FINAL PROGRESS REPORT

1. **DOE Award Number:** DE-FG02- SC0004200
   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:** December 9th, 2014
   Period Covered: 11/01/2011 – 12/31/2012.

4. **Brief Description of Accomplishments**:

The proposed research aims to achieve quantitative, molecular level understanding of charge carriers and traps in field-doped crystalline organic semiconductors via in situ linear and nonlinear optical spectroscopy, in conjunction with transport measurements and molecular/crystal engineering. Organic semiconductors are emerging as viable materials for low-cost electronics and optoelectronics, such as organic photovoltaics (OPV), organic field effect transistors (OFETs), and organic light emitting diodes (OLEDs). Despite extensive studies spanning many decades, a clear understanding of the nature of charge carriers in organic semiconductors is still lacking. It is generally appreciated that polaron formation and charge carrier trapping are two hallmarks associated with electrical transport in organic semiconductors; the former results from the low dielectric constants and weak intermolecular electronic overlap while the latter can be attributed to the prevalence of structural disorder. These properties have lead to the common observation of low charge carrier mobilities, e.g., in the range of 10^{-5} - 10^{-3} cm^2/Vs, particularly at low carrier concentrations. However, there is also growing evidence that charge carrier mobility approaching those of inorganic semiconductors and metals can exist in some crystalline organic semiconductors, such as pentacene, tetracene and rubrene. A particularly striking example is single crystal rubrene (Figure 1), in which hole mobilities well above 10 cm^2/Vs have been observed in OFETs operating at room temperature. Temperature dependent transport and spectroscopic measurements both revealed evidence of free carriers in rubrene. Outstanding questions are: *what are the structural features and physical properties that make rubrene so unique? How do we establish fundamental design principles for the development of other organic semiconductors of high mobility?* These questions are critically important but not comprehensive, as the nature of charge carriers is known to evolve as the carrier concentration increases, due to the presence of intrinsic disorder in organic semiconductors. Thus, a complementary question is: *how does the nature of charge transport change as a function of carrier concentration?*

To answer these questions, the PIs are extend their successful collaboration that combines transport measurements with in situ spectroscopy (Fig. 1); the new focuses are on single crystal organic semiconductor field effect devices gated with ionic liquid or ion gel for high charge carrier doping densities. The OFET structure provides control of surface charge concentration and the determination of carrier transport characteristics (e.g. mobility), while optical spectroscopy provides physical insight into the nature of charge carriers, as polarons and free carriers possess distinct optical signatures and also provide direct measurements of the energetics of charge carriers with respect to HOMO & LUMO bands. The establishment of synergistic collaboration between transport and spectroscopy of the two laboratories over the past funding period and the successful development of a set of powerful experimental tools and model systems have now set the stage for the two PIs to tackle the most fundamental and most important problems in organic semiconductor research. A long-term outcome will be rationally designed materials and interfaces for high performance OFETs and for the exploration of new physical phenomena in organic semiconductors.

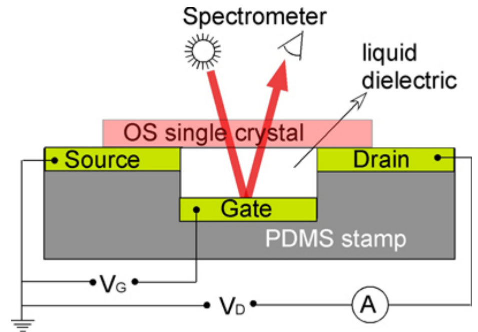

Figure 1. In situ optical absorption spectroscopy of an OFET structure with ionic liquid dielectric.

We have carried out transport measurements on ionic liquid (electrolyte) gating of two benchmark organic semiconductors, poly(3-hexylthiophene) and rubrene. The goal of these experiments is to use the giant capacitance of ionic liquids to induce large carrier densities in the organic semiconductors and to explore transport in the high carrier density regime. We find that in the case of P3HT, the mobility becomes high enough at the 3D highest charge densities, near 10^{21} cm^{-3}, that the Hall effect can be reproducibly observed. Furthermore, it is clear from extensive resistivity measurements versus temperature that a metallic state in P3HT is approached, though it is not realized likely due to gating induced disorder. In the case of rubrene single crystals, carrier mobilities as large a 4 $cm^2/V{\cdot}s$ are achieved at 2D hole densities of 0.15 charges/rubrene, ~3 x 10^{13} cm^{-2}. These large mobilities lead to an easily detected Hall signal that verifies the charge density estimated from capacitance-voltage measurements. Furthermore, at optimum carrier densities, the near-onset of metallic behavior is clearly observed for rubrene.

Concurrent with transport experiments, we carried out spectroscopic measurements to quantify the density of doping upon the formation of the rubrene/ionic liquid (ion gel) interface. Based on charge modulation FTIR spectroscopy, we discovered that there is an intrinsic doping of the rubrene capacitor with an ionic gel dielectric of ~1.5 x 10^{13} cm^{-2} holes (manuscript in preparation). Such an intrinsic density of doped holes can be removed with a positive gate bias of V_G = 0.8 V. These intrinsically doped holes are believed to result from the stabilization of hole carriers at the interface by counter ions (anions) in the ionic gel, a process similar to the trap healing mechanism discovered recently by Podzorov and coworkers. For negative gate bias up to V_G = -1.0 V, we find addition hole doping up to ~3 x 10^{13} cm^{-2}, in agreement with transport measurements. These findings suggest a new mechanism for gate doping of organic semiconductors with ionic liquid or ion gel dielectrics.

5. **Publications Acknowledging DOE support**

Wang, S; Ha, MJ; Manno, M; Frisbie, CD; Leighton, C. "Hopping transport and the Hall effect near the insulator-metal transition in electrochemically gated poly(3-hexylthiophene) transistors." *Nature Communications,* **2012***, 3,* 1210. DOI: 10.1038/ncomms2213

Morris, J. D.; Atallah, T. L.; Park, H.; Ooi, Z.; Dodabalapurd, A.; Zhu, X.-Y. "Quantifying space charge accumulation in organic bulk heterojunctions by nonlinear optical microscopy," *Organic Electronics* **2013**, *14*, 3014-3018.

Morris, J. D.; Atallah, T. L.; Lombardo, C. J.; Dodabalapur, A.; Zhu, X.-Y. "Mapping electric field distributions in biased organic bulk heterojunctions under illumination by nonlinear optical microscopy," *Appl. Phys. Lett.* **2013**, *102*, 033301.

Xie, W.; Wang, S.; Zhang, X.; Leighton, C.; Frisbie, C. D. "High Conductance 2D Transport around the Hall Mobility Peak in Electrolyte-Gated Rubrene Crystals", *Phys. Rev. Lett*., submitted, **2014**.

6. **People working on the project**

Graduate students:

Joshua Morris (graduate student, 100% on internal); Tim Atallah (graduate student, 100% TA/fellowship), W. Xie, (graduate student, 50% support, the other 50% on internal); S. Wang, (graduate student, 100% internal support)

7. **Current and pending support**

Current

National Science Foundation, Zhu (PI) 06/01/12-05/31/15
"Exceeding the limit in solar energy conversion with exciton fission", $461,000
The project is aimed at understanding exciton fission and energy transfer in organic semiconductors.

National Science Foundation, Zhu (PI); Liu (co-PIs) 08/01/12-07/31/15
"Dynamic Self-Assembly of Glycolipids for Unveiling Complex Glycan-Protein Interactions", ($300,000)
The project is aimed at developing fluidic glycan microarrays for large scale screening in glycomics.

Sandia National Lab – subcontract, Zhu (PI) 08/01/13-12/31/14
"Collaborative research on the Auger mechanism in semiconductor light-emitting diodes" $150,000
The project is aimed at understanding the Auger mechanism for the Droop phenomena in QW based white light LEDs. There is **no overlap** with the current proposal.

Department of Energy, Zhu (PI) 09/01/13-04/30/15
"Extracting hot carriers from photoexcited semiconductor nanocrystals" $352,759.
The project is aimed at understanding the charge separation mechanism in nanomaterial based photovoltaic.

Department of Energy, Zhu (PI); Frisbie (co-PI, UMN) 09/01/13-12/31/15
"Spectroscopy of charge carriers and traps in field-doped single crystal organic semiconductors" $470,103.
The project is aimed at obtaining direct spectroscopic signatures of charge carrier trapping in organic electronic materials and devices. There is **no overlap** with the current proposal.
Samsung Global Research Initiative, Zhu (PI) 11/01/13-10/31/14
"Probing Hot Electron Dynamics by Femtosecond Time-resolved Nonlinear Optical Spectroscopies**".** $100,000/yr
The project aims to develop and apply nonlinear optical spectroscopies to characterize hot electron dynamics in 2D nanomaterials. There is **no overlap** with the current proposal.
Air Force Office of Scientific Research, Nuckolls (PI); Zhu is 1 of 3 co-PIs. 09/01/13-08/31/16
"Artificial Atoms, Molecules, and Solids: Multiple Functions and Emergent Properties" $1,300,000.
The project explores the synthesis and emergent physical properties of new electronic materials from the assembly of super-atoms.

Pending:
National Science Foundation, Hone (PI); 11/01/14-08/31/19
(Zhu is an IRG leader and one of 14 co-PIs)
"Columbia University MRSEC (Materials Research Science and Engineering Center)" $16,819,346
The proposal consists of two independent research thrusts, designated IRG1 and IRG2. IRG1 will study the properties of van der Waals heterostructures while IRG2 will explore the design and synthesis of new electronic materials from the assembly of super-atoms (atomically precise nano-clusters).
Department of Energy, co-PIs: Zhu & Nuckolls 01/01/15-12/31/17
"Building a Toolbox of Singlet Fission Molecules for Solar Energy Conversion" $913,620.
The proposal aims to develop new strategies for the synthesis of molecular materials with high singlet fission yields.
Department of Energy, Zhu (PI) 05/01/15-04/30/18
"Charge carrier dynamics in hybrid organic-inorganic semiconductors" $689,820.
This proposal aims to probe the intrinsic mechanism of photo-induced charge carrier generation in hybrid organic-inorganic semiconductors.

8. **Unexpended fund**
none.