

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231667707>

Mixing at the Charged Interface of a Polymer Semiconductor and a Polyelectrolyte Dielectric

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · FEBRUARY 2010

Impact Factor: 7.46 · DOI: 10.1021/jz900471g

CITATIONS

5

READS

26

4 AUTHORS, INCLUDING:



Loren Kaake

University of California, Santa Barbara

18 PUBLICATIONS 815 CITATIONS

SEE PROFILE



C. Daniel Frisbie

University of Minnesota Twin Cities

226 PUBLICATIONS 14,770 CITATIONS

SEE PROFILE

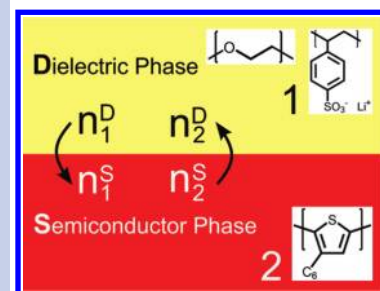
Mixing at the Charged Interface of a Polymer Semiconductor and a Polyelectrolyte Dielectric

Loren G. Kaake,[†] Bryan D. Paulsen,[‡] C. D. Frisbie,[‡] and X.-Y. Zhu^{*†}

[†]Department of Chemistry & Biochemistry, University of Texas, Austin, Texas 78712, and [‡]Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

ABSTRACT Electrolytes dissolved in ion conducting polymers are finding applications as dielectric materials with very high capacitance for electronic devices, particularly organic thin film transistors. A key mechanistic question concerning their application is whether mixing of electrolyte with the organic semiconductor occurs under gate bias. Here, we quantitatively analyze the interfacial-mixing problem within the framework of polymer solution thermodynamics. The model system studied consists of lithium poly(styrene sulfonate) dissolved in poly(ethylene oxide) as the dielectric and poly(3-hexylthiophene) as the polymeric semiconductor. A distinct transition between doping mechanisms is observed as a function of gate voltage (V_G). In situ optical spectroscopy, transistor measurements, and theoretical analysis strongly point to electrostatic double layer formation in one voltage regime ($0 > V_G > -1.8$ V) and electrochemical mixing across the interface in another regime ($V_G < -1.8$ V). The formalism developed also defines the maximum charge density ($2 \times 10^{14}/\text{cm}^2$) achievable in the electrostatic double layer regime.

SECTION Electron Transport, Optical and Electronic Devices, Hard Matter



One emerging subfield of organic semiconductor research is concerned with the development of high capacitance and solution processable dielectric materials.^{1–9} Although potentially of general use, these materials are especially important in the context of organic thin film transistors (OTFTs),¹⁰ where a premium is placed upon low voltage device operation. Electrolyte-based dielectrics¹¹ are one promising class of materials that use mobile ions to establish a large electric field at an interface through an electrostatic double layer.^{5–9} Capacitance values for an electrostatic double layer capacitor can be as large as $10\text{--}100 \mu\text{F} \cdot \text{cm}^{-2}$.^{5–9}

From a technological standpoint, the electrical characteristics of a transistor are the ultimate criteria for judging the effectiveness of a dielectric material. However, the use of electrolyte dielectric materials for organic transistor applications requires clarification regarding the importance of electrochemical doping and dedoping mechanisms when the transistor is switched.^{12–14} In electrochemical-based switching, mobile ions of the dielectric are incorporated into the semiconducting material. Electrochemical transistors,^{15,16} particularly those based on ion gels,^{7,14} may find niche applications where field effect transistors with more conventional dielectrics pose various difficulties either in fabrication or operation. However, the introduction of ions into the semiconductor during the electrochemical doping process can cause morphological changes,^{17,18} and the ions themselves act as Coulomb traps, reducing the mobility of charge carriers.^{19,20} As a result, creating an electrolyte dielectric

material that operates via electrostatic double layer charging is likely to be more attractive from a device perspective.

Is it possible to have an electrolyte dielectric material that operates only by a field effect mechanism? In cases where the semiconductor material is rigid and crystalline, such as ZnO or rubrene single crystals,^{21,22} the answer seems to be an emphatic “yes”, but in other cases, such as π -conjugated polymer thin films, the answer is not obvious. In principle, we would expect the formation of an electrical double layer and, thus, electrostatic doping at low gate voltages. However, the voltage threshold for electrochemical doping could be low enough to prevent transistor action in the electrostatic double layer regime. To complicate matters, no single, unambiguous signature delineating the onset of an electrochemical doping process has been discovered. This makes it difficult to distinguish between light electrochemical doping and electrostatic double layer charging. One possible way to reduce the aforementioned complications is to dramatically increase the size of the ions in the dielectric to prevent their facile incorporation into the film. This can be accomplished by the use of a polyanion or cation, i.e. a polyelectrolyte, which should be too large to easily penetrate the semiconductor layer. Polyelectrolyte dielectrics have been demonstrated as high capacitance materials in OTFTs.^{6,8}

Received Date: December 29, 2009

Accepted Date: February 3, 2010

Published on Web Date: February 12, 2010

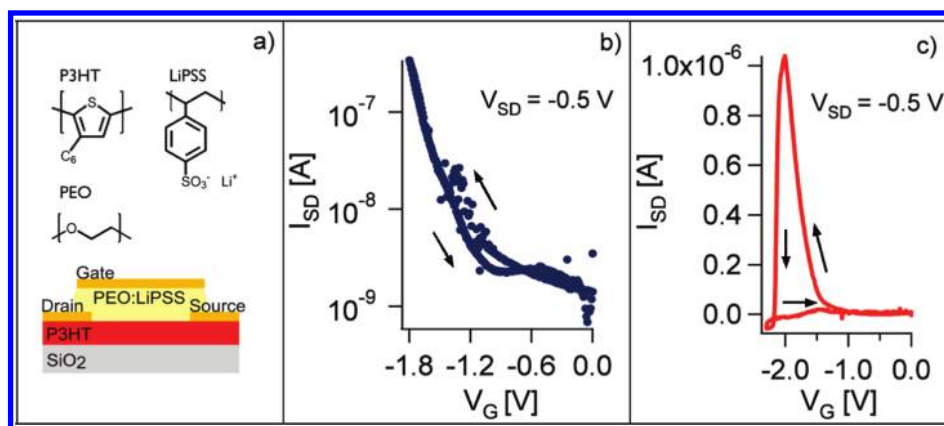


Figure 1. (a) Schematic of top gate transistor geometry employed and chemical structures of materials employed in the study. (b) Reversible trans-conductance traces occur when $0 \geq V_G > -2.0$. (c) Irreversible loss of trans-conductance occurs as the gate voltage is brought past -2.0 V.

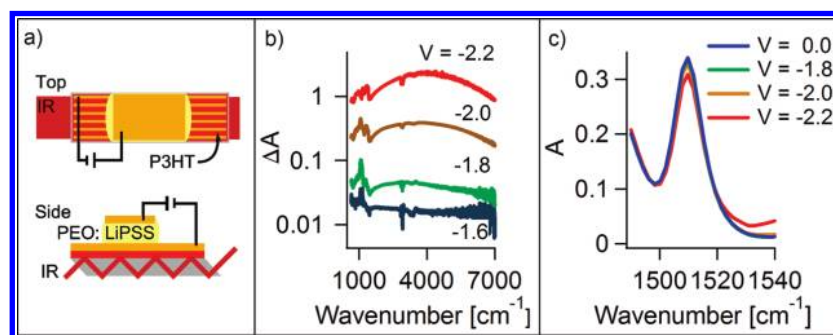


Figure 2. (a) Schematic of the in situ spectroscopic experiment showing a capacitor structure fabricated on an optical waveguide. (b) Difference spectra in the mid infrared range with gate bias voltage. Note the logarithmic increase in intensity above -1.8 V. (c) Changes in the neutral ring stretching modes of P3HT as a function of gate bias voltage.

The present study focuses on the charge injection mechanisms operating at the interface between a polyelectrolyte dielectric and a polymer semiconductor. We quantitatively analyze the interfacial mixing problem within the framework of the thermodynamics of polymer solutions. We choose as a model system the interface between the polymer electrolyte dielectric consisting of lithium poly(styrene sulfonate) (LiPSS) dissolved in poly(ethylene oxide) (PEO) and a polymeric semiconductor, poly(3-hexylthiophene) (P3HT). We characterize the system using transistor measurements (see Figure 1) and in situ optical spectroscopy (see Figure 2). In agreement with theoretical prediction based on polymer mixing, we show a distinctive transition from the electrostatic to an electrochemical doping mechanism when the gate voltage is above a critical value.

Figure 1b shows the output characteristic of a transistor for a measurement where the gate voltage was kept positive of -1.8 V throughout the sweep. The source–drain current shows very little hysteresis between forward and reverse sweeps of the gate voltage. Field effect mobilities were measured in the saturation regime for several devices and were found to be 0.1 ± 0.05 cm²/(V s). Note that, despite the relatively high mobility, the dielectric materials of this particular system are not suitable for OTFT application due to the

extremely slow response and, thus, low switching speed (< 1 Hz). While transistors with faster responses have been demonstrated,^{23,24} the present study is directed toward a mechanistic understanding of the charging process at the dielectric/polymer semiconductor interface, not developing a high performance transistor.

A completely different output characteristic is observed when the device is taken on a higher voltage excursion. The complete and irreversible destruction of channel conduction upon reaching a voltage of -2.0 V is seen in Figure 1c. This observation is in stark contrast with the reversible, low hysteresis sweeps depicted in Figure 1a where $0 \geq V_G > -1.8$ V. We believe that this finding is indicative of a distinct change in the operating mechanism of the device. At the lowest voltages, ($0 \geq V_G > -1.8$ V), an electrostatic double layer is formed between the holes in P3HT and the negatively charged polymer anion in the dielectric. In the first regime, the polymer semiconductor interface remains intact. The second regime occurs for gate voltages more negative than a certain voltage threshold ($V_G < -1.8$ V). In this regime the polymers mix, irreversibly damaging the interface and destroying the conductivity of the channel. Polymer mixing across the interface could also be termed electrochemical doping as positive charge carriers in P3HT are balanced by PSS counterions. This

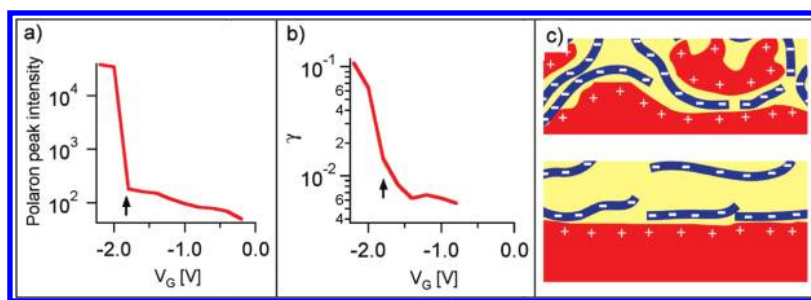


Figure 3. (a) Integrated intensity of the polaron band (see Figure 2b) as a function of gate. (b) The ratio of neutral thiophene ring stretch affected by charge injection (see Figure 2c and eq 1) as a function of gate. In each panel, the arrow indicates $V_C = -1.8$ V, the critical voltage for electrochemical doping/polymer mixing. (c) Schematic of the two proposed regimes of doping: electrically driven mixing (top) and electrostatic double layer charging (bottom).

conclusion is supported by in situ spectroscopic measurements and by analysis based on polymer mixing theory, as detailed below.

To verify the charging mechanisms, in particular the transition between electrostatic double layer formation and polymer mixing, in situ optical spectra of the semiconductor/dielectric interface were recorded as a function of gate bias. The model device used for this experiment is illustrated in Figure 2a, which is essentially an OFET similar to that in Figure 1a, but built on top of a waveguide, with the source and drain electrodes connected to electric ground. The main purpose of this experiment is to spectroscopically quantify the amount of charged polymer semiconductor based on spectroscopic signatures which are distinctive of charge carriers. In the electrostatic double layer regime, one would expect that the amount of charged polymer is not significantly greater than 1 monolayer. Conversely, when polymer mixing occurs, the amount of charged polymer can greatly exceed one monolayer, as the bulk of the polymer can now be electrochemically charged.^{12,13}

There are two types of absorptions sensitive to the presence of charge that can be used to estimate charge density: polaron absorptions and molecular vibrations of the neutral polymer. The presence of charge carriers causes broad electronic absorptions to appear. These absorptions, often referred to as polaron absorptions, are associated with the appearance of localized electronic states within the band gap of a polymer semiconductor.²⁵ Figure 2b shows difference spectra of the device at a few gate voltages. The rapid growth of a broad absorption feature centered at ~ 4000 cm⁻¹ accompanies charge injection. (Note the logarithmic scale.) This feature is assigned to the lowest polaron absorption of the doped P3HT molecule.^{25,26} There is clear evidence of a large increase in the number of carriers as the voltage is increased from -1.6 V to -2.2 V.

An alternative to quantify the concentration of injected charge is to monitor the loss of molecular signatures associated with the neutral molecule. Molecular vibrational modes associated with the conjugated core of a molecule are known to be strongly disrupted by the presence of charge.^{26,27} Figure 2c shows how the ring stretching mode of the thiophene monomer decreases with increasing gate bias voltage. This absorption can be used to estimate the percentage of molecules or monomer units that bear some portion of

charge. For this purpose, we determine the ratio (γ) of monomer units affected by the presence of carriers to the total number of monomer units in the film:

$$\gamma = \left(1 - \frac{A_V}{A_{V=0}}\right) \frac{a_{\text{tot}}}{a_G} \quad (1)$$

where A_V is the absorbance of a neutral mode at a particular voltage (V), here calculated as the integration of the ring stretching mode of a neutral thiophene. $A_{V=0}$ is the absorbance of the same mode when the voltage is equal to zero. The ratio outside the parentheses is a correction that takes into account the fact that the gated area of P3HT (a_G) is less than the total area of the P3HT film (a_{tot}).

Figure 3 shows a plot of (a) the integrated intensity of the polaron absorption peak (see Figure 2a) and (b) the γ value as a function of gate voltage. Both values remain low throughout the entire operating regime of the transistor ($0 \geq V_G > -1.8$ V), and suddenly increase between $V_G = -1.8$ V and $V_G = -1.9$ V. This voltage correlates well with the observed sharp decrease in the trans-conductance (Figure 1c), supporting the argument that polymer mixing occurs, resulting in the disruption of molecular packing in the P3HT semiconductor film. On the basis of the P3HT film thickness and structural parameters for crystalline P3HT, we can estimate that the γ value appropriate for the complete charging of one P3HT monolayer is $\sim 10^{-2}$. At the point of the transition ($V_G = -1.8$ V), this value is reached, indicating that, prior to device breakdown, a complete P3HT monolayer is charged. As we show below, the maximum charge density from electrostatic doping is 2×10^{14} /cm². Note that, in addition to the rapid increase in the amount of charge injected, we also observe that the dielectric mixture becomes dark red after the threshold voltage is breached, indicating the dissolution of P3HT in the LiPSS:PEO dielectric. Figure 3c illustrates the two regimes of device operation: electrostatic double layer charging and electrically driven mixing.

The observed electrically driven mixing process can be considered as a special case of polymer solution thermodynamics. Theories of polymer mixing are similar to those of liquid–liquid solutions, save the fact that the reduced translational entropy imposed by the fixed spatial configuration of monomer units implies a smaller entropic contribution. The enthalpic contribution to the free energy of mixing is

usually given in terms of the unitless Flory–Huggins parameter, χ , which describes, in essence, the comparative strength between polymer and solvent (ϵ_{ps}), versus polymer–polymer (ϵ_{pp}) and solvent–solvent (ϵ_{ss}) interactions.^{28,29}

$$\chi = \frac{Z}{k_B T} \left(\epsilon_{ps} - \frac{1}{2} (\epsilon_{pp} + \epsilon_{ss}) \right) \quad (2)$$

In eq 2, Z is the number of nearest neighbor interactions, k_B is the Boltzmann constant, and T is the temperature. A brief examination of eq 2 can be used to illustrate important aspects of the χ parameter. Should the strength of all the interactions be equal, there is no enthalpic penalty for mixing (the χ parameter will be zero), and the polymer will mix with the solvent. However, it is often the case that the polymer–polymer and solvent–solvent interactions are stronger (energetically more negative) than the polymer–solvent interaction. In such a situation, the χ parameter is positive, representing the increase in enthalpy that occurs when the two components mix.

The χ parameter for the P3HT/dielectric system can be calculated from the Hildebrand solubility parameter δ , which is defined as the square root of the cohesive energy density of a substance.^{28–30} In essence, this parameter describes the self-interactions of the polymer and the solvent, and assumes that the interaction between the components is the geometric average of their self-interactions. This assumption tends to be more valid when applied to weak, nondirectional interactions.²⁹ It is a convenient way to estimate solubility as values for this parameter have been tabulated for a variety of substances.³¹ In the following equation R is the ideal gas constant, and \bar{V}_1 is the molar volume of the solvent, taken in this case to be equal to that of PEO. In addition, the solubility parameters for PEO and P3HT are denoted with a subscript 1 and 2, respectively.

$$\chi = \frac{\bar{V}_1}{RT} (\delta_1 - \delta_2)^2 \quad (3)$$

Rigorously speaking, the semiconductor/dielectric system should be treated as a ternary mixture of PEO, LiPSS, and P3HT. However, since LiPSS is soluble in PEO and is a minor component, we can reduce the problem to the solvation of charged P3HT in PEO with the assistance of PSS anions. In essence, PSS anions are responsible for transporting positively charged P3HT to the PEO phase by forming PSS^{n-} : P3HT^{m+} ion complexes. In other words, electrostatic interaction between the positively charged P3HT and negatively charged PSS favors its dissolution into the PEO dielectric phase at the biased interface. We propose that this can be treated by the addition of an electrostatic energy of attraction. This treatment is similar to the treatment of solubility parameters according to Hansen,³² where additional terms to describe directional interactions such as dipole–dipole and hydrogen bonding are included, resulting in a general description of the enthalpic contributions to solubility. In other words, the polymer solvent interaction (ϵ_{ps}) of eq 2 is modified to include an electrostatic energy of attraction, \bar{E}_C , per unit volume. The addition of this term does not affect the

derivation of the solubility parameters (δ), allowing them to emerge unchanged for use in eq 4.

$$\chi = \frac{\bar{V}_1}{RT} [(\delta_1 - \delta_2)^2 - \bar{E}_C] \quad (4)$$

In the high molecular weight limit, the entropic contribution to mixing is negligible; this is approximately the case here for LiPSS and P3HT. This is due to the reduced entropy of polymers because of the fixed configuration of their monomer units. Mathematically, the entropic contribution for placing a polymer into a volume of solvent scales as N^{-1} where N is proportional to the number of monomer units. Thus, in the high molecular weight limit the entropic contribution to solvation is minimal and the mixing process is wholly determined by enthalpy. Thus, mixing occurs for $\chi < 0$, i.e., when \bar{E}_C exceeds $(\delta_1 - \delta_2)^2$.

Before mixing occurs, \bar{E}_C is given by the capacitance charging energy density,

$$\bar{E}_C = \frac{1}{2} \bar{C} V^2 \quad (5)$$

where \bar{C} is the specific capacitance; l_b is the thickness of the electric double layer, and V is the bias voltage. We point out that eq 5 represents the lower limit in the magnitude of the ion-pair interaction energy (in unit volume). When a P3HT chain (in the positive polaron state) is pulled into the PEO phase, the magnitude of the electrostatic interaction energy between the P3HT polycation and PSS polyanion is expected to increase, because of the structural flexibility in the PEO phase. In addition, the P3HT polycation is now accessible from all sides. Both arguments would suggest that eq 5 represents the lower limit. Thus, we use eq 5 to describe the critical voltage when mixing occurs. At the critical bias voltage, V_C , $\chi = 0$, and the interface becomes unstable. This corresponds to the transition from electrostatic to electrochemical doping (i.e., mixing).

$$\frac{\bar{C}}{l_b} = \frac{2(\delta_1 - \delta_2)^2}{V_C^2} \quad (6)$$

On the basis of our experimental value of $V_C = -1.8$ V and the literature values of $\delta_1 = 20.2$ (MPa)^{1/2} for PEO³¹ and $\delta_2 = 12.8$ (MPa)^{1/2} for P3HT,³³ we obtain $\bar{C}/l_b = 3.4 \times 10^7$ F/m³.

We attempted to measure \bar{C} in our model device, but the high leakage currents and noise of the capacitor prevented us from obtaining a reliable measurement. Previous measurement by Said et al. on a P3HT OFET gated with a poly(styrenesulfonic acid) dielectric gives a specific capacitance of 20 $\mu\text{F}/\text{cm}^2$.⁶ Since the electric double layer in this previous measurement is essentially the same as that in the present study, we take \bar{C} to be 20 $\mu\text{F}/\text{cm}^2$. This gives an electric double layer thickness of $l_b = 6.0$ nm, which is of the order expected for polyelectrolyte/polymer semiconductor interfaces.³⁴ The maximum charge density at the critical voltage is $Q_M = \bar{C} V_C = 2.2 \times 10^{14}/\text{cm}^2$, which is almost 1/4 of the density of thiophene rings for a planar interface.²⁷ In accordance with known behavior of weakly immiscible polymer interfaces,³⁵ we believe that roughening of the interface occurs as the critical voltage is approached. Thus, the actual interfacial area

must be larger than that of the planar geometry. The interfacial roughening phenomenon can be understood as a largely entropic effect where random walk statistics governing polymer chain configuration overcome repulsive interactions between the polymers at the interface.

As a corollary, it is worth noting that the situation encountered with polyionic dielectric is somewhat different than that encountered during the electrochemical oxidation of a polymer semiconductor with a small molecule or inorganic ion.^{12–16} In the latter cases, the size of the ion allows them to penetrate the semiconductor film without a major disruption to the film structure, allowing the heavily doped film to become quite conductive during the reversible doping process. However, despite important differences, the small ion doping process could also be theoretically treated in a fashion similar to the one outlined here.

To conclude, we quantitatively analyzed the transition from electrostatic to electrochemical doping at the model interface between a polymer semiconductor, P3HT, and a polymer electrolyte dielectric, LiPSS:PEO. In situ optical spectroscopy and field effect transistor measurements both show a distinct transition at a critical gate voltage of $V_C = -1.8$ V. For $0 > V_G > -1.8$ V, the interface is physically intact, corresponding to electrostatic double layer charging. For $V_G < -1.8$ V, electrochemical mixing occurs at the polymer interface and the density of injected charge rises rapidly until the entire P3HT/LiPSS:PEO volume is electrochemically mixed. This distinct transition can be well described from the thermodynamics of polymer mixing. It also defines the maximum charge density ($2 \times 10^{14}/\text{cm}^2$ in this case) achievable in the electrostatic doping region.

EXPERIMENTAL SECTION

The polyanion, LiPSS (see Figure 1), was obtained from Aldrich as a 30% w/w solution in water. The water was removed first by rotovap, then by dissolving in methanol and mixing with molecular sieves. Several cycles of freeze-drying and heating under vacuum was the final step employed to remove as much water as possible. PEO ($M_w = 300$) was obtained from Aldrich and used without further purification. LiPSS was mixed with PEO at a 3% mol ratio in methanol. The methanol was driven off first by rotovap, then by several cycles of freeze-drying. The resulting substance was a cloudy, viscous, liquid.

P3HT was obtained from Reike metals ($M_w = 76$ kD and 45 kD) and was used without further treatment. Also, a lower molecular weight sample ($M_w = 15$ kD) of P3HT was synthesized using a modified version³⁶ of the Grignard metathesis (GRIM) polymerization originally developed by the McCullough group.³⁷ No major difference between the three samples was observed; the conclusions and observations presented here apply to all three molecular weights.

The substrates used for transistor measurements were Si wafers with 3000 Å of thermally grown oxide, purchased from Silicon Valley Microelectronics (San Jose, CA), which were cut into ~ 1.5 cm \times 1.5 cm pieces. In an inert atmosphere glovebox (MBraun), the Si/SiO₂ substrates were spin-coated (Laurel) with P3HT from a 20 mg/mL solution in dichlorobenzene

(Aldrich) at 800 rpm for 120 s. While still under inert atmosphere, the resulting films were baked on a hot plate at 105 °C for ~ 20 min to drive off any residual solvent. Atop the P3HT film, Au source and drain contacts were thermally evaporated through silicon shadow masks, defining channel areas of either $200 \mu\text{m} \times 2000$ or $50 \mu\text{m} \times 2000 \mu\text{m}$ (length \times width). Under inert atmosphere, the polyelectrolyte dielectric was manually pasted over the channel region, and a Pt mesh or Au foil gate electrode, with an area much larger than the channel, was laminated atop the dielectric. The devices were left to set 24 h in a nitrogen glovebox.

Transistor measurements were made first by transferring the finished devices to a Desert Cryogenics (Tucson, AZ) vacuum probe station. Current–voltage measurements were carried out with two Keithley 236 source measure units and a Keithley 6517 electrometer. Measurements were preformed in the dark under nitrogen.

The devices used for in situ optical spectroscopy were fabricated on ZnSe waveguides. The raw ZnSe was purchased from photonic supply. The 1 mm thick wafer was cut into 1 cm \times 3.175 cm pieces. Beveled edges of 45° angles were polished by hand to enable the use of the attenuated total internal reflection (ATR) technique. Voltages were applied by a Keithley 6517A electrometer, and spectra were collected with a Nicolet 6700 spectrometer using a mercury–cadmium–telluride (MCT) detector. Voltages were applied for 30 min, during which several spectra were taken. After applying the voltage, the device was allowed to set without voltage for 30 min. Spectra were collected during this time as well. Voltages were stepped in -0.2 V increments, starting with -0.2 V. The experiments were conducted in an inert atmosphere glovebox (MBraun) where oxygen levels never reached higher than 3 ppm during device operation.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: zhu@cm.utexas.edu.

ACKNOWLEDGMENT This work was supported by the U.S. Department of Energy under Grant Number DE-FG02-05ER46252. Partial supports by the MRSEC Program of the National Science Foundation under Award Number DMR-0819885 and the EnTISE program of the University of Minnesota to B.D.P. are also acknowledged. We thank Prof. T. P. Lodge for valuable suggestions.

REFERENCES

- Gundlach, D. J. *Nat. Mater.* **2007**, *6*, 173–174.
- Yoon, M.-H.; Facchetti, A.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4678–4682.
- Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Dehm, C.; Schütz, M.; Maisch, S.; Effenberger, F.; Brunnbauer, M.; Stellacci, F. *Nature* **2004**, *431*, 963–966.
- Kim, C.; Wang, Z.; Choi, H.-J.; Ha, Y.-G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 6867–6878.
- Panzer, M. J.; Newman, C. R.; Frisbie, C. D. *Appl. Phys. Lett.* **2005**, *86*, 103503.

- (6) Said, E.; Crispin, X.; Herlogsson, L.; Elhag, S.; Robinson, N. D.; Berggren, M. *Appl. Phys. Lett.* **2006**, *89*, 143507.
- (7) Lee, J.; Panzer, M. J.; He, Y.; Lodge, T. P.; Frisbie, C. D. *J. Am. Chem. Soc.* **2007**, *129*, 4532–4533.
- (8) Herlogsson, L.; Crispin, X.; Robinson, N. D.; Sandberg, M.; Hagel, O.-J.; Gustafsson, G.; Berggren, M. *Adv. Mater.* **2007**, *19*, 97–101.
- (9) Panzer, M. J.; Frisbie, C. D. *J. Am. Chem. Soc.* **2007**, *129*, 6599–6607.
- (10) Ahn, C. H.; Bhattacharya, A.; Di Ventra, M.; Eckstein, J. N.; Frisbie, C. D.; Gershenson, M. E.; Goldman, A. M.; Inoue, I. H.; Mannhart, J.; Millis, A. J.; Morpurgo, A. F.; Natelson, D.; Triscone, Rev. *Mod. Phys.* **2006**, *78*, 1185–1212.
- (11) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH Publishers: New York, 1991.
- (12) Kaake, L. G.; Zou, Y.; Panzer, M. J.; Frisbie, C. D.; Zhu, X.-Y. *J. Am. Chem. Soc.* **2007**, *129*, 7824–7830.
- (13) Yuen, J. D.; Dhoot, A. S.; Namdas, E. B.; Coates, N. E.; Heeney, M.; McCulloch, I.; Moses, D.; Heeger, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 14368–14371.
- (14) Lee, J.; Kaake, L. G.; Cho, J. H.; Zhu, X.-Y.; Lodge, T. P.; Frisbie, C. D. *J. Phys. Chem. C* **2009**, *113*, 8972–8981.
- (15) Taniguchi, M.; Kawai, T. *Appl. Phys. Lett.* **2004**, *85*, 3298.
- (16) Shimotani, H.; Diguët, G.; Iwasa, Y. *Appl. Phys. Lett.* **2005**, *86*, 022104.
- (17) Tashiro, K.; Kobayashi, M.; Kawai, T.; Yoshino, K. *Polymer* **1997**, *38*, 2867–2879.
- (18) Prosa, T. J.; Winokur, M. J.; Moulton, J.; Smith, P.; Heeger, A. J. *Phys. Rev. B* **1995**, *51*, 159–168.
- (19) Shimotani, H.; Diguët, G.; Iwasa, Y. *Appl. Phys. Lett.* **2005**, *86*, 022104.
- (20) Arkhipov, V. I.; Emelianova, E. V.; Heremans, P.; Bassler, H. *Phys. Rev. B* **2005**, *72*, 235202.
- (21) Xia, Y.; Cho, J. H.; Lee, J.; Ruden, P. P.; Frisbie, C. D. *Adv. Mater.* **2009**, *21*, 2174–2179.
- (22) Yuan, H. T.; Shimotani, H.; Tsukazaki, A.; Ohtomo, A.; Kawasaki, M.; Iwasa, Y. *Adv. Funct. Mater.* **2009**, *7*, 1046–1053.
- (23) Cho, J. H.; Lee, J.; Xia, Y.; Kim, B.; He, Y. Y.; Renn, M. J.; Lodge, T. P.; Frisbie, C. D. *Nat. Mater.* **2008**, *7*, 900–906.
- (24) Hamedi, M.; Herlogsson, L.; Crispin, X.; Marcilla, R.; Berggren, M.; Inganäs, O. *Adv. Mater.* **2009**, *21*, 573–577.
- (25) Osterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. *Science* **2000**, *287*, 839–842.
- (26) Kaake, L. G.; Zhu, X.-Y. *J. Phys. Chem. C* **2008**, *112*, 16174–16177.
- (27) Mills, T.; Kaake, L. G.; Zhu, X.-Y. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *95*, 291–296.
- (28) Teraoka, I. *Polymer Solutions: An Introduction to Physical Properties*; Wiley-Interscience, New York, 2002; Ch. 2.
- (29) Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd ed.; CRC Press: Boca Raton, FL, 2007; Chapter 7.
- (30) Hildebrand, J. H.; Lane, S. R. *The Solubility of Nonelectrolytes*; Reinhold Publishing Corp.: New York, 1950; Chapter 8.
- (31) *Polymer Handbook*, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R., Eds.; Wiley-Interscience: New York, 1999.
- (32) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, 2000; Chapter 2.
- (33) Jaczewska, J.; Raptis, I.; Budkowski, A.; Goustouridis, D.; Raczowska, J.; Sanopoulou, M.; Pamuła, E.; Bernasik, A.; Rysz, J. *Synth. Met.* **2007**, *157*, 726–732.
- (34) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980.
- (35) Helfand, E.; Sapse, A. M. *J. Chem. Phys.* **1975**, *62*, 1327–1331.
- (36) Boudouris, B. W.; Molins, F.; Blank, D. A.; Frisbie, C. D.; Hillmyer, M. A. *Macromolecules* **2009**, *42*, 4118–4126.
- (37) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250–253.