IREE: Light Scattering Studies of Organic Semiconductor Based Devices

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ABSTRACT: The primary goal of the IREE supplemental award was to establish an international collaboration with a world-class chemistry department, *Department of Solid State and Structural Chemistry, Indian Institute of Science (IISc)-Bangalore, India* (in Prof. Satish Patil's group). The research group in IISc excels in the synthesis and characterization of novel conjugated polymers, polymer composites, and new organic-inorganic hybrid materials for organic optoelectronics. Several parallel projects involving novel donor-acceptor-donor molecules for application in light-emitting devices and thin-film transistors, composite organic-inorganic semiconductors for photovoltaic applications, and ionic liquid crystals have resulted out of the PI's three-month visit to IISc. In addition to opening up new routes for synthesis of organic-inorganic composites, our approach has the potential of moulding new material properties, which have unique potentials for technological applications. The goal is to develop these areas into a concise project on *functionalized hybrid organic-inorganic systems for optoelectronics applications*, involving theorists and other experimentalists.

INTRODUCTION

Our current NSF-ECCS 0523656 award at the *University of Missouri-Columbia* (MU) relies on probing metal-organic semiconductor interfaces using light scattering techniques. A major focus of this work is on electronic and vibrational spectroscopy from organic semiconductors to understand structure-property relationships and their influence on both charge-transport and photophysical properties. By engaging three graduate students and two undergraduate students we have achieved unique insights into charge transport properties in polymer-based light-emitting diodes and metal-insulating semiconducting structures using both optical and electrical probes. This has paved the way for diversifying into other applications of organic optoelectronics based on solution processable polymers. In addition to the core activities, we have established several new collaborative projects encompassing the disciplines of engineering, physics, chemistry and materials science.

Over the last three years we have expanded our research into other complementary techniques: capacitance-voltage measurements, interface trap density measurements, and new growth methods of polymer films being some of them. We have successfully performed electric-field induced light scattering studies from polymer-based light-emitting diodes (LEDs) to investigate the nature of polaronic states. In a nutshell, the significant achievements of our work funded by the NSF are:

- Resolving a long standing problem of a structural phase in polyfluorene using light scattering.[1,2]
- Devising Raman scattering techniques to probe electronic excitations in polymer-based LEDs and finding a new paradigm in charge transport mechanism in disordered materials.[3,4]
- Determination of interface trap density in polymer-based metal-insulator-semiconductors diodes.[5]

Reasons/Rationale for International Cooperation
Traveler: Dr. Suchi Guha
Dates: March 16-June 16, 2008

The IREE award was used to initiate a collaborative research project with Prof. Satish Patil, Department of Solid State and Structural Chemistry Unit (SSCU), Indian Institute of Science (IISc)-Bangalore, India. Prof. Patil's expertise is in synthesis and characterization of novel conjugated polymers, polymer composites, and new organic-inorganic hybrid materials for organic optoelectronics. IISc is one of the premier institutes of scientific research in India with a very high international standing. Additionally, Bangalore is one of the fastest growing cities with a stronghold of the semiconductor (both inorganic and organic) industry. Such an international collaboration opens up future possibilities of a liaison between academia/industry, situated in a part of the world that has a rapidly growing economy and a Midwestern US institution. Additionally, our current research lacked the expertise of a chemist, which this international cooperation has been able to overcome.

Selection of Researcher

Our initial selection of graduate students didn't work since both the domestic students that were supposed to join our research group last Fall went off in different areas. The current group has mainly international students who were involved with this project by working on experiments at MU, while the PI visited IISc. The PI, who is a new associate professor, was the best candidate for this visit. She is still at a stage where she does a lot of the actual experimental research in the laboratory by herself. The visit by the PI had a twofold advantage: involve synthetic chemists as part of the organic optoelectronics project and to learn a few synthetic skills that are easily transferable to the PI's research laboratory in the US.

Anticipated research and education outcomes

The three-month visit by the PI set the stage for fostering long term research ties with the Chemistry Dept. at IISc-Bangalore. Not only did this visit benefit from the original plan of a collaborative research with Prof. Patil's synthetic chemistry group but there were a couple of theory groups that the PI has tremendously benefited from. The PI had the opportunity to give formal and informal lectures to the faculty and students at the institute. During the three months there was a constant interaction with the PI and the graduate students at IISc.

Our long term goal is to submit a joint full-fledged proposal in the area of functionalized hybrid organic-inorganic systems to the Materials World Network program of the NSF and the Department of Science and Technology-India. This will also allow short term visits by the Indian graduate students from IISc to spend 3-6 months in the PI's research laboratory resulting in closer interaction with graduate students at MU. Moreover, such a collaboration provides a great platform for chemists, physicists and engineers to work as a team.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

The main thrust of our research carried out during the international research visit involved synthesis of functionalized organic molecules and hybrid organic-inorganic composites. These included:

- Conjugated polymer (MeHPPV, P3HT):TiO_2 nano-composites
- Donor-acceptor-donor materials with low band gap properties
- Red organic light-emitting materials

Composite materials rely on the material properties of both organic and inorganic semiconductors, such as processability of organic materials and high charge carrier mobilities in inorganic semiconductors. Most of these approaches are based upon mixing the conjugated polymers with inorganic semiconducting nanoparticles in the solution phase, resulting in a natural phase segregation that comprises a donor-acceptor type system. These composites provide an alternate solution to photovoltaic applications compared to using only organic blends or inorganic semiconductors. Our approach in the synthesis of organic-inorganic composites is quite different from the existing methodology; rather than mixing the organic and inorganic semiconducting materials, the conjugated polymers will be synthesized in the presence of inorganic semiconducting nanoparticles. This approach has the potential of moulding new material properties with potential technological applications. A second approach used was the formation of micron/nano particles of the polymer itself into which TiO_2 particles were synthesized. A micro-emulsion technique was used to form a uniform array of the polymer particles. As a starting point we used derivatives of polyfluorenes (PF), where the polymer particles form uniform sub-micron size as shown in the SEM image of Figure 1. The advantage of such blends of nanoparticles of polymers and oxide semiconductors is that the separation between the polymer (donor) and the oxide (acceptor) interfaces may be controlled for efficient charge transfer mechanisms needed for improving photovoltaic efficiencies. The next stage is to use these blended particles in devices, which is being currently carried out in the research laboratory at MU.

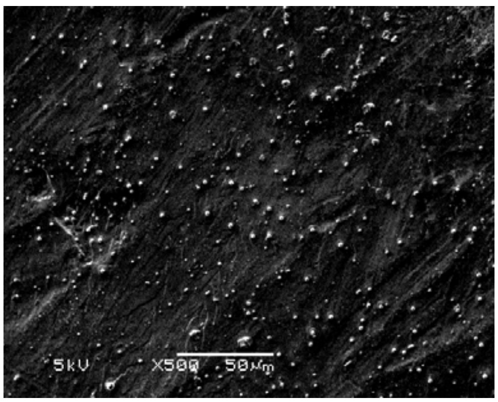

Fig. 1: SEM image of PF sub-micron size particles.

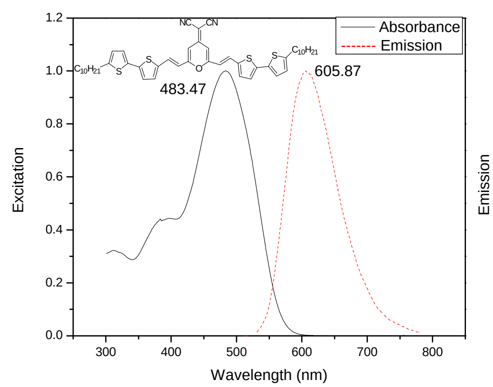

Fig. 2: Absorption/emission spectra of thiophene-based oligomer.

Another area that we made progress during the three-month visit was in the area of synthesis and characterization of low band-gap oligomers that have potential application as light-emitting materials. These new materials are superior to DCM and other dyes currently available, since they do not aggregate easily. Figure 2 shows the absorption and emission of a dilute solution of such a new red-emitting oligomer. The synthesis of these molecules takes between 3-6 weeks. Currently we are looking at the electroluminescence properties of these oligomers.

I also trained several of Prof. Patil’s graduate students in setting up an electrical characterization system and a photoluminescence setup for preliminary measurements at IISc before sending the materials to the US research lab for device fabrication.

Our current research involves fabrication of light-emitting diode structures to study charge-transport characteristics mainly in blue-emitting materials. We also have an initiative in photovoltaic application using these blue-emitters as the donor material to understand the process of charge separation along donor-acceptor heterojunctions. The international research experience has now made it possible to use a variety of new materials for understanding charge-transport properties at a fundamental level as well as to fabricate more efficient organic devices, such as organic solar cells.

During my stay at the IISc, I opted for an office space in the “wet” synthesis laboratory where the graduate students worked. This gave me an opportunity to directly interact with the students as well as to learn routine synthesis procedures. This was a particularly illuminating experience since it gave me a feel for what it entails to be a synthetic chemist and to also understand the nuances of chemistry at a basic “101” level that controls the entire field of organic optoelectronics.

The field of organic semiconductors is highly interdisciplinary, encompassing various areas of basic science and engineering. The research activities carried out at IISc during the international visit is just a stepping stone for the next level of collaboration, where we will focus on the fundamentals and applications of the new hybrid materials.

BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

The PI (traveler), a female scientist in the US, provided an excellent role model for female researchers in the host country. During the time of the visit, a female graduate student was working as a summer intern in the laboratory. The PI had many interactions with her and other female students at IISc and was able to convince them to continue their careers in science. The SSCU Department where the PI visited has over 20 faculty members but has no female faculty. In light of this it the PI's interaction with female graduate students at the institute was important to assure them that a career in science was not only just feasible but highly enjoyable too.

Fig. 3: Prof. Patil's research group.

The original scope of our NSF award was based upon blue-emitting polymers and molecules utilized in light-emitting diode structures for probing charge transport using light scattering techniques. Such materials are not ideal for solar cell applications due their large band gap. Organic solar cells belong to a class of "excitonic solar cells", where the absorption of photons results in the production of excitons. These solar cells are based on bulk heterojunction where excitons dissociate at the heterojunction interface, creating free charge carriers at the interface itself. Typically a band gap of less than 2.0 eV is ideal for the donor material, which is hard to achieve with many organic molecules and polymers. This new collaboration with Prof. Patil's group has opened up a whole new arena in the area of organic solar cells and red light-emitting diodes. The current NSF grant is based upon a strong collaboration between the Physics and the Electrical Engineering Depts. at MU. A big deficiency that we felt was there was no real dialogue with chemists. The travel award has tremendously helped us to overcome this deficiency. US physics/electrical engineering graduate students are now in constant contact with the chemistry graduate students at IISc; there are numerous discussions among them (mainly via electronic mail) regarding material preparation, device fabrication and characterization.

The visit by the PI has been a stepping stone for fostering long-term ties with Prof. Patil's group. The Department of Science and Technology (DST), equivalent of the NSF in India, has many funding opportunities for international collaborations. Currently, we are working towards gathering preliminary results on devices fabricated with the new materials that were synthesized during the three-month visit. Our goal is to develop a full proposal for the Materials World Network through the Office of Special Program at the NSF for Fall 2008. DST will act as the partner agency in India. This will enable Prof. Patil and students from his group to visit our institution for short research visits.

The Indian economy has been rapidly growing, which has resulted in a shift of many manufacturing and R&D units from the West to Southern India. In particular, the city of Bangalore has become a haven for the semiconductor industry. Along with this industrial growth, research and academic institutions in India have kept pace with the advancement of science and technology. The travel has given a wonderful opportunity to get first-hand knowledge of industrial research in India. Bangalore is the hub for many R&D units in the area of organic/hybrid electronics. We believe that in a few years down the road we may be able to extend our collaboration with semiconductor industries based in Bangalore.

Although the PI spent an early part of her education in India, she was completely new to the southern part of the country (where Bangalore is located). Culturally, different regions and states in India are more disparate than two different countries in Europe and the Americas. The IISc is one of the top research institutes in India with only a graduate program. The students go through various levels of competitive examination to be admitted to the institute. As a result the graduate students are heavily motivated and from the very beginning they are involved in research work. Many students have research publications in their very first semester. This is quite a contrast to the graduate program in Missouri; it usually takes at least a year before our students know what they want to do research-wise. At IISc when students join the institute they go through various levels of interviews with faculty members, which gives them a solid idea of the nature of research activities going on in their respective departments. Additionally, they take a short course on independent research and are required to participate in research presentations in areas that are completely different from their own research topic. As a result the breadth of knowledge of graduate students is amazingly high. Some of these ideas and practices are transferable and quite apt for US institutions as well. In the course of time, I plan to adopt some of these methods in our graduate program.

DISCUSSION AND SUMMARY

The international research experience has opened up many new avenues for us in the area of organic optoelectronics. Having chemists on board makes our research much more versatile and tunable. We believe that this visit has set the stage for long-term research collaborations not only with Prof. Patil's group at IISc but also with a group of quantum chemists at IISc. Additionally, there is now a constant connection between the US and Indian graduate students, which has been greatly advantageous in keeping up the interdisciplinary nature of this research field. In Winter 2008, we will most probably be able to have one of our new domestic students visit IISc for three months.

As a recommendation to the IREE program some flexibility could be provided to students such that they may spend one-two months at the foreign institution. Recruitment of graduate/undergraduate students to spend three months at the foreign institution proved somewhat difficult for us at a Midwestern institution.

The IREE program has opened up many options for us to apply for international funding in the area of functionalized organic-inorganic materials for optoelectronics with an emphasis on solar cells. Joint US-India proposals will be developed along the course of time. Such projects in the future will allow a two-way exchange of students and scientists. Additionally, this program is excellent for interdisciplinary collaboration, which in the normal course of events is difficult especially when the scientists are spread all across the globe. This program has also been extremely beneficial in understanding work ethics across cultures and disciplines.

ACKNOWLEDGEMENTS

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BRIEF BIOGRAPHIES OF RESEARCHERS

Suchi Guha is an associate professor at the Department of Physics and Astronomy, University of Missouri-Columbia. She earned her doctorate degree in physics from Arizona State University in 1996. Prior to that, she obtained master's and bachelor's degrees in physics from the Indian Institute of Technology-Delhi and the University of Delhi, respectively. Her current research interests include photophysics of conjugated polymers using light scattering techniques, charge transport mechanisms in polymeric semiconductors, development of organic field-effect transistors and photovoltaics, and high pressure optical studies of organic/inorganic semiconductors.