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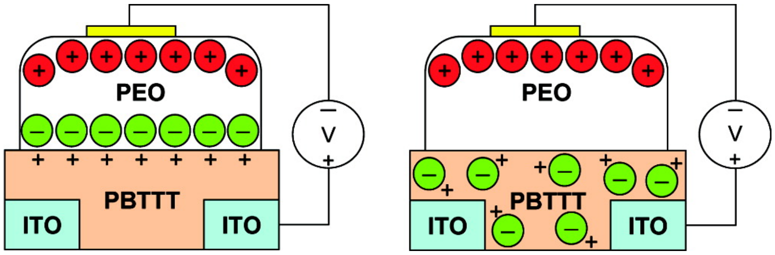

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Electrochemical Doping in Electrolyte-Gated Polymer Transistors

Jonathan D. Yuen,[†] Anoop S. Dhoot,[†] Ebinazar B. Namdas,[†] Nelson E. Coates,[†]
Martin Heeney,[‡] Iain McCulloch,[§] Daniel Moses,[†] and Alan J. Heeger*,[†]

Contribution from the Center for Polymers and Organic Solids, University of California, Santa Barbara, California 93106, Department of Materials, Queen Mary, University of London, Mile End Road, London, E1 4NS, United Kingdom, and Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

Received July 5, 2007; E-mail: ajhe@physics.ucsb.edu

Abstract: By comparing the changes in $\pi-\pi^*$ absorption with the transconductance in PEO−LiClO$_4$ electrolyte-gated FETs, we have demonstrated that the high channel currents obtained at low gate voltages result from reversible electrochemical doping of the semiconducting polymer film. At low temperatures, the conductivity of the electrochemically doped poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene), PBTTT-C14, is nonlinear with a crossover from $d\sigma(T)/dT > 0$ to $d\sigma(T)/dT \approx 0$ as a function of the source-drain voltage. High current densities, up to 10^6 A/cm^2 at 4.2 K, can be sustained in the electrochemically doped PBTTT-C14 films.

Introduction

Field effect transistors (FETs) fabricated from semiconducting polymers continue to be of interest as components of printable "plastic" electronic circuits.[1] Recent success in demonstrating light-emitting field effect transistors (LEFETs) has expanded the range of phenomena to enable gate-controlled light emission.[2,3] Moreover, within the ambipolar regime of the LEFET operation, there is population inversion in the semiconducting polymer.[4] Thus, the LEFET provides a possible route toward the fabrication of injection lasers from semiconducting polymers. In addition, the ability of FETs to laterally confine high densities of gate-induced (field-induced) mobile charge carriers enables experimental studies of the insulator-to-metal transition in pure conjugated polymers without the additional disorder and scattering that result from the insertion of charged impurity ions into interchain sites within the polymer.[5,6]

The concept of FETs fabricated with semiconducting polymers and gated with polymer electrolytes is of special interest because of the high capacitance of the double-layer near the electrolyte−semiconductor interface and the implied high density of field-induced carriers at low gate voltages ($\sim 10^{21}-10^{22}$ cm^{-3}, dependent on the applied voltage).[7,8] Initial results obtained from electrolyte-gated FETs using semiconducting polymers as the active material in the channel showed excellent performance at low gate voltages and low source-drain voltages.[7−9]

The mechanism of transconductance in electrolyte-gated polymer FETs has previously been discussed in the literature within the context of electrochemical FETs. In such devices, the carrier density was assumed to be controlled through reversible electrochemical doping.[10−11] It has been suggested, however, that because of the high capacitance of the double-layer, a significant field-effect can occur as a result of electrostatically induced carrier injection in the semiconducting polymer when a bias is applied to the electrolyte.[6−9,12] Because of the inherent difficulty in distinguishing between carriers generated by electrochemical doping throughout the bulk of the semiconducting polymer film and field-induced carriers confined to a few monolayers adjacent to the surface of the semiconducting polymer, the reality of the proposed mechanism in which the double-layer near the interface between the electrolyte and the semiconductor controls the carrier density has yet to be clearly established.

A schematic diagram of an electrochemical doping experiment with a semiconducting polymer is shown in Figure 1a. The electrolyte (e.g., Li$^+$ and ClO$_4^-$ ions in solution or dissolved in polyethylene oxide, PEO) is in contact with the surface of a semiconducting polymer film which, in turn, is in contact with an electrode at the opposite surface (e.g., indium/tin oxide, ITO,

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[†] University of California.
[‡] University of London.
[§] Imperial College London.

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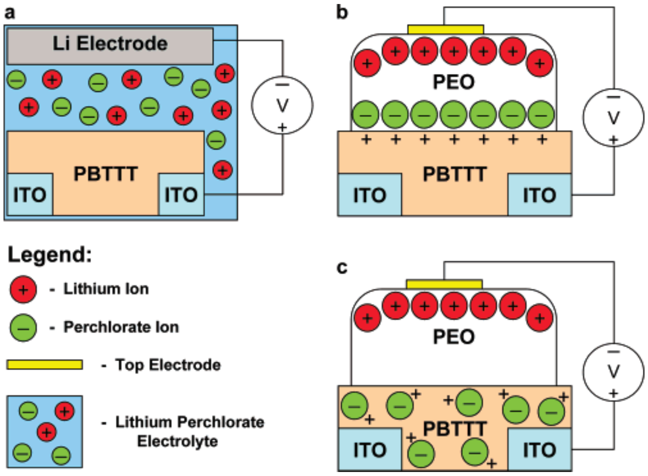

Figure 1. (a) Schematic diagram of an electrochemical doping experiment with a semiconducting polymer. (b) and (c) schematically show the electrolyte-gated transistor structure. (b) For gate voltages below the onset of oxidation, holes are field-induced near the surface. (c) Holes are generated throughout the bulk of the film by electrochemical doping (oxidation). Concurrently, Li$^+$ ions are reduced to neutral Li and plate out on the surface of the electrode.

shown in the diagram as split into two equivalent ITO electrodes). As indicated, a counter-electrode is inserted into the electrolyte; in Figure 1a, the counter-electrode is a strip of Li metal. Electrochemical p-type doping and the generation of hole polarons ("holes") occurs when the semiconducting polymer is oxidized (an electron is removed from the polymer through the back electrode), and simultaneously a negative ion moves from the electrolyte into the bulk of the polymer into an interchain site. The electrochemistry of conjugated polymers is typically reversible; i.e. intrachain chemical bonds are not disrupted during electrochemical doping. To initiate oxidation and p-type doping, the voltage applied to the back electrode must be sufficiently large to shift the Fermi level (the electrochemical potential) of the semiconducting polymer into the π-band.

When the voltage applied between the two electrodes is too small to oxidize the polymer, a double-layer is formed at the interface between the electrolyte and the semiconductor with the buildup of a high density of negative ions in the electrolyte (at distances within the Debye screening length of the interface) and an associated buildup of a high density of holes near the surface of the polymer, as shown schematically in Figure 1b. In this "electrolytic capacitor", the gate voltage appears across the double-layers. Figure 1b is the configuration that describes gate-induced (field-induced) carrier generation. If the holes in the semiconductor are mobile, one can generate an electronic current in the channel of the FET by applying a voltage between the split ITO electrodes (source and drain). Although one might expect the holes to be mobile, very little is known about the density of traps in a semiconducting polymer near the interface in the double-layer regime. Because of the large local electric field within the electrolytic capacitor (Figure 1a), any surface inhomogeneity can lead to the formation of traps that localize the holes.

When the voltage is increased to a value sufficiently large to shift the Fermi level into the π-band of the semiconducting polymer, oxidation occurs with associated injection of negative ions from the electrolyte. At electrochemical equilibrium, sketched in Figure 1c, a uniform density of holes exists throughout the bulk of the semiconducting polymer. Each hole is associated with, and weakly bound to, a negative counterion in direct analogy with the donor states in a conventional inorganic semiconductor. Note that the doped semiconducting polymer is everywhere neutral; the charge associated with each hole is compensated by the charge on a negative counterion. At finite temperature, as determined by the Boltzmann factor, a fraction of these donor states will be ionized giving rise to mobile carriers. At sufficiently high carrier densities, however, the screening of the Coulomb attraction between the holes and the negative ions and the energy gained through delocalization can cause a transition to a metallic state (the Mott transition). In the regime of electrochemical doping, oxidation of the polymer is electrochemically balanced by reduction at the counter-electrode; in the configuration shown in Figure 1a with Li metal as the counter-electrode, Li$^+$ ions are reduced to neutral Li and plate out on the surface of the electrode.

The p-type doping process is described in detail above; the corresponding n-type doping process is identical except that the charges in the double-layer regime and in the doped polymer are reversed, and the Fermi level must be shifted into the π^*-band to enable injection of electrons.

Thus, in any experiment with the general configuration shown in Figure 1a, there will be two regimes:

(1) the double-layer regime with gate-induced carriers near the surface of the semiconductor;

(2) the electrochemically doped regime with both carriers and counterions in the bulk of the polymer.

The double-layer regime can be extended to higher voltages if, for example, the negative ions in the electrolyte are immobile (as was suggested for the perchlorate ions in PEO[6]), the semiconductor is crystalline and has sufficiently high-density that ion diffusion into the bulk of the semiconductor is inhibited (as would be expected for an inorganic semiconductor such as Si), or if there is an overpotential in the electrochemistry arising from, for example, using a high dielectric constant solvent for dissolving the ions in the electrolyte.

We report here the results of an investigation of the $\pi-\pi^*$ absorption and the carrier transport properties in electrolyte-gated FETs made with poly(2,5-bis(3-tetradecylthiophen-2-yl)-thieno[3,2-*b*]thiophene)[13] (PBTTT-C14) as the semiconductor in the channel; the molecular structure of PBTTT-C14 is shown in Figure 2a. UV−vis absorption was measured as a function of the wavelength at different applied voltages using the polymer-electrolyte/semiconductor/ITO structure shown in Figure 2b.[6] We find that electrochemical doping, raised as a possibility in an earlier publication,[6] dominates the device performance.

In Situ Measurements of the Absorption and the Electrical Conductivity

PBTTT-C14 in chlorobenzene (Sigma-Aldrich) was first heated to 120 °C and then spin-cast onto an ITO/glass substrate at 3000 rpm in a nitrogen atmosphere and subsequently annealed at 150 °C, resulting films with thickness of 30 nm. The PEO:Li$^+$(ClO$_4$)$^-$ electrolyte was prepared by dissolving a 1:1.36

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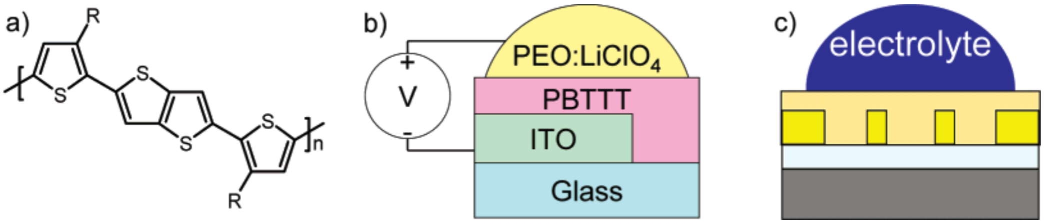

Figure 2. (a) Molecular structure of PBTTT-C14 ($R = C_{14}H_{29}$), (b) schematic illustration of the polymer-electrolyte/semiconductor/ITO device configuration used for spectroscopic measurements, and (c) schematic illustration of the device structure used for measurement of the temperature dependence of electrical conductivity.

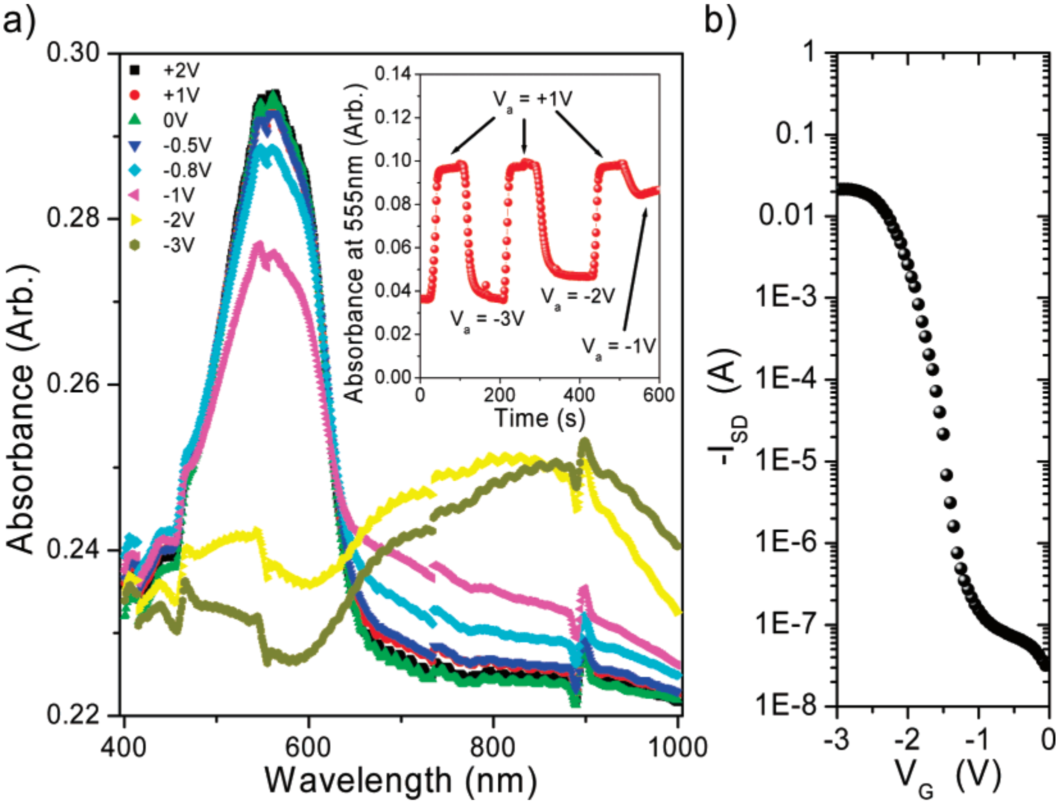

Figure 3. (a) Absorption spectra of the device biased at various gate voltages. The inset shows the absorption at 555 nm versus time in response to step changes in the gate voltage. (b) Transfer characteristics of the polymer electrolyte-gated transistor.

weight ratio of $LiClO_4$ (Fluka) and poly(ethylene oxide) (Sigma-Aldrich) in acetonitrile (Sigma-Aldrich) at 30 mg/mL. After filtering, the solution was drop-cast directly onto the device and left overnight to dry under vacuum at room temperature. Samples were then connected to a Keithley 2400 Sourcemeter in the polarity shown via gold-tipped clips and placed in a Beckman Coulter DU800 UV/vis spectrophotometer. After the bias was set at a specific applied voltage and 3 min was allowed for the system to come to electrochemical equilibrium, the absorbance of the PBTTT-C14 film was recorded over the wavelength range from 400 to 1000 nm at a scan rate of approximately 500 nm/min.

The absorption spectra of PBTTT-C14 at a series of gate voltages are shown in Figure 3a. At $V_G = 0$, the spectrum is typical of a pure semiconducting polymer. For PBTTT-C14, the onset of absorption is at $h\nu = 660$ nm (implying an energy gap of approximately $E_g \approx 1.9$ eV) and the maximum absorption is approximately at 555 nm.[14] The spectra obtained under positive bias ($V_a = +1$ and $+2$ V) overlap with the 0-V spectrum, indicating that the semiconductor is structurally and electronically unperturbed. At biases starting at $V_G = -0.8$ V, however, the spectrum changes: the $\pi-\pi^*$ absorption of PBTTT-C14 steadily decreases in magnitude with increasing negative bias, while the oscillator strength shifts to a long wavelength absorption with peak in the near IR centered at approximately 800 nm. On the basis of these spectroscopic data, the double-layer regime is limited to $-0.8 < V_G < 0$ V; for larger negative gate voltages, the changes in the absorption spectrum are characteristic of electrochemical p-type doping.[15]

The time required to reach electrochemical equilibrium was determined by monitoring the absorption at the spectral peak (555 nm) following a change in the applied gate bias; the results are shown in the inset in Figure 3. Electrochemical doping and dedoping are observed to be relatively rapid processes at all bias levels. Electrochemical doping of the PBTTT-C14 in contact with a liquid electrolyte, Li^+ and ClO_4^- ions in acetonitrile, occurs in a few seconds (data not shown), similar

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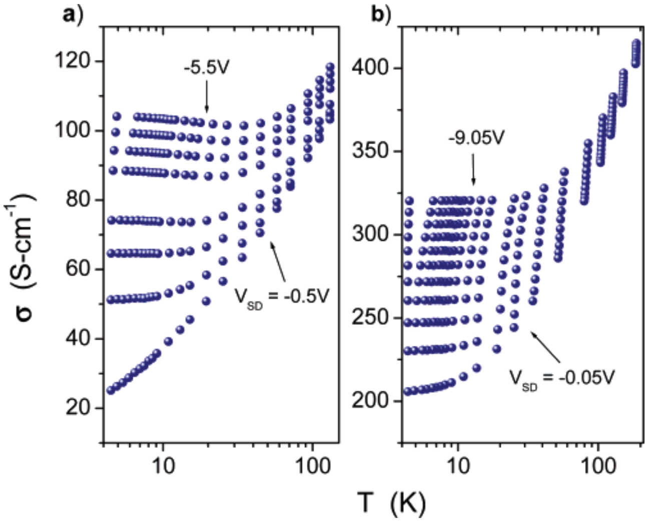

Figure 4. Temperature dependence of the conductivity for two polymer electrolyte-gated PBTTT-C14 devices (A and B) at various V_{SD} values. For device A, V_{SD} increases from $V_{SD} = -0.5$ V to $V_{SD} = -5.5$ V in steps of -0.5 V, and for device B, V_{SD} increases from $V_{SD} = -0.05$ V to $V_{SD} = -9.05$ V in steps of -1.125 V. Both devices were first cooled to 4.2 K while holding the gate voltage constant at $V_G = -3$ V and with $V_{SD} = -1$ V.

to other thiophene-based materials.[16] The doping process for the PEO/electrolyte in contact with a PBTTT-C14 film requires approximately 10−20 s and therefore appears to be limited by the diffusion of ions in the gating PEO solid electrolyte.

For electrical transport measurements, top-gate, bottom-contact, electrolyte-gated FETs with channel lengths and widths of 16 and 1000 μm, respectively, were used (see Figure 2c). The channel resistance was measured using the four-probe method, with two long parallel electrodes, 2 μm wide and 4 μm apart, placed inside the transistor channel for voltage measurements. A tungsten probe tip provided the external contact to the electrolyte. The four-probe devices were lithographically defined on heavily n-type doped Si (n^{2+}-Si) substrates covered with 200-nm-thick SiO_2. The source and drain electrodes (5 nm Ti followed by 50 nm Au) were deposited by e-beam evaporation. The substrates were sonicated with acetone followed by 2-propanol, dried at 120 °C for 5 min, exposed to oxygen-plasma for 4−5 min, and then soaked in an octadecyltrichlorosilane solution (1% dilution in toluene) at 80 °C for 10 min before the PBTTT-C14 was spin-cast as described above. The PEO:$LiClO_4$ electrolyte layer was then deposited as decribed previously. Completed devices were characterized using three Keithley 2400 Sourcemeters, with internal impedance $>10^{10}$ Ω. For the measurements of the temperature dependence of the conductivity in the channel, devices were inserted directly into a dewar containing liquid helium. The device temperature was monitored using a Lake Shore Cryotronics sensor soldered to the copper sample holder (see ref 5 for details).

Figure 3b shows the transconductance, I_{SD} vs V_G. The two regimes discussed above and observed through the spectroscopic changes in Figure 3a are evident in the data: the double-layer regime at negative gate voltages between 0 and −0.8 V and the electrochemical doping regime at negative gate voltages for

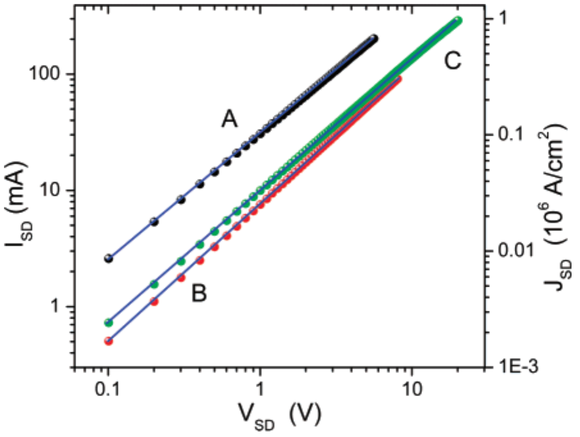

Figure 5. (a) Log−log plot of current and current density versus V_{SD} for three polymer electrolyte-gated PBTTT-C14 devices. The data labeled A and B were obtained from the same devices used to obtain the temperature dependence shown in Figure 4.

$|V_G| > 0.8$ V. Note that the source-drain current at $V_G = -0.8$ V is only 10^{-7} A. Thus, in the double-layer regime, the conductivity in the first few monolayers is less than 1 S/cm. Since the surface charge density is estimated to be $>10^{21}$ cm^{-3} in the first few monolayers, it appears that the mobility of these double-layer-induced charges is quite small, possibly because of a high density of traps in the conducting polymer near the interface with the electrolyte. At the onset of electrochemical doping (for V_G between −0.8 and −2.0 V), the current increases by more than 5 orders of magnitude from 10^{-7} to 2.5×10^{-2} A.

Figure 4 shows the temperature dependence of the doping-induced conductivity in the channel versus temperature for two nominally identical devices, A and B. Assuming the PBTTT-C14 layer is uniformly doped, the conductivities at 300 K are 200 S/cm (device A) and 450 S/cm (device B) at $V_G = -3$ V and $V_{SD} = -1$ V. The variation in the measured conductivity obtained from different devices presumably arises from minor differences in the quality of the spin-cast PBTTT-C14 films. These conductivity values are typical of doped semiconducting polymers at relatively high carrier densities $\sim 10^{21}$ cm^{-3} close to the insulator−metal transition.

Temperature Dependence of the Electrical Conductivity of Electrochemically Doped PBTTT-C14

For measurements of the temperature dependence of the channel resistance, the devices were first cooled to 4.2 K with the gate voltage held fixed[17] at $V_G = -3$ V and with $V_{SD} = -1$ V. Although the conductivities decrease with decreasing temperature, the conductivity remains high even at 4.2 K; for device B, $\sigma(4.2\ \mathrm{K})/\sigma(300\ \mathrm{K}) \approx 0.5$. The weak temperature dependence and the high conductivity at low temperature are consistent with the assertion that electrochemically doped PBTTT-C14 is close to the insulator−metal transition; see Figure 4. Note that the measured conductivity values and $\sigma(T)$ are field dependent at low temperatures. As shown in Figure 4, $\sigma(4.2\ \mathrm{K})$ increases as the source-drain voltage is increased. At high V_{SD}, the conductivities are temperature independent (device B) or even increase slightly as the temperature is lowered (device A). While nonlinearity at low electric fields in FETs has been attributed to injection barriers, the 4-probe measurements of $\sigma(T)$ are

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(17) V_G was not varied at low temperatures ($T < 260$ K) due to ion immobility in the electrolyte.

insensitive to the contact resistance. Moreover, in the high carrier density regime characteristic of the data in Figure 4, the contact resistance is much smaller than the channel resistance.[6] The apparent crossover from “insulator” with $d\sigma(T)/dT > 0$ to “metal” is reminiscent of the electric-field-induced insulator to metal transition observed in metal-gated FETs fabricated from semiconducting polymers.[5] For the metal-gated (conventional) FETs, where electrochemical doping is completely eliminated, it has been suggested that the nonlinearity is the result of field-induced delocalization in two dimensions.[5]

Figure 5 shows $I-V$ characteristics for devices A and B and a third device, C, all obtained at 4.2 K. All three devices showed high conductivity at low temperatures. The straight lines in Figure 3 indicate power law behavior, I_{SD} proportional to $(V_{SD})^n$, where $n = 1.1-1.2$. All three devices were capable of carrying high current densities at low temperatures. For device C, $I_{SD} = -0.3$ A at $V_{SD} = -20$ V, which corresponds to a conductivity of 350 S/cm at 4.2 K and a current density of 10^6 A/cm^2.

Conclusion

By comparing the changes in $\pi-\pi^*$ absorption with the transconductance in PEO$-$LiClO$_4$ electrolyte-gated PBTTT-C14 FETs, we have demonstrated that the high channel currents obtained at low gate voltages result from reversible electrochemical doping of the polymer film. In the double-layer regime below the onset of electrochemical doping, the associated conductivity is small (1 S/cm). At low temperatures, the conductivity of electrochemically doped PBTTT-C14 is nonlinear with a crossover from $d\sigma(T)/dT > 0$ to $d\sigma(T)/dT \approx 0$ as a function of the source-drain voltage. High current densities, up to 10^6 A/cm^2 at 4.2 K, can be sustained in heavily doped films of PBTTT-C14.

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