FINAL PROJECT REPORT

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"Optical, Electrical and Magnetic Studies of Pi-Conjugated Organic Semiconductor Systems"

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Institution: The University of Utah

Address: Sponsored Projects, 1471 Federal Way, Salt Lake City, Utah 84102

Principal Investigator: Z. Valy Vardeny

Title: Distinguished Professor of Physics

Address: Physics Department, 115 South 1400 East, room 201,

Salt Lake City, Utah 84112

Tel: (801) 581-8372; **Fax**: (801) 581-4801; **e-mail address**: val@physics.utah.edu

DOE office of Science Program: Office of Basic Energy Sciences

Division: Materials Science and Engineering; (a) Materials Chemistry

Program Directors: Dr. Dick Kelley; and from 2012 Dr. Michael Sennett

Address: SC-22.2/ Germantown Building

1000 Independence Avenue, Washington DC 20585-1290

Tel: (301) 903-6051

e-mail addresses: michael.sennett@science.doe.gov

Executive Summary

Over the duration of this grant our group has studied the transient and cw optical response of various π-conjugated polymers, oligomers, single crystals, fullerene molecules and blends of organic donor-acceptor molecules. We have been also involved in complementary experiments such as magneto-optical studies and spin-physics. We have advanced the field of photophysics of these materials by providing information on their excited state energies and primodal and long-lived photoexcitations such as singlet excitons, triplet excitons, polaron-pairs, excimers and exciplexes. We also fabricated various organic optoelectronic devices such as organic light emitting diodes (OLED), electrochemical cells, organic diodes, organic spin-valves (OSV), and organic photovoltaic (OPV) solar cells. These devices benefited the society in terms of cheap and energy saving illumination, as well as harnessing the solar energy.

In addition, we have synthesized novel π-conjugated polymers in which the proton nucleus (^{1}H; nuclear spin ½) in the hydrogen atoms closest to the backbone chain carbon atoms is substituted by deuterium nucleus (^{2}H; nuclear spin 1)); we have also substituted ^{12}C atoms (nuclear spin zero) by ^{13}C isotope atoms (nuclear spin ½) in some polymer backbone chains. We also synthesized various π-conjugated polymers that contain intrachain Pt atoms for increasing the spin-orbit interaction. These new compounds have been used to investigate the spin-orbit interaction that leads to phosphorescence in the organics, and also to provide white-light illumination.

Research on "Organic Spintronics", which was initiated by us (Nature 2004) during this DOE support period as one of our focused research avenues, has transformed in the meanwhile into a field by itself, with enormous interest that has led to numerous grants extended to interdisciplinary groups all over the world.

A. <u>Achievements</u>

A1. Materials, Devices, and new Experimental Capabilities

(1) We synthesized polymers that contain *deuterium nucleus* (^{2}H) that replace the hydrogen atoms close to chain backbone carbon atoms, as well as exchanging ^{12}C by ^{13}C isotope atoms. We continued to improve the synthetic route of these polymers that consequently reduce the impurity density in these materials. The isotope exchange has brought a new control element to our research endeavors, namely 'HFI tunability'.
(2) We acquired the knowhow of fabricating *miniature* OLED and OPV cells. The device area that is usually used in other studies is 1x1 mm^2; we routinely fabricated devices with area of 50x50 μm^2. Such 'miniature devices' were needed for studying *mesoscopic phenomena* in organic electronics. This was a new direction in our research that we wanted to emphasize, especially for electrical and magneto-electrical noise, and 'telegraphic fluctuations' in the current density of the devices.
(3) We fabricated organic spin valves in which for the hole injection anode we used an LSMO spin injector (a ferromagnet (FM) at low temperature); whereas the other FM electrode we used a

Co thin film. We demonstrated that such a C_{60}-based spin-valve show magneto-resistance at low temperature of up to 20%, and at room temperature up to 0.3%.

(4) We purchased a new glove-box for fabricating cleaner organic spintronics and optoelectronic devices. This glovebox was put in operation in a new laboratory space that we received. We also purchased a new evaporation system that gave us the capability of co-evaporation few organic layers in series. With this new system we were capable of studying new organic optoelectronic devices such as OPV cells that do not have the usual bulk heterojunction (BHJ) configuration, but instead are composed of alternating layers of donor and acceptor (for example pentacene/C_{60}).
(5) We also synthesized Pt-polymers, where the π-conjugation in the chain is interrupted by Pt atoms with large spin-orbit (SOC). Using these polymers we were able to study magnetic response in polymers with tunable SOC.
(6) We acquired the knowhow to grow organic inorganic perovskite materials that are known to yield high PCE in PV cells. We routinely fabricated perovskite cells with ~ 15% PCE. Also LED devices based on these materials have been fabricated.

A2. Picosecond transient spectroscopy studies

(1) Using our unique fs OPO laser system in the mid-IR spectral range we studied the transient response of polythiophene (P3HT) with different regio-regularities and its blend with fullerene in a broad spectral range from 0.15- 1.12 eV using the photomodulation (PM) spectroscopy. This donor-acceptor (D-A) system is characteristic of blends used for OPV applications. We concluded that the charge photogeneration process in these blends proceeds in two steps. The first step is intrachain exciton photogeneration in the polymer donor. The excitons subsequently diffuse towards the D-A interfaces in the blend in about 10 ps, where they form charge-transfer (CT) excitons. In the next step the CT excitons dissociate. We saw a surprising difference in the charge photogeneration mechanism in P3HT/PCBM blend that depends on the regio-regularity of the polymer backbone. This translates in significant difference in solar cell power conversion efficiency (PCE) of blends based on RR-P3HT and RRa-P3HT. OPV cells based on the former blend reach ~ 4% PCE; whereas cells based on the latter blend show PCE of only ~ 0.1%. The reason for this surprising finding is the film morphology. RR-P3HT/PCBM blend contains separate donor and acceptor nano-domains; whereas RRa-P3HT/PCBM blend shows D-A domain separation of lesser degree. Consequently in RRa-P3HT/PCBM blend the photogenerated CT excitons cannot dissociate as easily as in RR-P3HT/PCBM blend.

(2) We have also completed ps transient studies on newer copolymers with lower bandgap (~1.6 eV), that give PCE of up to 10%. These copolymers have intrachain D-A geometry based on two molecular moeities, where one moiety serves as 'donor' whereas the second moiety serves as acceptor. The singlet exciton and polaron excitations in this type of copolymers are quite different from the more regular polymers, since there are two different moieties in the chain. Thus there are *two excited state* mA_g *states* that lead to two photoinduced absorption bands from the photogenerated singlet excitons. Also the polaron excitation show *three different bands*, compared to two bands in more regular polymers, because the charge may be localized either on one moiety or the other.

(3) For the strong excitation intensity regime, where our laser amplifier system is used in the spectral range of 1.3-2.7 eV, we successfully measured the transient photomodulation (PM) spectra of several polymer films at moderately high excitation intensities, and compared the PM spectrum with that of two-photon absorption (TPA) spectrum. We completed such studies on the novel polymer regio-regular PTV. This study was focused on the relationship between the primary photoexcitations in the polymer and the order of the excited state. *We found that if the odd-parity symmetry exciton ($1B_u$) in the polymer lies below the even-parity symmetry ($2A_g$) then the polymer shows a strong photoluminescence band. However if this order is reversed, then the polymer is dark (namely PL efficiency < 10^{-4}).* **This is the most important conclusion of our studies**.

(4) We also completed a study on the uniquely synthesized Pt-rich polymers, in which there are Pt atoms at each monomer. This polymer shows increase SOC that results in faster intersystem crossing (ISC) from the singlet to the triplet manifolds. We obtained a record fast ISC time < 2 ps that depends on the number of monomers in between two adjacent Pt atoms in the chain. These measurements were complemented by two-photon absorption measurements and electro-absorption spectroscopy. We found that the Pt-related band lies below the π-π* band when the Pt atoms are close enough to each other (namely on each monomer). In this work we have collaborated with a theoretician from LANL, namely Dr Sergei Tretiak.

(5) In the transient PM spectrum of π-conjugated polymer thin films we recently found a surprising phenomenon caused by the formation of *ps transient strain waves* in the polymer films subjected to strong pulse irradiation (i.e. using the fs laser amplifier system). Because of the different deformation potential of the ground and excited states of the polymer, upon pulse excitation a stress pulse is formed that leads to a transient strain in the film. The strain in the films is composed of two components; (i) a static strain that simply decays with time, but which dramatically influences the ps transient response in the film; and (ii) a dynamic strain wave that bounces back and force in the film due to acoustic reflections at the film boundaries. The dynamic strain induces an oscillatory response in the PM transient decay, from which the sound wave velocity and attenuation can be measured.

(6) We also studied various types of organic *laser action* in random and engineered microcavities. For example in disordered films of DOO-PPV we measured '<u>random</u> <u>lasing</u>' from single random laser 'cavities', and its evolution with increasing excitation intensity. We found that at excitation intensity at threshold there is usually only one natural 'cavity' that shows laser action, because of its maximum Q-value within the illuminated area on the polymer film. In this case the laser emission spectrum is straight forward to analyze because it contains few correlated laser lines that can be studied using fast Fourier transform. However, when the excitation intensity increases above the threshold, then other 'natural resonators' within the illuminated area of the film start lasing, and consequently the RL spectrum contains a myriad of sharp laser lines which are difficult to analyze. We designed an imaging optical set-up, where the laser emission from the various random cavities in the illuminated area is collected separately, and mapped onto the entrance slit of a monochromator for providing a map of the illuminated area upon laser action.

A3. CW Spectroscopy studies

(1) We completed a study in which we showed that is possible to scrutinize polymer/fullerene blends for OPV applications using cw spectroscopies such as photoluminescence (PL) and quasi steady-state PM spectra. The PM spectrum can show the amount of impurities in the polymer, whereas the PL spectrum shows the degree of polymer aggregation in the film. Both properties influence carrier mobility in the donor domains of the D-A blend; a property with immense influence over the power conversion efficiency of organic solar cells.

(2) We studied the photophysics of two Pt-polymers that were synthesized in-house. We found that photogenerated triplet excitons dominate the PM spectrum of these polymers starting from time t~1ps. We measured the excitation spectrum of the phosphorescence emission band in these polymers and found that is composed of two components separated by below-gap and above-gap excitations. From the below-gap excitation we clearly could identify the triplet level in the gap of these polymers; a new spectroscopy that has not been tried before in π-conjugated polymers. We also measured the PM spectrum of these polymers and from the frequency dependence could infer the triplet exciton lifetime. We also found that the phosphorescence emission spectrum contains a super-fluorescence band at the 0-0 line.

(3) We have also succeeded in measuring the absorption spectrum of carriers injected in nanotubes [NT]. It has been difficult to get a clean spectrum of the absorption from carriers in NT because the primary photoexcitations (excitons) quickly recombine, leaving behind spectral artifacts caused by strain and thermal modulation from the excitation laser. Thus steady state PM spectroscopy is unable to help here. On the contrary we found that carriers can be readily *injected* into NT films from electrodes (as opposed to photogenerated). We therefore used the technique of cw <u>charge induced absorption</u> (CIA) to measure the spectrum of charge carriers in NT films for the first time in fact.

(4) In light of the immense interest in 'singlet fission' that leads to enhanced PCE of OPV solar cells, we measured the excitation spectra of the known triplet PA band in several π-conjugated polymer films. We expected that the PA excitation spectrum would show a step-like increase at photon energy that corresponds to $2E_T$, where E_T is the triplet energy level in the gap. We measured the PA excitation spectrum in MEH-PPV and RR-P3HT. We found that the PA excitation spectra of these polymers are not flat; there is a step increase at the optical gap, followed by another step increase at $2E_T$. This work continued by measuring the magneto-PA spectrum.

A4. Spin Physics and Magneto-transport

(1) Perhaps the most attractive achievement during the 12 years support period in the field of OPV solar cells is that spin ½ radical additives can enhance the OPV efficiency cells based on donor/acceptor (D-A) cells such as RR-P3HT/PCBM blends. This is due to the induced spin exchange between the spin ½ radicals and the photogenerated CT excitons at the D-A interfaces in the organic blend. We found that the OPV efficiency increases by ~ 15% at optimum D-A ratio, but is enhanced more than 300% in organic D-A blends that are rich with acceptor molecules.

(2) One of the fascinating phenomena in the field of organic spin effect is the organic magnetic field effect (MFE), which include magneto-conductivity (MC) and magneto-electroluminescence (MEL) in OLEDs and magneto-photoconductivity in OPV cells. The organic MFE may enhance (or reduce) the device output (current, photocurrent or electroluminescence by few tens of % when a relatively small magnetic field is applied on the device [ref. B1]. This phenomenon has been furiously debated during the last ten years. During the DOE support period we succeeded to synthesize deuterated- and ^{13}C-rich DOO-PPV polymers, where the hyperfine interaction (HFI) is smaller (for the former compound) and larger (for the latter compound). We proved that the HFI plays a major role in the mechanism that leads to the MFE. We also showed that there is an ultra-small MFE component (at fields of order 2 Gauss) that was not seen before; and this component might explain how birds navigate.

(3) We also found (ref. B28) that the MFE can be also obtained in the photoinduced absorption (PA) spectra in organic films. This happens since the magnetic field changes the recombination rate of various photoexcitations that leads to change in their steady state density, and, in turn to change in the PA intensity. We dubbed this technique as magneto-PA or MPA, and this effect allows one to measure MFE in films rather than in devices, which is much more convenient. For example we found that the PA spectrum in C_{60} films is substantially magnetic field dependent (i.e. MPA), showing that other mechanisms than HFI may contribute to the MFE in this material. We identified this mechanism as Δg, the difference in the g-value of electron and hole polarons in C_{60}, and a contribution from the triplet excitons known to dominate the photophysics in C_{60}. Our work shows that the organic MFE is quite diverse and merits the DOE funds extended to us.

(4) Organic spin valve (OSV) devices were fabricated during the DOE support period. In our research we focused our attention to films and devices based on the fullerene C_{60}. These compounds are composed of 99.8% carbon nuclei that are spinless in nature, and therefore the average HFI in this carbon allotrope is about two orders of magnitude smaller than in any other organic semiconductor. We have fabricated OSV devices based on C_{60} and found that the magneto-resistance (MR) response in these devices is very clear; we even could measure MR of ~ 0.3% at room temperature. However we also found that the spin diffusion length in these devices is of the order of 12 nm, which is quite small. This is surprising since the HFI is very small in C_{60}, and this may lead to enhanced spin diffusion length. It turns out that the C_{60} films in fact contain crystalline nanosize grains that depend on the deposition temperature. It is therefore conceivable that these nanocrystallites contribute to the spin relaxation rate, and thus diminish the spin diffusion length in C_{60} films.

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(C) Patents and Patent Disclosures that resulted from this project

1. Invention disclosure No. U-4008: *“Π-conjugated heavy metal polymers for organic light emitting diodes*”. Inventors: Z. V. Vardeny, L. Wojcik, and T. Drori.

2. Invention disclosure No. U-4015: “*OLEDs based on π-conjugated polymers incorporating heavy metals as illuminators for hydroponics applications*”. Inventors: Z. V. Vardeny, L. Wojcik, T. Drori, and M. Delong.

3. Patent No. 7682707; “*Organic light-emitting devices using spin-dependent processes*”; issued 03/23/2010.

4. Provisional patent; “Spin-organic light emitting diodes”, submitted July 2012, inventors: T.D. Nguyen, E. Ehrenfreund, and Z. V. Vardeny.

Comment: We do not have anything to report on:

b. Web site or other Internet sites that reflect the results of this project;
c. Networks or collaborations fostered;

d. Technologies/Techniques;
e. Inventions/Patent Applications, licensing agreements; and
f. Other products, such as data or databases, physical collections, audio or video, software or netware, models, educational aid or curricula, instruments or equipment.