-probe experiments revealed a considerable shift of the surface potential of P(NDI2OD-T2) coated on low work-function metals, indicative of a transfer of electrons from the metal to the polymer under equilibrium conditions.<sup>9</sup>

Recently Rivnay *et al.* demonstrated using x-ray diffraction that face-on oriented crystallites with respect to the substrate surface are present in P(NDI2OD-T2) films.<sup>14</sup> It was proposed that the alignment of intramolecular dipoles could cause a lowering of the LUMO level within the oriented

domains with respect to surrounding material. Shifts in energy levels due to such orientation effects of the order of several tenths of an eV have been predicted in other conjugated polymers.<sup>15</sup> While this film microstructure would favor electron injection into the face-on oriented crystallites, the domains are only  $\sim 30$  nm in size, and these films also contain edge-on oriented crystallites and amorphous regions.<sup>16</sup> Unless the entire  $2.8 \mu\text{m}$  film has the same polymer chain orientation, electrons will have to move into amorphous regions or regions having different chain orientations. The interface between face-on oriented and differently oriented regions will present an energetic barrier to electrons. Crucially, this barrier will be located inside the polymer film, some distance away from the contact. Band bending due to charge injected into the face-on on regions raises the LUMO of the randomly oriented regions above the Fermi level of the contact. Thus, we propose an “internal energetic barrier” model to explain vertical transport in these devices. While x-ray scattering data on this material is not conclusive, establishment of an internal-barrier could have alternative origins, such as local variations of the energetic spread (disorder) of states, impurities, or small oligomer chains in the vicinity of the injecting contact.

We simulated P(NDI2OD-T2) devices using a one-dimensional drift-diffusion model.<sup>7</sup> A Gaussian distribution of conduction states was assumed with a width of 40 meV and a total density of states of  $2 \times 10^{27} \text{ m}^{-3}$ . A region of thickness  $d_0$  next to the electrodes represented the oriented regions, in which the center of the distribution (LUMO) was set to 3.8 eV. Next to this, an internal energetic barrier of height  $\Delta E_b$  was introduced by raising the energy of the LUMO in graduated steps over a distance  $d_1$  (see inset of Fig. S2 in Ref. 5). The value of  $\Delta E_b$  directly controlled the activation energy of the current at low voltages, while increasing  $d_0$  reduced the voltage required to overcome the barrier. Values of  $\Delta E_b = 320$  meV,  $d_0 = 20$  nm, and  $d_1 = 30$  nm were chosen to fit the data. Work functions of 3.2 and 2.8 eV were assumed for the Al and Sm contacts, respectively. The metal-polymer interface was modeled by assuming thermal equilibrium at the interface under neglect of interface dipoles. Step changes in LUMO levels were handled by assuming continuity of quasi-Fermi levels across the steps. Mobilities in the low carrier-density limit were taken from the Arrhenius fit to the TOF data, with no electric field dependence, and the mobility and diffusion constant were increased with increasing carrier density as appropriate for a Gaussian DOS with a width of 40 meV.<sup>7</sup> The complete  $2.8 \mu\text{m}$  active layer was modeled using 6000 grid points.

The model reproduces very well the observed Arrhenius temperature dependence of the current density. The simulated activation energy for different biases is plotted in Figure 3. It provides a good description of the measured current densities in the linear regime at low electric fields where the current is primarily diffusion-driven. Above about 10 V, the simulated device tends towards quasi bulk-limited current and the simulation begins to overestimate the increase in

current; however, the qualitative behavior is still well reproduced. Many of the features of the observed behavior in sandwich-type P(NDI2OD-T2) electron-only devices are predicted, such as, the current plotted against electric field does not depend on the device thickness for devices less than about  $10 \mu\text{m}$  thickness;<sup>5</sup> and the current density is approximately independent of the contact work-function for work functions less than about 4.2 eV, but drops rapidly if the work function is increased above this value.<sup>5</sup>

In conclusion, we have measured a very high TOF electron mobility for P(NDI2OD-T2) films. The weak temperature dependence of mobility is indicative of little energetic disorder. Vertical conduction through similarly-prepared films was found to be injection limited at low voltages, with the injection efficiency increasing at higher voltages. The large activation energy of current at low voltages could be explained by an internal barrier possibly caused by different orientation of polymer domains in the proximity to the metal contact. Such internal barriers might be a general problem for conduction in any conjugated polymer that has well ordered domains.

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<sup>5</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3657827> for the electric-field dependence of TOF mobility, simulated current as a function of electrode work function, and simulated current as a function of device thickness.

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