

FINAL PROGRESS REPORT

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Institutions: University of Texas at Austin, University of Minnesota at Minneapolis

Contact Info:

Prof. Xiaoyang Zhu
Department of Chemistry
Columbia University
New York, NY 10027
Email: xyzhu@columbia.edu
Tel: 212-851-7768

2. Project Title: Spectroscopy of Charge Carriers and Traps in Field-Doped Single Crystal Organic Semiconductors

Principal Investigator: Xiaoyang Zhu, C. Daniel Frisbie

3. Date of the Report: June 13th, 2013

Period Covered: 03/01/2008 – 10/31/2011.

4. Brief Description of Accomplishments:

Research achievements during this funding period are in two areas. The first is the development of absorption spectroscopy as a probe of charge carriers in gate-doped OFETs. We have focused on a model polymeric semiconductor, poly (3-hexylthiophene), and high capacitance dielectric materials (polymer electrolyte or ionic liquid) to probe gate-doping mechanisms. We have established fundamental limits and transitions in electrostatic and electrochemical doping regions using polymer mixing theories. The second achievement is on the development of displacement current measurement (DCM) in studying the transient behavior of charge carriers and traps. We used the model system of polycrystalline pentacene thin film in a long-channel capacitor (LCC) geometry. The DCM techniques allowed us to determine not only charge carrier mobility, but more importantly, the nature of charge carrier traps at the pentacene-dielectric interface. Eight papers (see list below) in these two areas have been published during this funding period and two more are in progress and one is submitted. We also present some highlights from these research achievements.

A. Electrostatic vs. Electrochemical Doping. A key focus during this funding period is the application of absorption spectroscopy to understand the molecular mechanism of gate-doping in OFETs with liquid dielectrics (ionic liquids & polymer electrolytes). A major

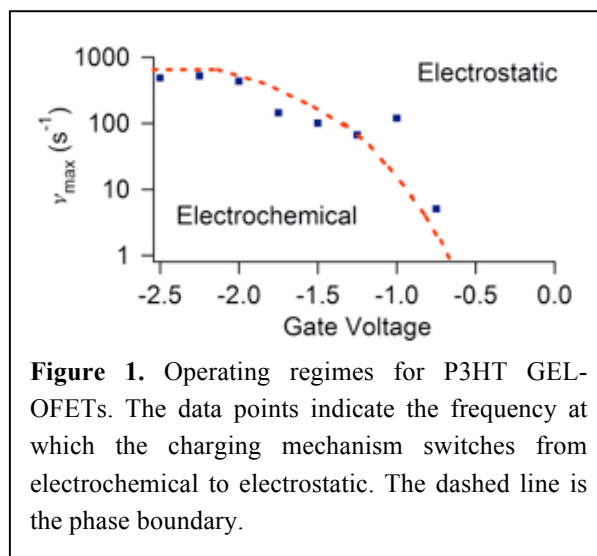
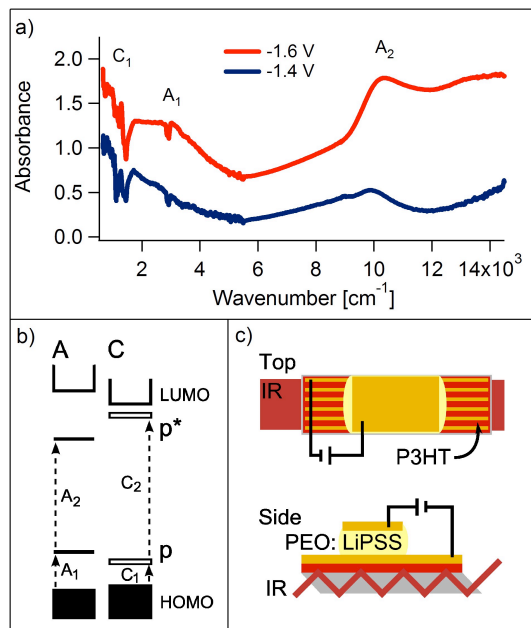
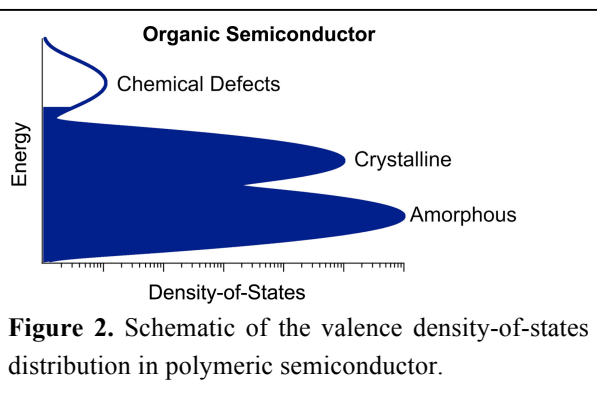


Figure 1. Operating regimes for P3HT GEL-OFETs. The data points indicate the frequency at which the charging mechanism switches from electrochemical to electrostatic. The dashed line is the phase boundary.

advantage of these dielectric material is the exceptionally high capacitance ($\geq 1 \text{ mF/cm}^2$) which allows one to achieve charge carrier density as high as $10^{14}/\text{cm}^2$ and transistor operation at gate voltages as low as 1 V. The low voltage operation is particularly important to the practical application of OFETs and the high doping level allows one to explore interesting new carrier physics in organic semiconductors. The presence of mobile ions in these dielectric materials raises the critical question of whether the gate-doping mechanism is purely electrostatic or electrochemical (mixing). Using in situ absorption spectroscopy for a $\text{LiClO}_4/\text{PEO}$ polymer electrolyte gated device, we can quantitatively measure the concentration of carriers in the organic semiconductor, in this case poly-3-hexyl-thiophene (P3HT). By monitoring the time-dependent buildup of charged species, we can determine the diffusion constants of carriers injected from a source electrode and that of mobile ions from the dielectric into the organic semiconductor (electrochemical doping) as function of gate voltage. This allows us to estimate the time scales (t_m) for mixing for the first organic semiconductor molecular layer in contact with the dielectric and to construct a “phase” diagram for two doping mechanisms, as illustrated for an ion-gel gated P3HT OFET, Fig. 1. Here, we compare the maximum OFET switching speed (g_{max}) with $1/t_m$. When $g_{\text{max}} > 1/t_m$, we are in the electrostatic region. When $g_{\text{max}} < 1/t_m$, we have electrochemical doping.

B. The bimodal electronic energy landscape.

The application of in situ spectroscopy to polymeric semiconductors has also allowed us to understand the complex electronic energy landscape in these materials. We suggest the presence of a two-tier electronic energy landscape: a bimodal majority landscape due to two dominant structural motifs and a minority electronic energy landscape from intrinsic charged defects, Fig. 2. The bimodal majority electronic energy landscape results from a combination of amorphous domains and micro-crystalline or liquid-crystalline domains. The minority tier of the electronic density of states is comprised of deep



Coulomb traps embedded in the majority electronic energy landscape. This minority electronic energy landscape may dominate transport properties at low charge carrier densities, such as those expected for OPVs, while the bimodal majority electronic energy landscape becomes significant at high carrier densities, e.g., in OFETs.

To probe the majority electronic energy landscape, we carry out spectroscopy measurement on a model device: the interface between a polymeric semiconductor, P3HT, and a polymer electrolyte dielectric consisting of lithium poly(styrene sulfonate) dissolved in poly(ethylene oxide), LiPSS:PEO. As a function of gate bias voltage (V_G), in situ optical spectroscopy reveals a distinct transition from electrostatic ($0 > V_G > -1.8$ V) doping to electrochemical ($V_G < -1.8$ V) mixing. Here we focus on the electrostatic double-layer charging region. Based on a previously measured capacitance density of 20 mF/cm^2 at the P3HT/PSS interface, we can calculate a maximum charge density of $\sim 2 \times 10^{14} \text{ /cm}^2$ at the highest bias voltage of $V_G = -1.8$ V. Since this charge density is confined within a few nanometers from the interface, we can convert this 2D density to a 3D carrier density of 10^{20} - 10^{21} /cm^3 . Such a high carrier density samples the majority electronic energy landscape and can be observed spectroscopically. The two spectra in Fig. 3 are obtained from the model device at two different bias voltages. At the lower bias voltage, charge carriers (hole polarons) predominantly reside in crystalline regions of the polymer. As the bias voltage and thus injected charge density increase, charge carriers start to populate states more associated with the 1D disordered regions. This presents clear evidence for the bimodal electronic energy landscape in P3HT and the preferential population of the 2D crystalline domains at low charge carrier densities.

C. Displacement Current Measurements. In the area of transport, a principal directions has been to employ gate displacement current measurements on OFETs to understand transient charging and discharging dynamics in organic semiconductors, trapped charge concentrations, and total gate-induced charge. In standard transistor measurements, the DC current running through the conducting channel from source to drain electrode is measured either as a function of gate voltage or as a function of drain voltage.

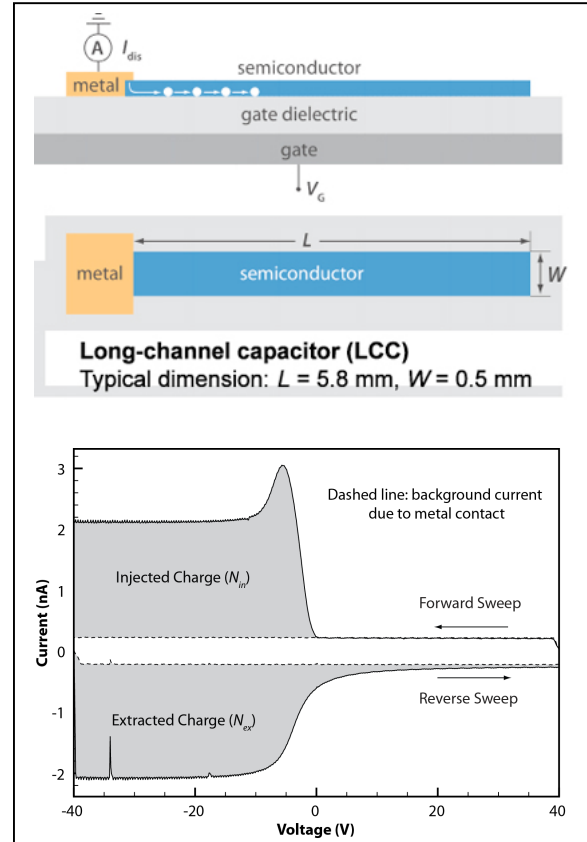


Figure 4. (Top) Device geometry for displacement current measurements in which application of a gate bias causes a front of carriers to be injected from the grounded metal contact and to sweep along the organic semiconductor channel. (Bottom) Measured displacement current (at either the top contact or the gate) as a function of the gate voltage. Integration gives injected and extracted charge; the difference between these gives trapped charge.

These traditional measurements give important device parameters, such as field-effect mobility, ON/OFF ratio, and threshold voltage. However, *transient* processes – including the injection of charge carriers from metal contacts into the OSC layer, the redistribution of carriers in the OSC layer to form the conducting channel, and the extraction of carriers from the OSC layer during the channel annihilation - are not explored in typical OFET measurements. Study of transient processes through displacement current measurements (DCM) provides additional information on carrier injection/extraction dynamics and trapping/detrapping properties.

A typical device geometry we employed is shown in Fig. 4; it is a two-terminal device structure resembling a simplified field-effect transistor with either source or drain electrode removed. Carrier transport occurs in the direction parallel to the dielectric surface. In contrast to the transistors, one source/drain contact was removed in these structures and much longer channels were used, which increased both the transit time and the displacement current and resulted in better signal-to-noise ratio in electrical measurements.

The displacement current associated with charging and discharging the OSC layer was measured and is also shown in Fig. 4. By integrating this current, the concentrations of injected, extracted, and trapped carriers were estimated. For example, the concentration of trapped carriers (p_{trap}) is the difference between the total injected and extracted charge concentrations:

$$\bar{p}_{\text{trap}} = N_{\text{trap}} / A_{\text{pen}} = (N_{\text{in}} - N_{\text{ex}}) / A_{\text{pen}} \quad (1)$$

Where A_{pen} is the organic semiconductor (e.g., pentacene) area, and

$$N_{\text{in}} = \left| \frac{1}{er_v} \int_{V_1}^{V_2} (I_{\text{dis}}^f - I_{\text{dis}}^{\text{Au},f}) dV \right| \quad N_{\text{ex}} = \left| \frac{1}{er_v} \int_{V_2}^{V_1} (I_{\text{dis}}^r - I_{\text{dis}}^{\text{Au},r}) dV \right| \quad (2)$$

where r_v is the gate voltage sweep rate and I_{dis} stands for displacement current in either the forward (f) or reverse (r) gate voltage sweep directions.

In addition, the transient processes of conducting channel formation and annihilation were identified in the current vs. voltage (I-V) characteristics. With device simulation it was possible to understand quantitatively the origin of these transient effects in terms of the channel carrier dynamics and trapping and detrapping processes. A central finding was that the commonly observed peak in the displacement current on channel formation (see Fig. 10) is directly related to the magnitude of the carrier mobility and the presence of a transient lateral electric field that drives an initial front of charge carriers across the semiconductor channel from the injecting contact.

Similar DCM measurements were also employed to examine contact effects on channel charging and discharging. Specifically, we observed that more carriers were trapped in devices with Au

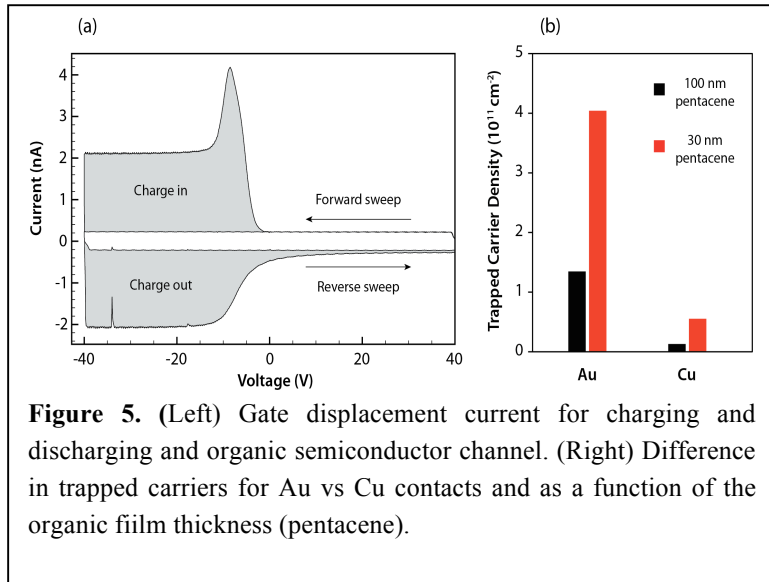


Figure 5. (Left) Gate displacement current for charging and discharging and organic semiconductor channel. (Right) Difference in trapped carriers for Au vs Cu contacts and as a function of the organic film thickness (pentacene).

contacts than in devices with Cu contacts, Fig. 5. We proposed that carrier trapping in the long channel of the Au devices is indirectly caused by the deep trap states at the pentacene-dielectric interface *in the contact region* generated by Au penetration. Such trap states are minimal when Cu is used as the contact metal. Importantly, we were also able to observe electron displacement currents when we contacted pentacene with Al.

5. Publications Acknowledging DOE support

“Charge transport, Nanostructure and the Mott insulator-to-metal transition in poly (3-hexylthiophene),” L. Kaake, X.-Y. Zhu, *J. Phys. Chem. C* 112 (2008) 16174–16177.

“Ion gel gated polymer thin-film transistors: operating mechanism, characterization of gate dielectric capacitance, hole mobility, switching speed, and stability,” J. Lee, L. G. Kaake, J. H. Cho, X.-Y. Zhu, T. P. Lodge, C. D. Frisbie, *J. Phys. Chem. C* 113 (2009) 8972–8981.

“Polaron and ion diffusion in a poly(3-hexylthiophene) thin film transistor gated with a polymer electrolyte dielectric,” T. Mills, L. Kaake, X.-Y. Zhu, *Appl. Phys. A* 95 (2009) 291-296.

“Conducting channel formation and annihilation in organic field-effect structures,” Y. Liang, C. D. Frisbie, H-C Chang, P. P. Ruden, *J. App. Phys.* 105 (2009) 024514.

“Mixing at a Charged Interface Between a Polymer Semiconductor and a Polyelectrolyte Dielectric,” L. Kaake, B. Paulson, C. D. Frisbie, X.-Y. Zhu, *J. Phys. Chem. Lett.* 1 (2010) 862-867.

“Intrinsic charge trapping in organic and polymeric semiconductors: a physical chemistry perspective,” L. Kaake, P. F. Barbara, X.-Y. Zhu, *J. Phys. Chem. Lett.* 1 (2010) 628–635.

“Transient effects controlling the charge carrier population of organic field effect transistor channels.” Chang, H.C.; Ruden, P.P.; Liang, Y.; Frisbie, C.D. *J. Appl. Phys.* 107 (2010), 104502.

“Quantify interfacial electric fields and local crystallinity in polymer/fullerene bulk heterojunction solar cells,” I. R. Gearba, J. Morris, T. Mills, D. Black, R. Pindak, X.-Y. Zhu, *Adv. Funct. Mater.* 21 (2011) 2666-2673.

6. People working on the project

Graduate students:

Loren Kaake (graduate student, 50% support; the other 50% on internal); Travis Mills (graduate student, 50% support, the other 50% on TA); Y. Liang (graduate student, 100%)

7. Current and pending support

Department of Energy, Zhu (PI); Frisbie (co-PI)

01/01/12-12/31/14

“Spectroscopy of charge carriers and traps in field-doped single crystal organic semiconductors” \$540,000.

This project is aimed at obtaining direct spectroscopic signatures of charge carrier trapping in organic electronic materials and devices.

This project.

Department of Energy, Zhu (PI) 09/01/10-08/31/13
“Extracting hot carriers from photoexcited semiconductor nanocrystals” \$630,000.

Role: PI

This project is aimed at understanding the charge separation mechanism in nanomaterial based photovoltaic.

No overlap.

National Science Foundation, Zhu (PI) 06/01/12-05/31/15
“Exceeding the limit in solar energy conversion with exciton fission”, \$461,000

This project is aimed at understanding exciton fission and energy transfer in organic semiconductors.

No overlap.

National Science Foundation, Huffaker (PI); Ratsch, You, Zhu (co-PIs)
09/01/11-08/31/14

“SOLAR Collaborative: Designing and modeling advanced nanostructure based hybrid solar cells”, (\$347,999 to Zhu)

This project is aimed at fundamental mechanisms underlying organic-GaAs heterojunction solar cells.

No overlap.

Department of Energy, Yardley (PI); Zhu is one of 17 co-PIs. 08/01/09-07/31/14

Energy Frontier Research Center - High Efficiency Nanosystems for Photovoltaics: Moving Beyond the Shockley-Queisser Limit,” ~\$600,000 to Zhu

This project is aimed at understanding molecular control on nanomaterial based photovoltaic. Zhu’s effort in this project focuses on singlet fission materials based on organic semiconductors. These are crystalline van der Waals solids, e.g., pentacene & tetracene, and are fundamentally different from inorganic nanomaterials in the current DOE project.

No overlap.

National Science Foundation, Zhu (PI); Liu (co-PIs) 08/01/12-07/31/15

“SOLAR Collaborative: Designing and modeling advanced nanostructure based hybrid solar cells Dynamic Self-Assembly of Glycolipids for Unveiling Complex Glycan-Protein Interactions”, (\$300,000)

This project is aimed at developing fluidic glycan microarrays for large scale screening in glycomics.

No overlap.

8. Unexpended fund

none.