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14. ABSTRACT This program was focused on several novel experimental approaches to investigating charge injection and charge transport in organic semiconductors all using infrared (IR) spectroscopy. IR spectroscopy was employed to characterize polymer systems integrated in the architecture of organic field-effect transistors (OFET). These experiments allowed the PI to determine: i) the excitations of the studied organic semiconductors, and ii) their dynamics in high mobility OFETs. The PI proposed to investigate modification of the electronic properties at the surface of organic semiconductors controlled by self-assembled monolayers (SAM) and has completed this work. In addition, the PI has completed a comprehensive study of high mobility, low band gap of Donor-Acceptor (D-A) copolymers that are of high interest in view of ambipolar transport in these systems.						
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AFRL-OSR-VA-TR-2013-0095

An infrared probe of charge dynamics in high mobility organic semiconductors

Basov

University of California

FEBRUARY 2013

Final Report

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**AIR FORCE RESEARCH LABORATORY
AF OFFICE OF SCIENTIFIC RESEARCH (AFOSR)/RSA
ARLINGTON, VIRGINIA 22203
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An Infrared probe of charge dynamics in high mobility organic semiconductors

D.N. Basov, *University of California San Diego* dbasov@physics.ucsd.edu,
<http://infrared.ucsd.edu/>

Final report

This program was focused on several novel experimental approaches to investigating charge injection and charge transport in organic semiconductors all using infrared (IR) spectroscopy. IR spectroscopy was employed to characterize polymer systems integrated in the architecture of organic field-effect transistors (OFET). These experiments allowed the PI to determine: *i*) the excitations of the studied organic semiconductors, and *ii*) their dynamics in high mobility OFETs. The PI proposed to investigate modification of the electronic properties at the surface of organic semiconductors controlled by self-assembled monolayers (SAM) and has completed this work. In addition, the PI has completed a comprehensive study of high mobility, low band gap of Donor-Acceptor (D-A) copolymers that are of high interest in view of ambipolar transport in these systems.

1. Infrared signatures of high carrier densities induced in poly(3-hexylthiophene) by fluorinated organosilane molecules

Conjugated polymers, and specifically polythiophenes, have emerged as attractive materials for low-cost, large-area, and flexible electronics applications due to their solution processability, superior film-forming properties, and high mobilities. Since most polymeric systems are intrinsic insulators with a moderate energy gap, it is necessary to introduce mobile charges through electrostatic or electrochemical doping in order to initiate electrical transport: a precondition for functional electronic devices. A comprehensive understanding of charge carrier dynamics in conjugated polymer films remains elusive, especially in the high carrier density regime near the insulator-to-metal transition (IMT). The IMT region is of both practical and fundamental interest, and is difficult to reach in polymers given the constraints of conventional methods of charge injection.

Recently, it became possible to achieve very high carrier densities in organic semiconductors through the use of fluorinated organosilane molecules. Exposure to a vapor of these highly polar molecules (known to self-assemble on surfaces) results in a chemical oxidation (ie hole doping) of the organic semiconductor host, and a several orders of magnitude increase in the DC electrical conductivity. The PI has carried out a thorough infrared and DC transport investigation of a prototypical polymer, poly(3-hexylthiophene) (P3HT), whose electronic properties were modified by a fluoroalkyl trichlorosilane (FTS). The FTS molecules incorporate into the polythiophene structure, hydrolyze, and partially cross-link, forming a 3D network that induces a very strong p-type doping of P3HT.

The PI performed infrared transmission measurements on thin films of P3HT that were treated with FTS, shown in Figure 1. The PI has also fabricated organic field-effect transistors based on

P3HT to directly compare the merits of FTS modification vs electrostatic doping on the same testbed. For FTS-

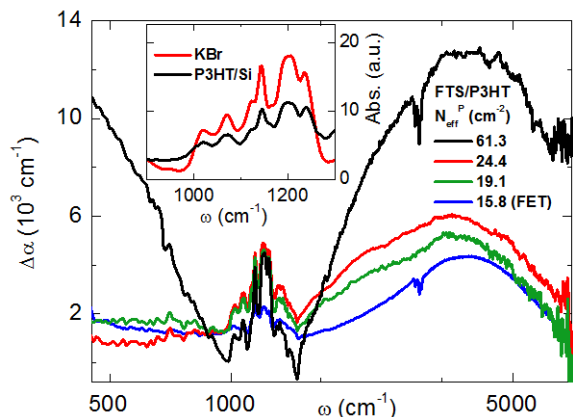


Figure 1: IR absorption of FTS-treated P3HT thin films. The most highly-doped films (black curve) display both polaronic and Drude absorption, indicative of metallic transport.

directly comparing FTS-doping to electrostatic charge injection via field-effect on the same device, we found at least an order of magnitude improvement in the maximum achievable carrier density. Using a simple capacitor model of an OFET, the PI extracted carrier densities exceeding 10^{14} holes/cm² for FTS-treated P3HT, surpassing the charge density limits imposed by use of conventional oxide insulators (roughly 10^{13} /cm²).

In the most highly-doped films, the PI observed both Drude absorption (indicative of delocalized states in a metal) and strong polaron absorption (associated with self-localized states). This intriguing result has implications for several possible theories on the evolution of the electronic structure of conjugated polymers through the IMT involving merging of the valence band with mid-gap polaron or bipolaron bands. Alternatively, coexistence of metallic and localized states may also be indicative of phase separation, possibly a common attribute among conducting polymers. The use of FTS molecules to achieve ultra-high carrier densities near the IMT has afforded us the opportunity to further study this relatively unexplored regime containing rich physics and many outstanding questions. This work is published in the *Journal of Applied Physics*.

2. An infrared probe of charge injection in ambipolar organic field effect transistors (OFETs)

A new generation of Donor-Acceptor (D-A) copolymers based on electron acceptor benzobisthiadiazole (BBT) are of high interest in view of potential applications for photovoltaic and light-emitting devices. These polymers possess extremely narrow band gaps below 1 eV, and when employed in OFET structures as active semiconductors reveal ambipolar transport with relatively high electronic mobility. Experimental studies of the electronic transport in these polymers are still in its infancy. Using infrared spectroscopy, the PI has performed systematic investigations of ambipolar charge injection in a family of BBT-based DA copolymers including polybenzobisthiadiazole-dithienopyrrole [PBBTPD], polybenzobisthiadiazole-

doped films, we observed a prominent absorption band in the mid-IR indicative of polarons, supporting the assertion of hole doping via a charge-transfer process between FTS molecules and P3HT. Additionally, in the most highly-doped films with a significantly enhanced polaron band, we observed a monotonic Drude-type absorption in the far-IR, signifying delocalized states (black curve in Fig. 1).

The significance of this work is two-fold: the PI has demonstrated a novel approach to achieving ultra-high carrier densities in polymers, as well as providing a unique way to study the insulator-to-metal transition in polythiophenes. By

dithienocyclopentane [PBBTCD], and polydiketopyrrolopyrrole-benzobisthiadiazole [PDPPBBT]. The latter polymer, with a DPP as donor unit, exhibits electron and hole mobilities exceeding $1 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$.

The PI designed and fabricated OFETs compatible with simultaneous electrical measurements and infrared monitoring of injection processes. The PI employed devices using OFET structures with SiO_2 and high-dielectric constant Ta_2O_5 gate insulators. Figure 2 displays voltage-induced changes in IR transmission for PBBTPD and PBBTCD-based OFETs. We discovered a significant modification of the absorption edge under the applied electric field. The absorption edge reveals hardening under electron injection and softening under hole injection. This behavior is reproduced in all copolymer-based OFETS (including PDPPBBT).

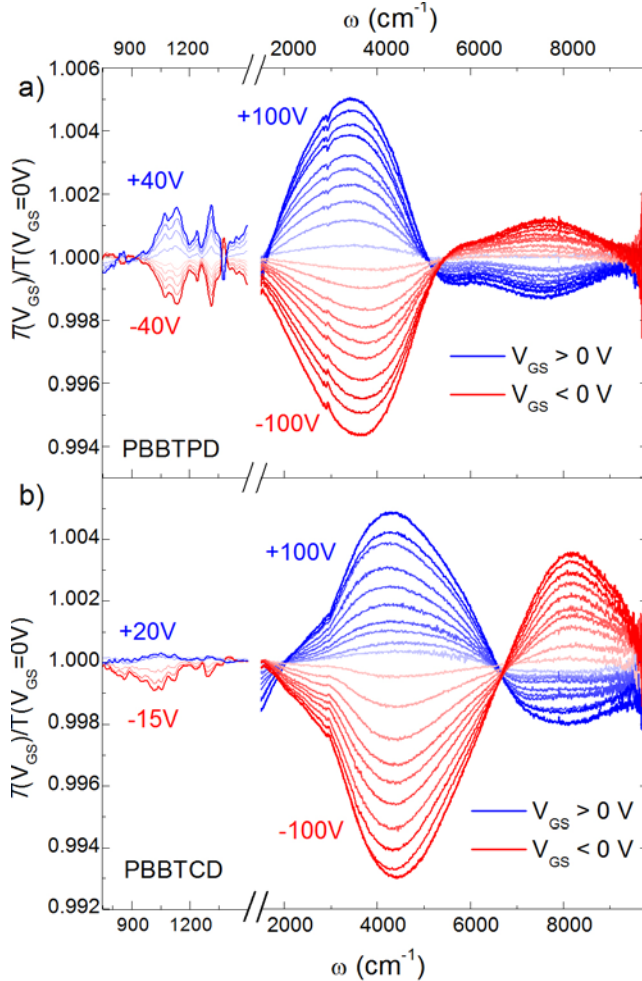


Figure 2: Voltage-induced change in transmission spectra $T(\omega, V_{GS})/T(\omega, V_{GS} = 0 \text{ V})$ for structures employing (a) PBBTPD and (b) PBBTCD as the active semiconductor. Blue curves indicate n-type operation ($V_{GS} > 0 \text{ V}$); red curves indicate p-type operation ($V_{GS} < 0 \text{ V}$).

Increased absorption under negative gate bias is consistent with hole-doping of the polymer host, revealing both polarons and vibrational modes absorptions: IR signatures of charge injection. A suppression of the same spectral features is found at positive gate voltages, however, inconsistent with the notion of absorption due to injected electrons.

The experimental data indicate a self-doping of holes in the polymer that is modified by charge injection. The PI found a correlation between the suppression of hole-induced IR features under positive gate voltage, and the mobility of the polymer. In PDPPBBT-based OFET devices with high electron and hole mobility, this ‘asymmetry’ in the IR transmission spectra is much more pronounced than in PBBTPD or PBBTCD. The observation of both hole-induced IR absorption and electronic transport in OFET data suggests phase separation.

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The importance of these results is in the implication of a phase-separated, strongly inhomogeneous conducting polymer, and its relation to the intrinsic ambipolarity seen in these systems. This work is published in *Physical Review B*. Exploring the role of inhomogeneities, and understanding the origin of high charge carrier mobility in these ambipolar polymers requires high-resolution real-space probes currently developed in our laboratory.

3. Development of Infrared Microscopy for OFET characterization.

The PI designed, developed and built a new optical microscope enabling infrared monitoring of the spatial profile of the injection density in the channel of organic transistors (Fig. 3a). Figure 3b shows IR transmission spectra for a PBBTPD-based OFET biased in “ambipolar” mode, where the conduction channel is populated by both holes and electrons. The evolution of the spectra from source to drain directly reflects the electric potential across the channel, and thus the carrier density. The ability to glean spatial information about the distribution of both positive and negative charge carriers for ambipolar polymer-based OFETs is crucial in assessing theoretical models to describe charge transport during such device operation.

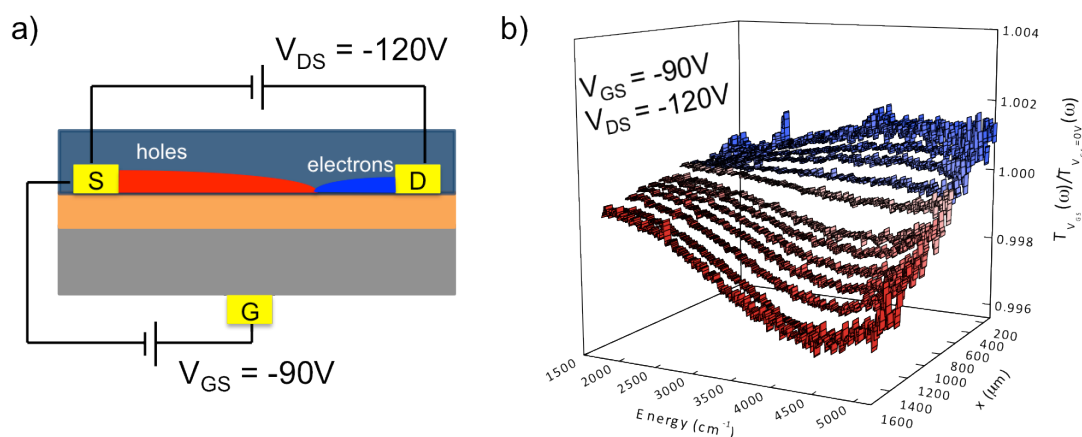


Figure 3: a) Schematic of OFET biased in “ambipolar” mode of operation. b) Voltage-induced change in transmission spectra $T(\omega, V_{GS})/T(\omega, V_{GS} = 0 \text{ V})$ for PBBTPD OFET across the conduction channel. Red (blue) curves indicate a negative (positive) electrical potential in the channel.

The use of several tunable mid-infrared lasers in conjunction with our home-built microscope has allowed for diffraction-limited measurements without the use of a synchrotron light source. This entirely novel capability is instrumental in understanding the injection length scales in organic ambipolar transistors. The knowledge of injection length scales has a direct impact on design and implementation of a wide variety of organic electronic components including inverters, CMOS circuits, light-emitting structures, and organic laser diodes.

4. Review on Many-Body Effects in Organics Materials.

The PI has written a comprehensive review on electrodynamics of correlated electron materials published in Reviews of Modern Physics. In this article he overviewed studies of the electromagnetic response of various classes of correlated electron materials including organic and molecular conductors, intermetallic compounds with d and f electrons, and others. Optical inquiry into correlations in all these diverse systems is enabled by experimental access to the fundamental characteristics of an ensemble of electrons including their self-energy and kinetic energy. Steady-state spectroscopy carried out over a broad range of frequencies from microwaves to UV light and fast optics time-resolved techniques provides complimentary

prospectives on correlations. Because the theoretical understanding of strong correlations is still evolving, the review is focused on the analysis of the universal trends that are emerging out of a large body of experimental data augmented where possible with insights from numerical studies. This review covers monumental amount of literature on the optical phenomena in both organic and inorganic correlated electron systems and contains about 400 references.

5. Publications.

O. Khatib, J. D. Yuen, J. Wilson, R. Kumar, M. Di Ventura, A. J. Heeger, and D. N. Basov
· “*Infrared spectroscopy of narrow gap donor-acceptor polymer-based ambipolar transistors*”
Phys. Rev. B 86, 195109 (2012).

D. N. Basov, Richard D. Averitt, Dirk van der Marel, Martin Dressel, and Kristjan Haule
“*Electrodynamics of correlated electron materials*” Reviews of Modern Physics 83, 471 (2011)

O. Khatib, B. Lee, J. Yuen, Z. Q. Li, M. Di Ventura, A. J. Heeger, V. Podzorov, and D. N. Basov
“*Infrared signatures of high carrier densities induced in semiconducting poly,,3-hexylthiophene by fluorinated organosilane molecules*” JOURNAL OF APPLIED PHYSICS 107, 123702 (2010).