Based on work supported by the National Science Foundation
under grant NSF-DMR-1523463

University of Puerto Rico at Humacao
Call Box 860, Humacao, PR 00791
(787) 850-0000, ext. 9027
prem.uprh@upr.edu

University of Puerto Rico at Humacao

# 15th ANNUAL MEETING

**November 22, 2019**

Wyndham Candelero Beach Resort
170 Candelero Dr., Palmas del Mar
Humacao, PR 00791

PENN-UPR Partnership for Research and Education in Materials

## Abbreviations

| | |
|---|---|
| **UPRH** | University of Puerto Rico at Humacao |
| **UPRC** | University of Puerto Rico at Cayey |
| **PENN** | University of Pennsylvania |
| **CMU** | Carnegie Mellon University |

**Legend**:

Names of undergraduates and high school students: Underlined

**Names of PREM faculty**: bold

**P-15** "Chromo-fluorogenic detection of aromatic aldehydes in solid and liquid phase", Andrea N. Marcano Delgado and Ezio **Fasoli**, UPRH

Aromatic aldehydes are widely used as solvents, flavoring materials in foodstuffs, fragrances and as precursors in the organic synthesis of a plethora of compounds. The goal of this work is to develop a simple, fast and sensitive chromogenic and fluorogenic assay for the detection of aromatic aldehydes at nanomolar concentrations. The assay involves the reaction between benzamidine and glyoxal bisulfite. The so formed intermediate undergoes to aldolic condensation with aromatic aldehydes leading to a fluorescent benzyl imidazolone. The method was optimized with structurally different aldehydes to detect aromatic aldehydes between 0.2 and 100 μM in aqueous solution. The fluorophores were characterized by NMR, UV-VIS and fluorescence spectroscopy. The same reaction was carried out in solid phase using benzamidine linked to cellulose paper strip. This work is the first example of the use of the glyoxal reaction as an assay for the detection of aromatic aldehydes and discusses its application for the development of paper strip fluorescent assays.

**P-14** "Current-voltage-temperature characteristics of a $WSe_2$/Si heterostructure", Ahmad Matar Abed, Anmaris Meléndez, Nicholas J. **Pinto**, José O. **Sotero Esteva**, and Idalia **Ramos**, UPRH

A tungsten diselenide ($WSe_2$)/silicon (Si) pn diode was fabricated by using a simple method of transferring a p-type two-dimensional $WSe_2$ film onto a cleaved n-Si/$SiO_2$ wafer. The current-voltage characteristics of the device were measured, and the conduction mechanisms analyzed over a temperature range of 80 K–300 K. At high temperatures, the current–voltage characteristics of the diode show that thermionic emission transport dominates. However, tunneling also contributes at low temperatures. To explain the transport behavior of the heterojunction, a model that takes into consideration both thermionic emission and tunneling will be presented. Furthermore, the device was tested as a half-wave rectifier at room temperature at low frequencies. The rectification ratio and low turn-on voltages of the diode makes it suitable for optoelectronic applications.



# Program

Friday November 22, 2019
Wyndham Candelero Beach Resort ▪ Humacao, Puerto Rico

**8:30 AM** Registration and Breakfast

**9:30 AM** Welcome Messages

**9:40 AM** Overview PREM 2018-2019

## IRG-2 Progress Reports

**9:50 AM** **O-1** "Cellulose based affinity membranes: Characterization of pores size and protein binding", Vibha **Bansal**, UPR Cayey

**10:05 AM** **O-2** "Fluorescent labelling of chemically modified cellulose membranes and aromatic aldehydes via glyoxal reaction", Ezio **Fasoli**, UPR Humacao

**10:20 AM** **O-3** "Molecular dynamics modeling of affinity membranes and interactions between their ligands and proteins", José **Sotero-Esteva**, UPR Humacao

**10:35 AM** **O-4** "Albumin/β-cyclodextrin-modified gold nanoparticles and GFP-Ferritin interactions: A fluorescence fluctuation spectroscopy study", Rolando **Oyola** and Nitza V. Falcón, UPR Humacao

**10:50 AM** Group Discussion

## IRG-1 Progress Reports

**11:15 AM** **O-5** "Carbon-polymer composites for energy storage and sensing applications", Idalia **Ramos**, Angelo Porcu, Luis Rivas, and Enrique González, UPR Humacao

PREM

**Group Photo and Lunch**

**11:40 AM** Group Photo

**12:00 PM** Working Lunch

**IRG-1 Progress Reports (cont.)**

**1:30 PM** **O-6** "CVD grown 2-D materials characterized in a field effect transistor configuration with ferroelectric gating", Nicholas **Pinto**, UPR Humacao

**1:45 PM** **O-7** "Length dependent thermoelectric properties of molecular junctions", Natalya **Zimbovskaya**, UPR Humacao

**2:00 PM** **O-8** "Studies on the Electrical Properties of Novel Organic Borazines and Applications of Azaborine compounds as Beta-amyloid Fluorescence Sensors", Margarita **Ortiz Marciales**, UPR Humacao

**2:15 PM** Group Discussion

**Education Progress Report**

**2:45 PM** Gilda **Jiménez**[1], Ricardo E. Morales[1] and Edgardo Sánchez[2], [1]UPRH, [2]UPRC

**3:00 PM** Group Discussion

**Poster Session, Advisory Board Meeting, and Closing**

**3:15 PM** Poster Session

**4:30 PM** Advisory Board Meeting with PIs

**5:00 PM** Closing



PREM

**P-13** "Effect of polyethylene oxide on camphor sulfonic acid doped polyaniline thin film field effect transistor with ionic liquid gating", Luis M. Rijos, Anamaris Melendez, Rolando **Oyola**, and Nicholas J. **Pinto**, UPRH

Field effect transistors (FET) using camphor sulfonic acid (CSA) doped polyaniline (PANi) blended with several polyethylene oxide (PEO) concentrations were investigated via ionic liquid gating. The pure PANi-CSA FET could not be turned "off" and had an on/off ratio of 2. Blending with 22 wt%-PEO retained a high "on" state throughput current and improved the mobility, while the on/off ratio increased by 103. Superior film quality and PEO assisted electrostatic interactions with the PANi chains led to device parameter enhancement. For higher PEO concentrations the field effect was suppressed due to disorder. Analysis of the UV/Vis spectra polaron band peak area near 810 nm show an increase in the mobility with decrease in the peak area, consistent with the observed results. Enhanced device parameters, high throughput current and low operating voltages (±2 V), make PANi-CSA/PEO blends attractive materials for use in low power consumption electronics.

PREM

**P-12** "Electrical characterization of polyaniline synthesized in a confined environment", Ricardo E. Morales, Luis M. Rijos, Melvin de Jesus, Margarita **Ortiz**, Rolando **Oyola**, and Nicholas J. **Pinto**, UPRH

Polyaniline was synthesized at 0°C in a confined environment *via* oxidation of the monomer. The purpose of confinement was to reduce chain disorder during polymerization. Confinement was achieved by placing a drop of aniline dissolved in 1M HCl between two coverslip slides that were held tight with a tweezer. The clamped slides were then inserted in a beaker containing 1M HCl solution (at 0°C) in which the oxidant ammonium peroxydisulfate was dissolved. Capillary forces permitted the entry of the oxidant into the confined space initiating the polymerization. This was evident from the green film that slowly began to appear between the slides during the synthesis. UV/Vis spectroscopy of the as synthesized polymer film show characteristic absorption peaks at 356nm, 435nm and 887nm corresponding to emeraldine salt form of polyaniline. The film conductivity was measured as a function of temperature, and it decreased as the temperature was lowered. Analysis of the data showed a quasi 1D conduction mechanism of charge transport in the temperature range 150K < T < 300K. Results on additional experiments to test the semiconducting properties of this polymer will also be presented.



## Student Poster Presentations

PREM

**P-1** "Sensing interactions between gold nanoparticles and Human Serum Albumin at single molecule level in the long red visible region", Nitza V. Falcón[1], Nicole M. González[1], Arusha Achayya[2], **Feng Gai**[2], and Rolando **Oyola**[1], [1]UPRH, [2]**PENN**

**P-2** "Temperature dependent charge transport in graphene with ferroelectric gating", Kelotchi S. Figueroa[1], Luis M. Rijos[1], Nicholas J. **Pinto**[1], Srinivas Mandyam[2], Meng–Qiang Zhao[2], and A.T. Charlie **Johnson**[2], [1]UPRH, [2]PENN

**P-3** "Coarse-Graining of Atomistic Models Using Neural Networks", Bernardo A. Roque Carrión, and José O. **Sotero Esteva**, UPRH

**P-4** "Granules: A Pandas-Based Package for Analysis of Molecular Dynamics Simulation", Lyxaira Glass Rivera and José **Sotero Esteva**, UPRH

**P-5** "Characterizing the Effect of Chemical Modification on Pore Size and Structural Integrity of Cellulose Membranes", Edgardo J. Sánchez Rivas[1], Zhiwei Liao[2], Ezio **Fasoli**[3], Daeyeon **Lee**[2], and Vibha **Bansal**[1], [1]UPRC, [2]PENN, [3]UPRH

**P-6** "Study of the binding affinity between para aminobenzamidine functionalized cellulose nanocrystals and t-PA", Jordan A. Caraballo Vega, José O. **Sotero Esteva**, and Ezio **Fasoli**, UPRH

**P-7** "Ligand Density Effects on Protein Binding Capacity of Chemically Modified Cellulose Membranes", Guillermo A. Correa Otero[1], Edgardo J. Sánchez Rivas[1], Shermain Aponte Rosario[1], Ivan J. **Dmoschowski**[2], Ezio **Fasoli**[3], and Vibha **Bansal**[1], [1]UPRC, [2]PENN, [3]UPRH

**P-8** "Polymer-Infiltrated Carbon Nanoparticle Films", Enrique O. González[1], Luis D. Rivas[1], Anamaris Meléndez[1], Idalia **Ramos**[1], and Daeyeon **Lee**[2], [1]UPRH, [2]PENN.

**P-9** "Fabrication and characterization of conducting polymer/single wall carbon nanotube aerogels", Angelo Porcu Madau[1], Luis Rivas Baguer[1], Anamaris Meléndez[1], Idalia **Ramos**[1], Arjun **Yodh**[2], and Mohammad **Islam**[3],[1]UPRH, [2]PENN, [3]CMU

**P-10** "Fluorescence Analysis of the Interaction between Azaborine Derivatives and Human Serum Albumin", Yareslie Cruz Rivera[1], Naomi Rivera Martínez[1], Melvin De Jesús[1], Rolando **Oyola**[1], Gary A. **Molander**[2], and Margarita **Ortiz**[1], [1]UPRH, [2]PENN

**P-11** "Synthesis of a Novel Organic Borazine Compound derived from Ortho-phenylenediamine as a Potential Semi conductive Material and its Chemical and Physical Properties Studies", José L. Rosario, Melvin De Jesús, Anamaris Meléndez, Idalia **Ramos**, Nicholas **Pinto**, and Margarita **Ortiz Marciales**, UPRH

**P-12** "Electrical characterization of polyaniline synthesized in a confined environment", Ricardo E. Morales, Luis M. Rijos, Melvin de Jesus, Margarita **Ortiz**, Rolando **Oyola**, and Nicholas J. **Pinto**, UPRH

**P-13** "Effect of polyethylene oxide on camphor sulfonic acid doped polyaniline thin film field effect transistor with ionic liquid gating", Luis M. Rijos, Anamaris Melendez, Rolando **Oyola**, and Nicholas J. **Pinto**, UPRH

**P-14** "Electrical characterization of a tungsten diselenide/silicon heterostructure", Ahmad Matar Abed, Anamaris Meléndez, Nicholas J. **Pinto**, José O. **Sotero Esteva**, and Idalia **Ramos**, UPRH

**P-15** "Chromo-fluorogenic detection of aromatic aldehydes in solid and liquid phase", Andrea N. Marcano Delgado, and Ezio **Fasoli**, UPRH



**P-11** "Synthesis of a Novel Organic Borazine Compound derived from Ortho-phenylenediamine as a Potential Semi conductive Material and its Chemical and Physical Properties Studies", José L. Rosario, Melvin De Jesús, Anamaris Meléndez, Idalia **Ramos**, Nicholas **Pinto**, and Margarita **Ortiz Marciales**, UPRH

PREM

Organic borazine compounds are benzene analogues containing alternating B and N atoms substituted with carbon groups. Recently, new interest on organic borazines have emerged due to their potential for new materials due to their optoelectronic and mechanical characteristics. Our research group is highly interested on the synthesis of novel organic borazine compounds to study their semi conductive properties. The borazine derived from *O*-phenlylenediamine was prepared by stirring the diamine and acid boric in toluene under reflux for 4 days. The solid borazine was recrystallized and characterized by IR, NMR and melting point. A conductivity analysis of the crystals was carried out using a gold electrode obtaining an average current of 2.24 mA at 0.1 Volts, and the average resistance was 43.5 Ohms, indicating that this borazine has a semi-conductor behavior. Further studies of this *O*-phenylenediamine borazine is underway. In the future, similar polymeric borazines will be prepared and their chemical properties and conductivity behavior will be studied.

**P-10** "Fluorescence Analysis of the Interaction between Azaborine Derivatives and Human Serum Albumin", Yareslie Cruz Rivera[1], Naomi Rivera Martinez[1], Melvin De Jesús[1], Rolando **Oyola**[1], Gary A. **Molander**[2], and Margarita **Ortiz**[1], [1]UPRH, [2]PENN

Azaborines are organic molecules composed of aromatic six-membered heterocycles, substituted with a B-N isosteric array in place of the C=C bond. The chemistry of organoboron compounds are currently being studied for their potential as optoelectronic materials and in biomedical applications. Recently, azaborines have demonstrated in vivo bioactivity that have addressed previous challenges in drug development, such as water solubility. Our research focuses on the analysis of aromatic polycyclic azaborines that can work as fluorescent organic labels for Human Serum Albumin (HSA) protein for bioactivity studies and further drug development. The azaborine compounds were characterized by $^{1}$H-NMR, $^{11}$B-NMR, UV-vis analysis and fluorescence spectroscopy. The absorbance of the drug was within the range of 310-330 nm. In addition, fluorescence characterization of the molecules showed a high fluorescent signal at low concentrations of these compounds between 330-375 nm. Successful binding results were obtained from the study of the interaction between the protein and some of the azaborine derivatives. The most significant benefit of these azaborine compounds is that they can also serve as fluorescent markers for the binding analysis with the protein. Further studies are in progress to show the effectiveness of the binding interactions between HSA and other novel azaborine compounds.



PREM

# Abstracts

**P-9** "Fabrication and characterization of conducting polymer/single wall carbon nanotube aerogels", Angelo Porcu Madau[1], Luis Rivas Baguer[1], Anamaris Meléndez[1], Idalia **Ramos**[1], Arjun **Yodh**[2], and Mohammad **Islam**[3], [1]UPRH, [2]PENN, [3]CMU.

Aerogels are highly porous solid nanomaterials with very low density, large pores, and high surface area. These characteristics make them ideal for energy storage, and for the fabrication of electronic devices. Here, we report on preparation and characterization of conductive gels composed of co-networks of single wall carbon nanotubes (SWCNTs) and the conducting polymer poly (3,4-ethylenedioxythiophene) – poly(styrene sulfonate) (PEDOT:PSS), at ratios of 1:5 to 1:9 using concentration dependent sol-gel method. High resolution scanning electron microscopy imaging, conducted at PENN, validated the porous, filamentous microstructure of these gels. Four-point conductivity measurements, done at UPRH, show gels prepared with the 1:7 concentration ratio have the best combination of mechanical robustness and high electrical conductivity (~100 S/cm).

PREM

**P-8** "Polymer-infiltrated carbon nanoparticle films"
Enrique O. González Delgado[1], Luis Rivas Baquer[1], Anamaris Meléndez[1], Idalia **Ramos**[1], and Daeyeon **Lee**[2], [1]UPRH, [2]PENN

Polymer-infiltrated composite films were fabricated using leaching-enabled capillary rise infiltration (LeCARI), a film of carbon spheres (CS) and the elastometer poly(dimethylsiloxane) (PDMS). LeCARI is a simple and solvent free method to fabricate nanoparticle composites. CS with average diameters of ~600 nm where fabricated by hydrothermal carbonization of sucrose, and then sintered at 200°C to reduce oxygen and enhance conductivity. A thick film (average ~ 30μm) of CS was prepared using spin coating. A piece of the PDMS was brought into contact with the top of the CS film and held in place for up to 48 hours. Then, the PDMS was removed and polymer infiltration into the CS film was confirmed by scanning electron microscopy (SEM). The electrical conductivity of the films was calculated using 2-point current-voltage measurements. Ongoing work includes enhancing the preparation method using UV-PDMS, understanding and controlling infiltration of PDMS on the CS film, and preparing flexible composites that can be used as mechanical sensors.



**O-1** "Cellulose based affinity membranes: Characterization of pores size and protein binding", Vibha **Bansal**[1], Ezio **Fasoli**[2], José **Sotero**[2], Ivan **Dmochowski**[3], and Daeyeon **Lee**[3], [1]UPRC, [2]UPRH, [3]PENN

Membrane discs have emerged as attractive alternatives to micro bead-based chromatography columns. The poor economy and performance-related problems associated with chromatographic separations add significantly to the cost of the final protein product, particularly in case of clinical applications. Membranes, on the other hand, offer higher accessible surface area, lower diffusional resistance, and pressure drop problems. The goal of this project is to develop affinity membranes for protein capture from biological mixtures. Towards this end, the study being reported here focused on understanding: i) the effect of chemical modification on the structural integrity of the membranes; and ii) the effect of ligand density on the protein binding capacity of the affinity membranes. Commercially available cellulose acetate membranes were chemically modified to obtain amidine as the end group, using protocols previously established in our laboratory. The pore size of modified membranes, as determined using a gravity driven water flow through the membranes, was observed to decrease with increase in ligand density. SEM analysis indicated that the membranes' structural integrity was not affected adversely by the modification process. The model proteins chosen for protein binding experiments included Trypsin and Tissue type Plasminogen Activator (tPA), both trypsin type serine proteases. The proteins were fluorescently labeled to facilitate the protein monitoring during binding experiment. Experiments performed using membranes in ligand density range of 0- 5.0 μmol per ml showed that protein binding increases with increase in ligand density up to amidine concentration of 4.0 μmol per ml. After this point a saturation effect was observed.



PREM

**O-2** "Fluorescent labelling of chemically modified cellulose membranes and aromatic aldehydes via glyoxal reaction", Ezio **Fasoli**[1], Vibha **Bansal**[2], José **Sotero**[1], and Ivan **Dmochowski**[3], [1]UPRH, [2]UPRC, [3]PENN

The glyoxal reaction has been established in our laboratory as a method for the quantification of aromatic amidine linked to solid support as well as for imaging affinity membranes with confocal laser scanning microscopy. In this talk new applications of glyoxal reaction will be discussed. We report the development of a simple, fast, and sensitive colorimetric and fluorometric assay for the detection of aromatic aldehydes at nanomolar concentrations. The assay is based on the reaction between benzamidine and glyoxal that forms an intermediary, 2-phenyl-4,5-dihydroxy-2-imidazolone. The intermediary reacts with the benzaldehyde forming the final fluorophore, 2-aryl-4-arylidene-2-imidazolin-5-one. The fluorophore was characterized by NMR, UV-VIS and fluorescence spectroscopy. The effect of different substituents on spectroscopic properties was analyzed. The assay quantifies aldehydes up to 100 µM. The limit of detection is 79 nM, and the limit of quantification is 263 nM. The assay was optimized on a para amino benzamidine chemically modified paper strip to develop a solid phase fluorescent assay. Another application of the glyoxal reaction was established, wherein it can be used as an enzymatic assay for alcohol oxidase and alcohol dehydrogenase. This provides a new tool for enzyme discovery and kinetic studies in microbial cultures in both liquid and solid media.



**P-7** "Ligand Density Effects on Protein Binding Capacity of Chemically Modified Cellulose Membranes", Guillermo A. Correa Otero[1], Edgardo J. Sánchez Rivas[1], Shermain Aponte Rosario[1], Ivan J. **Dmoschowski**[2], Ezio **Fasoli**[3], and Vibha **Bansal**[1], [1]UPRC, [2]PENN, [3]UPRH

Chemical modification of membranes with ligands that have affinity and selectivity for the target protein offers potentially advantageous alternatives for protein purification over traditional chromatographic processes based on microbead packed columns. The industrial processes have a clear preference for traditional chromatographic techniques, due to lack of availability of appropriately modified or end-group modifiable membranes. But more importantly, it can be attributed to a lack of understanding of the factors that affect protein binding capacity of such membranes. We have been involved with trying to understand factors that affect membrane performance in bioseparations. Here we describe a fast, economic, and effective approach to study the effects of ligand density on protein binding capacity of affinity membranes. Cellulose acetate membranes (1.2µm) were chemically modified with para-aminobenzamidine (pABA) to obtain an amidine as the end group that binds the active site of the protein of interest (trypsin type serine proteases). A range of ligand densities on membrane surface were obtained by adding different amounts of epichlorohydrin as the spacer arm and resulting amidine was quantified with the glyoxal method. The binding capacity was tested using fluorescently labeled tissue-type plasminogen activator (tPA) and trypsin. Results showed a linear increase in protein binding with an increase in ligand density until a ligand concentration of approx. 2.7 µmol per mL of membrane volume was reached. At this point, a saturation effect was observed. This research provides a valuable insight towards the understanding of factors that affect membrane binding capacity and promotes membrane-based processes in industrial separations.



PREM

PREM

**P-6** "Study of the binding affinity between para-aminobenzamidine functionalized cellulose nanocrystals and t-PA", Jordan A. Caraballo Vega, José O. **Sotero Esteva**, and Ezio **Fasoli**, UPRH

Affinity membranes are receiving extensive studies as an attractive, competitive, and affordable method for purifying biomolecules because of its renewability and cost efficiency. Applications such as fiber mat filters and antibody purification are just a small range of its applicability in the health industry. The study described in this work models by means of molecular dynamics simulations the interaction between para-aminobenzamidine (pABA) functionalized cellulose nanocrystals and tissue-type plasminogen activator (t-PA) at different ligand concentrations and sizes to determine the membrane parameters for optimal protein binding. Affinity ligands were developed by combining carbon based spacer arms of different lengths (5-atoms, 7-atoms, and 14-atoms) and pABA as the affinity ligand. Classical and steered molecular dynamics methods were employed using NAMD2 constant force pulling algorithms to model the absorption and desorption process. Frequency charts and unsupervised clustering algorithms were used to classify the folding structure of the affinity ligands, while binding affinity measurements were applied to quantify this protein-ligand interaction. Notably, spacer arms fold in three different ways depending on their ligand densities: straight, leaning, and twisting folds. Binding affinity results have shown an increase in energy during the absorption process, and the convergence of the energies to zero during the desorption process. Thus, the proposed optimal combinations of spacer arm length and ligand density of the system, the one that maximizes binding energies, are derived from this model.



**O-3** "Molecular dynamics modeling of affinity membranes and interactions between their ligands and proteins", Jordan A. Caraballo Vega, Bernardo A. Roque Carrión, Lyxaira Glass Rivera, José O. **Sotero-Esteva**, and Ezio **Fasoli**, UPRH

PREM

Experimental results have demonstrated that the performance of affinity membranes for chromatography may vary depending on factors such as the ligand density, and the length of the spacer arm separators used to increase the reach of the active component of the membrane and its underlying structural matrix. In this work we report on techniques used to simulate and analyze both the conformation of the spacer-arm and the affinity ligand, and their interactions with a protein. Possible research paths to improve these techniques including applications of data science methods, including machine learning are also discussed. In particular, we studied para-aminobenzamidine (pABA) functionalized cellulose membranes as produced in the lab by **Bansal** et. al. and their interaction with tissue plasminogen activator protein (tPA). Molecular dynamics simulations were setup with varying ligand densities and spacer arm lengths. In order to study spacer arm-pABA conformations, a set of simple geometric transformations were used to reduce the degrees of freedom of the structures that allowed us to effectively apply principal component analysis to classify the main conformations. The binding strength between the affinity membrane and tPA was then studied by incorporating the protein to the ends of the trajectories of the previous simulations. With the aim of improving the simulation, trajectory analysis and general applicability of the techniques applied here, two new paths of inquiry are discussed: the use of machine learning to compute force fields of coarse grain simulations and the development of a new software package for applying methods from data science to the analysis of molecular dynamics trajectories.

**O-4** "Albumin/β-cyclodextrin-modified gold nanoparticle and GFP-Ferritin interactions: A fluorescence fluctuation spectroscopy study", Rolando **Oyola**, and Nitza Falcón, UPRH

*Collaborators*: Anamaris Meléndez[1], Melvin De Jesús[1], Idalia **Ramos**[1], Arusha Achayya[2], Feng **Gai**[2], Joshua Bulos[2], and Ivan J. **Dmochowski**[2], [1]UPRH, [2]PENN

Supramolecular interactions are fundamental in nanotechnology. Our interest is to better understand the interaction of protein/metal-nanoparticles and protein/protein interactions at single molecule level. In this presentation, we discuss the current updates of the two main projects in our group: 1) albumin and gold nanoparticles interactions and 2) GFP/Ferritin. Protein corona formation is present when nanoparticle is in contact with biological fluids. In this work, the fluorescence probe, Atto655, is under free diffusion in open volume concept. Our results indicate that free Atto655 concentration in the confocal volume decreases in the presence of β-cyclodextrin or citrate gold nanoparticles but not with thiomethyl-PEG NP. In addition, an increase in the average number of molecules in the confocal volume was observed in the presence of HSA which we attribute to Atto655 displacement from the NP surface. The GFP/Ferritin project aims to develop a simple quantitative method to determine the stoichiometry of this protein/protein interaction. The results show that at low GFP/Ferr concentration the presence of NaCl changes the photostability of the complex.



**P-5** "Characterizing the Effect of Chemical Modification on Pore Size and Structural Integrity of Cellulose Membranes", Edgardo J. Sánchez Rivas[1], Zhiwei Liao[2], Ezio **Fasoli**[3], Daeyeon **Lee**[2], and Vibha **Bansal**[1], [1]UPRC, [2]PENN, [3]UPRH

PREM

Pore size is an important determinant of membrane performance in a downstream process. In case of membranes that have been chemically modified, the modification process can have a significant effect on membrane morphology. We have been researching factors affecting affinity membrane performance in our laboratory. Commercially available cellulose acetate membranes are chemically modified to obtain amidine linked as the terminal group. This membrane can then be used to isolate trypsin-like serine proteases from biological fluids. Here we report the study where membranes modified with increasing concentrations of ligand were characterized for any changes in their structural integrity post the modification process. Due to the characterization of their general morphology, SEM analysis of non-modified cellulose acetate membranes shows a complex network of cellulose fibers that result in pores of irregular geometry. This kind of non-cylindrical pore structure rendered it impossible to determine pore size by Scanning Electron Microscopy. A method was thus designed based on Darcy's Law to perform micropore analysis of the chemically modified cellulose membranes. This Gravity-Driven Setup (GDS) was based on gravity-driven flow of water through the membrane. When pore size measurements were performed on membranes modified with different concentrations of ligand, the pore size was found to increase with an increase in ligand density. The pores were also characterized using scanning electron microscopy to observe for any changes in structural integrity of the membranes.

**P-4** "Granules: A Pandas-Based Package for Analysis of Molecular Dynamics Simulation", Lyxaira Glass Rivera and José **Sotero Esteva**, UPRH

Molecular Dynamics (MD) is an effective technique for understanding molecular structure relationships throughout their respective simulations. Granules is a Python-based package developed with the aim of allowing analysis from molecular dynamics simulations into the means of concise and clear syntax constructions. In this way, 'Granules' may accelerate the analysis of MD experiments and increase performance of previous work. The package is built on top of the Pandas library for Python. Obtained data is accommodated into Pandas DataFrames for better data management and is purposed to exploit Pandas data analysis capabilities. Granules is currently capable of obtaining data through CHARMM force field Parameter files, NAMD Protein Structure files, and Protein Data Bank Files. In this work, we present examples of the analysis of atoms and molecules through MD Analysis using Granules.



**O-5** "Carbon-polymer composites for energy storage and sensing applications", Angelo Porcu[1], Luis Rivas[1], Enrique González[1], Anamaris Meléndez[1], Idalia **Ramos**[1], and Daeyeon **Lee**[2], [1]UPRH, [2]PENN.

PREM

We will report on two UPRH-PENN collaborative research efforts on the preparation of Single Wall Carbon Nanotubes (SWCNT)-poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT:PSS) gels and Carbon Spheres (CS)-Polydimethylsiloxane (PDMS) films. In the first project, co-gels of SWCNTs and PEDOT:PSS were fabricated using sol-gel methods. Characterization using high resolution scanning electron microscopy (SEM) and four-point current-voltage measurements shows the formation of co-gels with high porosity, filamentous microstructures, and high conductivity (~100 S/cm). We will also present preliminary results on the fabrication of mechanically robust, highly electrically conducting electrospun fibers using the co-gels. In the second project, CS-PDMS films were fabricated using leaching-enabled capillary rise infiltration method. The carbon spheres were prepared by hydrothermal characterization of sucrose. SEM images of cross-sections of the films show infiltration of PDMS as the time of exposure increases from 0 to 48 hours.

**O-6** **"**CVD grown 2-D materials characterized in a field effect transistor configuration with ferroelectric gating", Nicholas J. **Pinto**, UPRH

Results on CVD grown graphene and $MoS_2$ samples characterized in a FET configuration with ferroelectric gating will be presented. The ferroelectric co-polymer poly(vinylidene fluoride-trifluoroethylene)-PVDF-TrFE was used as the gate insulator. In the case of graphene, we studied the temperature dependence of charge transport in the range 300K < T < 350K. Two charge neutrality points (CNP) were observed during the gate voltage sweep from -50V to 50V that correspond to the up/down polarization of the ferroelectric material. The CNP was seen to occur near the coercive voltage of the ferroelectric allowing some tuning of the Dirac point. The advantage of using a FE gate is the ability of the dielectric to store charge. This was used to perform write and erase functionality on graphene. In a separate experiment, monolayer $MoS_2$ was also characterized as a FET with FE gating, and the effects of varying the gate voltage scan rate from 200 mV/s to 4 mV/s on device performance were investigated. Prior to the device switching on, a negative trans-conductance was observed for all scan rates. It was followed by a rapid increase in the channel current to the on state, corresponding to the polarized down configuration of the FE. This effect was independent of the drain-source voltage. Our results revealed a narrowing in the memory window width, an increase in the mobility (μ) from 0.02 – 10 $cm^2$/V-s, and a decrease in the sub-threshold voltage swing (SS) as the scan rate was lowered. These parameters appeared to stabilize at slower scan rates suggesting an asymptotic limit to their values. A model based on nucleation and unrestricted domain growth was used to explain these results. By lowering the gate voltage scan rate, the performance of polymer based FE-FET's can therefore be improved.



**P-3** "Coarse-Graining of Atomistic Models Using Neural Networks", Bernardo A. Roque Carrión and José O. **Sotero Esteva**, UPRH

PREM

Classical Molecular Dynamics simulations contain the desired molecule as a solute in a solution. Simulating protein and solvent atoms requires many computational resources. One proposed method of reducing the computational expense of these simulations is a technique known as Coarse Graining, which reduces the total number of atoms to a smaller number of Coarse-Grained beads. In this project test a technique to derive the force fields in the Coarse-Grained Molecular Models from the all-atoms force field using Artificial Neural Networks. For the test, a small hairpin protein is used. Its corresponding coarse grain model atoms are the Ca atoms of the original molecule. A Neural Network is trained to compute the forces acting on the atoms of the Coarse Grain model. Energy measures of the all-atom and coarse grain models comparisons serve as measure of the accuracy of the coarse grained representation.

PREM

**P-2** "Temperature dependent charge transport in graphene with ferroelectric gating", Kelotchi S. Figueroa[1], Luis M. Rijos[1], Nicholas J. **Pinto**[1], Srinivas Mandyam[2], Meng–Qiang Zhao[2] and A.T. Charlie **Johnson**[2], [1]UPRH, [2]PENN

CVD graphene was electrically characterized in a field effect transistor configuration with ferroelectric (FE) gating in the temperature range 300K < T < 350K. Saturated hysteresis loops of the FE co-polymer poly (vinylidene fluoride-trifluoroethylene)-PVDF-TrFE (75/25) showed that the memory window width decreased as temperature increased. Device trans-conductance (I-Vg) curves exhibit hysteresis behavior with two charge neutrality points (CNP) corresponding to the up/down polarization of the ferroelectric gate. Increasing the temperature decreased the change of the gate voltage and increased the change in the channel current measured between the two CNP's. The electron mobility showed a steeper decrease compared to the hole mobility as temperature was increased. Desorption of $O_2$ and $H_2O$ was used to explain these observations. Finally, non-volatile switching was realized using the charge storage property of the gate insulator.



**O-7** "Length dependent thermoelectric properties of molecular junctions", Natalya **Zimbovskaya**, UPRH

PREM

The results of theoretical studies of steady state thermoelectric transport through a single-molecule junction with a long chain-like linker are reported. Electron transmission through the system may be computed using a tight-binding model for the linking molecule. In the reported studies Coulomb interactions between electrons and the effect of phonon bath representing the molecular surroundings were omitted from consideration. We concentrated on the analysis of molecule length dependences of thermally induced charge current and of thermoelectric efficiency given by the figure of merit ZT. We have studied length dependent thermoelectric properties in unbiased and biased single molecule junctions operating within and beyond linear response regime. It was shown that the thermally induced charge current and ZT strongly depend on the molecular bridge length. They both may be significantly affected by the lineshape of electron transmission in the interval corresponding to HOMO/LUMO transport channel. Also, it was demonstrated that electron interactions with molecular vibrations may bring noticeable changes in the behavior of the length-dependent thermally induced charge current.

**O-8** "Studies on the Electrical Properties of Novel Organic Borazines and Applications of Azaborine compounds as Beta-amyloid Fluorescence Sensors", Margarita **Ortiz Marciales,** José Luis Rosario Collazo, and Yareslie Cruz Rivera, UPRH

*Collaborators*: Naomi M Rivera[1], Rolando Oyola[1], Nicholas **Pinto**[1], Anamaris Meléndez[1], Melvin De Jesús[1], Idalia **Ramos**[1] and Gary **Molander**[2], [1]UPRH, [2]PENN

Organic boron compounds are presently key entries in biomedical and electronic materials. Our aim was to synthesize and characterize novel planar borazine compounds derived from 1,2-aminophenol, 3-amino-2-naphthol and o-phenlylenediamine and study their physical and chemical properties for possible semi conductive materials. Initial attempts to prepare the oxazaborolidine precursors derived from 2-aminophenol and 2-amino-1-naphthol failed due to their moisture sensitivity. However, the direct synthesis of the borazine derived from the 1,2-diamino benzene was successfully achieved and the stable product was characterized by IR, $^{1}H$, $^{13}C$ and $^{11}B$ NMR. The characteristic signal for the borazine ring appeared at ~20.0 ppm in the $^{11}B$ NMR. Further studies are in progress to study the electronic properties of these types of polyaromatic borazines. In collaboration with **Oyola** and **Molander**, our second project study key aromatic azaborine compounds, synthesized by **Molander**'s group at PENN, as biosensor for the analysis of Human Serum Albumin (HSA). Selected azaborines were fully characterized by IR, $^{1}H$, $^{13}C$ and $^{11}B$ NMR. Azaborine I6 has a high fluorescence behavior at low concentrations (15μM). Moreover, in the presence of HSA, the radiation emitted by this compound increased. We are studying the interaction of other azaborines with HSA by a fluorescence method to use this as an effective sensor of gold nano particles covered with HSA.



**P-1** "Sensing interactions between gold nanoparticles and Human Serum Albumin at single molecule level in the long red visible region", Nitza V. Falcón[1], Nicole M. González[1], Arusha Achayya[2], Feng **Gai**[2], and Rolando **Oyola**[1],[1]UPRH, [2]PENN

PREM

Gold nanoparticles (AuNPs) have remained a research topic because of their extensive range of applications which includes biosensing, cancer therapy, and drug delivery. In biological applications one of the most pertinent interactions is the corona formation (proteins/NPs complex). This project focused on studying the interactions of human serum albumin (HSA), the most abundant protein in human blood, with AuNPs using fluorescence correlation spectroscopy (FCS). Atto655 was used as a probe, because its absorption and emission are in the red region, away from AuNP plasmonic absorption. We proposed that through FCS detailed information could be obtained about the interaction of HSA with AuNP and how these interactions change with NPs' surface modification at the single molecule level. Results demonstrate that the emission of Atto655, i.e. the average number of molecules (<N>) decreases in the presence of β-cyclodextrin-AuNP (βCDAuNP) and Citrate-AuNP (cAuNP). Addition of HSA (0-100nM) to Atto655:βCDAuNP induces a recovery of free <N>, while for Atto655:cAuNP remains low. When HSA is added to poly(ethylene glycol) methyl ether thiol (PEGT) modified AuNPs, <N> remains constant. Thus, the information gathered at single molecule level provides a better understanding of the binding mechanism of macromolecules to AuNPs.