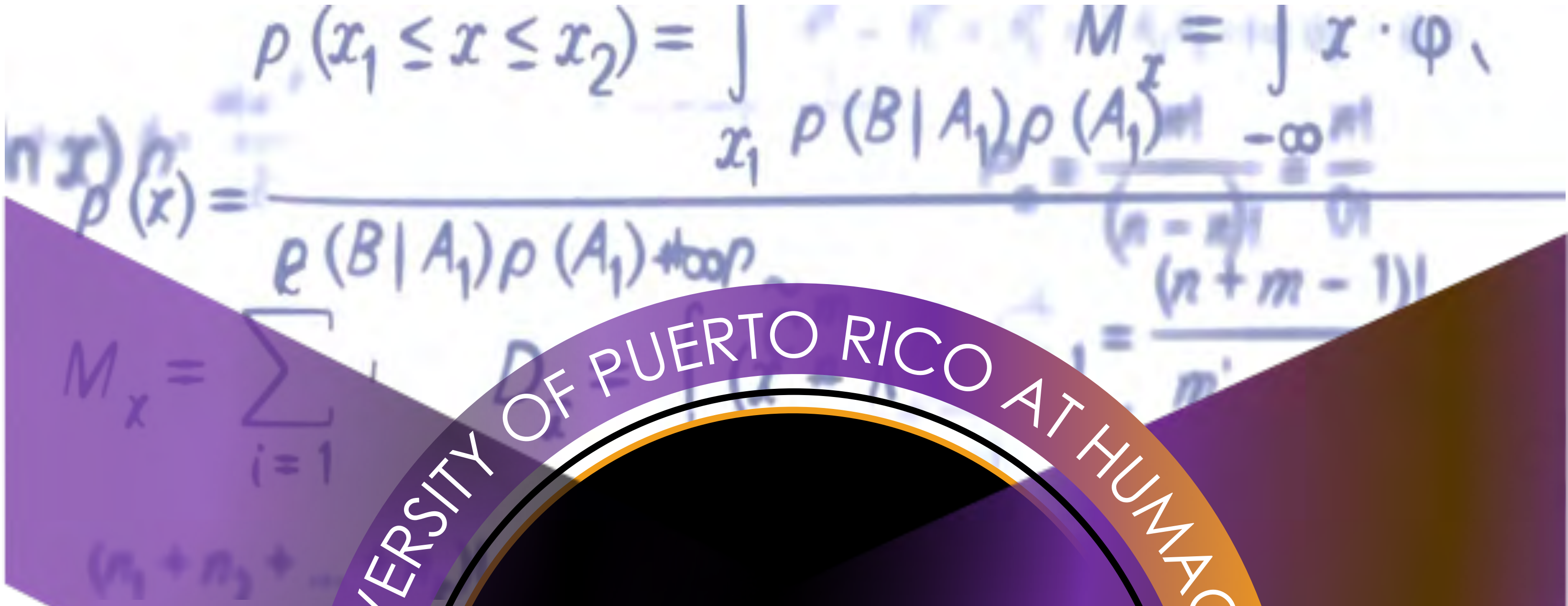


UNIVERSITY OF PUERTO RICO AT HUMACAO

PREM

13TH ANNUAL MEETING

PARTNERSHIP FOR RESEARCH AND EDUCATION IN MATERIALS

December 16, 2016

Wyndham Garden at Palmas del Mar

Program

13th PREM Annual Meeting
December 16, 2016
Wyndham Garden at Palmas del Mar
Humacao, Puerto Rico

9:00 AM **Registration** and **Breakfast**

9:45 AM **Welcome Messages & Presentation of Participants**
Idalia Ramos, Program Director, UPR-Humacao
Arjun Yodh, PREM Co-PI and Director PENN MRSEC
Andrew McGhie, Associate Director PENN MRSEC

10:00 AM **Parallel Sessions**

Room Roble: IRG-1, "Multifunctional Nanodevices from Optoelectronic Materials" (**Abstracts**, **O-1**:**O-4** page 9)

10:00 **Overview**: Idalia Ramos & Nicholas Pinto, Group Leaders

10:10 **O-1**: **Synthesis and Characterization of Organic Borazine Compounds**, Margarita Ortiz, UPR-Humacao

10:30 **O-2**: **Liquid ion gel gating of organic and inorganic devices**, Nicholas Pinto, UPR-Humacao

10:50 **Coffee Break**

11:00 **O-3:** **Carbon materials derived from sucrose for electronic devices, sensors and energy storage**, Idalia Ramos, UPR-Humacao

11:20 **O-4:** **Electron transport mechanisms in the assembly of carbon microspheres**, Natalya Zimbovskaya, UPR-Humacao

11:40 Discussion and plans for the future.

Room Laurel: IRG-2, "Nanoscale Interactions of Macromolecules at Soft and Hard Interfaces" (**Abstracts O-5**:**O-7**, page 12)

10:00 **Overview**: Rolando Oyola & José Sotero, Group Leaders

10:10 **O-5:** **Understanding the effect of ligand density and pore size on protein binding capacity of affinity membranes**, Vibha Bansal[1], Ivan Dmochowski[2], Ezio Fasoli[3], Rolando Oyola[3] & José Sotero[3], [1]UPR-Cayey, [2]PENN, [3]UPR-Humacao

10:50 **Coffee Break**

11:00 **O-6:** **Nanoscale interactions with cellulose-based materials**, Pantojas[1] & JoseeVedrine[2], [1]UPR-Cayey, [2]UPR-Humacao

11:30 **O-7:** **Protein/peptide interactions with nanoparticles**, Rolando Oyola[1], Anamaris Meléndez[1], Idalia Ramos[1] & Feng Gai[2], [1]UPR-Humacao, [2]PENN

12:00 Closing remarks and plans for the future

12:15 PM **Working Lunch**

1:30 PM **IRG's** and **Education Group Reports**

1:30 **IRG 1:** Idalia Ramos & Nicholas Pinto
1:50 **IRG 2:** Rolando Oyola & José O. Sotero
2:10 **Education:** Gilda Jiménez

2:40 PM **Group Photo**

3:00 PM **Student Poster Presentations** (**List of Posters**, page 5, **Abstracts**, page 15)

4:30 PM **Advisory Committee meets to write report**

5:30 PM **Closing**

Student Poster Presentations

IRG-1: Multifunctional nanodevices from optoelectronic materials (**Abstracts** page 15)

P-1 **Synthesis of the organic borazine derived from 2-aminophenol using sodium borohydride and boron trifluoride-etherate**, Yareslie Cruz, Melvin De Jesús-Flores & Margarita Ortiz-Marciales, UPR-Humacao

P-2 **Synthesis and characterization of borazines derived from 2-aminophenol and norephedrine using borane and trimethylborate**, Leeza M. Santiago-Millán, Melvin De Jesús-Flores & Margarita Ortiz-Marciales, UPR-Humacao

P-3 **Synthesis and Characterization of the Borazine derived from 2-Aminophenol and Triisopropylborate**, Jonathan Ramos Agosto, Melvin de Jesús-Flores & Margarita Ortiz-Marciales, UPR-Humacao

P-4 **p-n Junction Diodes Fabricated using Poly (3-hexylthiophene-2,5-dyil) (P3HT) Thin Films and Nanofibers**, Shamir Maldonado-Rivera & Nicholas J. Pinto, UPR-Humacao

P-5 **Electro-spun PEDOT-PSS nano-ribbon transistor using ion-gel gate dielectric**, Deliris Ortiz & Nicholas J. Pinto, UPR-Humacao

P-6 **Green Preparation of Graphene Oxide and Carbon Nanospheres for Gas Sensing Applications**, José L. Pérez Gordillo[1], Ahmad Matar[2], Anamaris Meléndez[2], Nicholas Pinto[2] & Idalia Ramos[2], [1]Petra Mercado High School, [2]UPR-Humacao

P-7 **Temperature-dependent charge transport in carbon-based polymer composites**, Cesar A Nieves-Sanabria, Luis M. Martínez, Anamaris Meléndez, Idalia Ramos & Nicholas J. Pinto, UPR-Humacao

P-8 **Preparation of carbon foams from sucrose**, Orlando Carromero, Anamaris Meléndez & Idalia Ramos, UPR-Humacao

IRG-2: Nanoscale interactions of macromolecules at soft and hard interfaces (**Abstracts** page 19)

P-9 **The study of the oligomerization process of IAPP in presence of modified Gallium nanoparticles**, Ambar S. Delgado-Carrión & Rolando Oyola, UPR-Humacao

P-10 **Protein/ Peptide Interactions with Gold Nanoparticles**, Lilliana I Ortiz- Rodriguez, Ambar Delgado & Rolando Oyola, UPR-Humacao

P-11 **Laser scanning confocal microscope as a tool for ligand density and protein binding estimation in affinity membranes**, Junellie L. Cruz-Lebrón & Ezio Fasoli, UPR-Humacao

P-12 **Confocal Laser Scanning Microscopy Image Analysis Using Python and Matplotlib**, Joshua Cruz-Cintrón[1] & José Sotero-Esteva[2], [1]Petra Mercado High School, [2]UPR-Humacao

P-13 **Fluorescent assay for determination of ligand density in para aminobenzamidine affinity membranes**, Christian J. Ortiz-Hernández & Ezio Fasoli, UPR-Humacao

P-14 **Effects of pore size on protein binding capacity of affinity membranes**, Adriana N. Santiago-Ruiz[1], Christian Ortiz[2], Rolando Oyola[2], Ezio Fasoli[2], Vibha Bansal[1], [1]UPR-Cayey, [2]UPR-Humacao

P-15 **Characterization and analysis of bamboo cellulose nanocrystals,** Nicole Ramos-Solis, Carolyn Carradero & Josee Vedrine, UPR-Humacao

P-16 **Ligand mediated interaction between hard metal nanoparticles and cellulose polymer fibers**, Jorge L. Berrios-Rivera & Víctor Pantojas, UPR-Cayey

P-17 **Study of nanoscale adhesion of different metal nanoparticles on the surface of cellulose nanocrystals**, Milagros M. Rivera-Cruz & Víctor Pantojas, UPR-Cayey

Other Non-IRG (**Abstracts** page 25)

P-18 **Shearing of an Organic Polymer Film for Improved Solar Cell Devices,** Luis A. Ortiz-Flores, Gabriel Calderón-Ortiz & Josee Vedrine-Pauleús, UPR-Humacao

P-19 **Purification, characterization and synthetic applications of an esterase from a moderately halophilic microorganism**, Mahmoud Matar, Steven J. Toro, José Sánchez, Ángel Miranda Iris Flores, Ezio Fasoli, UPR-Humacao

P-20 **Electrochemical Studies of Ferrocene Compounds**, Francisco Velázquez-Alvarez, Jorge Castillo-Ramírez & Mirna Claudio-Rivera, UPR-Humacao

Abstracts

O-1: Synthesis and Characterization of Organic Borazine Compounds,

Leeza Santiago, Johnathan Agosto, Yaresly Cruz, Melvin de Jesús &
Margarita Ortiz-Marciales, UPR-Humacao

Organic borazines are compounds with a six-member ring of alternating boron and nitrogen atoms, which have new applications in the material sciences. Following our previous methodology, the borazine derived from 2-aminophenol was synthetized by the reaction of borane-DMS or borane-THF at room temperature, followed by the trimerization of the oxazaborolidine intermediate by heating the reaction mixture up to 150 ºC. The resulting product was characterized by IR, ^{1}NMR, ^{13}C NMR and by UV-Vis and fluorescence spectroscopy. However, this borazine was obtained in the crude form since the purification by sublimation and/or recrystallization to obtain this compound in a highly pure form has been difficult due to its low solubility in organic solvents, low volatility, and susceptibility to atmospheric moisture. A second alternative, using sodium borohydride ($NaBH_4$) and boron trifluoride in THF, was attempted for the synthesis of this borazine with modest success. It was also explored the use of triisopropyl borate as a boron source in a less hydroscopic medium such as toluene, xylene and in a polar solvent like diglyme. The formation of the borazine was evidenced by the melting point, ^{1}H, ^{13}C and ^{11}B-NMR, and IR analysis, however it partially decomposed under the work-up and purification process. Currently, we are preparing other borazines derived from norephedrine, 2-aminoindanol using borane-dimethyl sulfide or trimethyl-borate that can be easily purified. We expect to obtain new borazines using novel chemistry and environmentally safety boron compounds in a pure form for possible future applications in advanced semi conductive materials. Future work includes the preparation of new borazines containing other polyaromatic and heterocyclic aromatic rings, synthetizing borazines derived from ferrocenyl amino ethanol and 2-aminonaphthol and stuyding the photochemical and semiconductive properties of the prepared borazines.

O-2: Liquid ion gel gating of organic and inorganic devices, Nicholas J. Pinto, UPR-Humacao

In a typical field effect transistor, the gate dielectric is SiO_2 which has a specific capacitance of ~20 nF/cm^2 for a 150nm thick layer. When used in organic field effect transistors, the operating voltages are several tens of volts making them impractical for commercial applications. Ionic liquids are organic/inorganic salts that are air stable, have low vapor pressure and exhibit high ionic conductivity. The advantage of using these materials as the gate dielectric is the high specific capacitance (10 microF/cm^2), which dramatically lowers the operating voltages in devices. The ionic liquid solution used was prepared by dissolving 9wt% of 1-ethyl-3-methylimidazolium bis (trifluromethylsulfonyl) amide – $(EMI)^+(TFSA)^-$ and 1wt% of poly(styrene-b-methyl methacrylate-b-styrene) triblock copolymer-SMS-15-81-15 in 90wt% of methylene chloride. Gelation of the triblock polymer in the ionic liquid (EMITFSA) through non-covalent association of the polystyrene blocks lead to a viscous low vapor pressure liquid ion gel. Results on devices fabricated from electro-spun PEDOT:PSS nano-ribbons and from monolayer WS_2 using this ion gel as the gate dielectric will be presented. In the case of PEDOT:PSS, the proposed mechanism is an electrochemical process due to penetration of ions into the polymer in the "depletion" mode and perhaps a combination of electrochemical and field effect in the "enhancement" mode. For the WS_2 based device, the operation is due to the field effect since ions could not penetrate the WS_2 film. In both cases however the operating voltages are under 2V which is ideal for use in hand held devices. The use of ion gels as the gate dielectric is new to the lab, and thus opens up several possibilities of expanding collaboration with other groups in the PREM project.

O-3: **Carbon materials derived from sucrose for electronic devices, sensors and energy storage**, Idalia Ramos, UPR-Humacao

Carbon spheres (CS) were prepared by hydrothermal carbonization of sucrose and annealing under a nitrogen atmosphere. The CS have smooth surfaces, diameters ranging from nanometers to micrometers, and are electrically conductive. CS/polymer composites have been implemented as Schottky diodes and aliphatic gas sensors. This research is done in collaboration with Nicholas Pinto (UPRH) and Anamaris Meléndez (UPRH), and has promoted interactions with other PREM partners. Jorge Santiago-Avilés (PENN) and his students have been working on the CS characterization through Raman scattering and electronic transport properties of CS/polyethylene oxide (PEO) composites. Margarita Ortiz (UPRH) has synthesized polyaniline (PANI) for the preparation of CS/PANI composites. Natalya Zimbovskaya (UPRH) is theoretically studying electron transport mechanisms in CS/PEO and CS/PANI composite to understand temperature-dependent experimental results (see abstract O-4). Finally, in collaboration with Exio Fasoli (UPRH), the CS has been functionalized for future applications in biosensors and drug delivery. In a second project, carbon foams were produced by increasing the time for hydrolysis of the sucrose. The high surface area and electrical conductivity make these foams promising as electrodes for supercapacitors and pseudocapacitors.

O-4: **Electron transport mechanisms in the assembly of carbon microspheres**, Natalya Zimbovkskaya, UPR-Humacao

Electron transport mechanisms in the composite compiled out of carbon microspheres glued together by polyethylene oxide (CS/PEO) are theoretically analyzed basing on experimental data. It is shown that the electron transport in the considered CS/PEO sample is mostly governed by two transport mechanisms, namely, thermally activated transport through chains compiled of adjoining spheres and thermally induced tunneling between the spheres separated by gaps. The interplay between these mechanisms results in unusual temperature dependence of the sample conductivity observed in experiments.

O-5: Understanding the effect of ligand density and pore size on protein binding capacity of affinity membranes, Vibha Bansal[1], Ivan Dmochowski[2], Ezio Fasoli[3], Rolando Oyola[3] & José Sotero-Esteva[3], [1]UPR-Cayey, [2]PENN, [3]UPR-Humacao

The goal of this project is to develop membrane based separation processes that can eventually translate into time-and cost-effective tools. Specifically, we are trying to develop cellulose based affinity membranes for protein capture from biological mixtures. Bansal, Fasoli and Oyola's group are developing a fluorescent assay for the estimation of ligand density (PABA) on cellulose membrane surface. The fluorescent probe 2-aryl-4-arylidene-2-imidazolin-5–one (Ex 385 nm, Em 455 nm) was synthesized starting from benzamidine, glyoxal, and benzaldhyde, and characterized by ^{1}HNMR. In order to measure the ligand density of PABA on cellulose membranes, a standard curve was obtained by submerging unmodified cellulose membranes in solution containing increasing concentration of fluorescent probe. The method was found to be linear up to 5 mM amidine concentration. Bansal, Dmochowski, Fasoli, and Sotero's group are developing a method for qualitative and quantitative analysis of the ligand density and protein binding using a laser scanning confocal microscope (LSCM). Chemically modified cellulose membranes were dyed with Rhodamine B (Ex 545nm, Em 580 nm) which allows the visualization of membrane structure and porosity. The bound affinity ligands (PABA) were fluorescently labeled by a reaction with glyoxal and Fluorene-2-carboxaldehyde (Ex 488 nm, Em 530 nm). *Substilisin carlsberg* was fluorescently labeled with Fluorescein isothiocyanate (Ex 480, Em 520 nm) and used as model protein for the study. Different images using LSCMS were taken on membrane carrying different ligand density, and protein concentration. Bansal is now using this method developed by Fasoli in UPENN for protein binding experiments in her lab. Analysis of images was done using a custom made computer application developed by the group of Sotero which allows to experiment with different image analysis techniques to determine the degree of membrane functionalized with the affinity ligand and the amount of protein bound to the ligand. Bansal and Sotero's group are focusing on studying the effect of pore size and ligand density on protein binding to cellulose membranes. Using the model previously described, a five-atoms long spacer arm was attached to the regenerated cellulose membrane, followed by the linking of PABA as the terminal group. Preliminary studies showed a successful capture of the protein from a pure protein solution using these affinity membranes. As a second step, cellulose acetate membranes of different pore sizes were purchased (0.2 – 7.0 microns) and modified similarly with para-aminobenzamidine. An accurate quantification of PABA is needed to evaluate the protein binding capacity of the membranes. No clear correlation was seen between the ligand concentration and pore size. Experiments are being performed now to determine the protein binding capacities of these membranes and understand the role of pore size in it. Sotero is developing a molecular dynamics model to predict the ligand orientation on the cellulose membrane in relation to ligand density. His simulation will be compared with experimental methods to predict the optimum ligand density for an efficient separation.

O-6: **Nanoscale interactions with cellulose-based materials**, Victor Pantojas[1] & Josee Vedrine[2], [1]UPR-Cayey, [2]UPR-Humacao

The nanoscale interaction between hard metal nanoparticles and cellulose polymer and/or nanocrystals is explored. The chemically tunable hydroxyl group present along the surface of cellulose can act as an anchoring site to immobilize metal species. Chemical modifications can increase availability and strength of the interaction at these sites. In this work, cellulose fibers were produced by electrospinning and deacetylation of cellulose acetate. The fibers were chemically modified after treatment with sodium chloroacetate to functionalize the surface and assist in the adhesion of atomic metals. After dipping the fibers in a solution of the metal salt, and subsequent reduction, the formation of metal nanoparticles is expected. The effect of variations on the concentration of Cobalt metal salt on the amount of atomic Co metal attached to the fibers is evaluated by Energy Dispersive Spectroscopy. Surface morphology is characterized by Scanning Electron Microscopy. A similar functionalization procedure is applied to the surface of nanocrystalline cellulose thin films for the attachment of Copper and Nickel metals. Applications of metal nanoparticles supported on polymeric fibers includes catalysis, sensing, environmental decontamination, amongst others.

Additional routes to understanding the nanoscale interactions of macromolecules at soft and hard interfaces can be obtained by aligning or orientating CNCs nanostructures on surfaces; particularly, their nanoscale interactions with macromolecules or the assembling of nanomaterials into macroscopic structures that have designed properties and functionality. In this work, we extracted and characterized cellulose nanocrystals from Bambusa vulgaris Schrad. ex Wendl Bamboo from Puerto Rico using a four-step process composed of alkaline, bleaching, hydrolysis and dialysis. We performed zeta potential analysis to measure the magnitude of the electrostatic or charge repulsion/attraction between dispersed bamboo cellulose nanocrystal particles in aqueous suspension, and characterized CNCs using analysis tools such as AFM XRD, SEM/EDS and IR. Upon obtaining fundamental CNC properties, we applied orientation techniques such as Flow Coating, and Langmuir Blodgett to organize CNCs monolayers on substrate surfaces. Future work will include the mechanical and packing properties of CNCs on surfaces.

O-7: **Protein/peptide interactions with nanoparticles**, Rolando Oyola[1], Anamaris Meléndez[1], Idalia Ramos[1] & Feng Gai[2], [1]UPR-Humacao, [2]PENN

Studies have shown that nanoparticles (NP) can have an impact on the aggregation properties of proteins, including fibril formation. Protein-NP interaction may change protein orientation, conformation and packing arrangement. Therefore, developing fundamental knowledge of the aspects that direct the protein/NPs interaction is relevant for future nanomaterials. Our research is focused in two major projects: (1) interaction of Gallium nanoparticles with islet amyloid polypeptide (IAPP) and (2) the interaction of modified-gold nanoparticles (AuNP) with human serum albumin (HSA). It is well known that misfolding of islet amyloid peptide (IAPP) takes place, insoluble fibril aggregates that are toxic to the pancreatic beta cells form, and induce a decline on the insulin secretion (diabetes type 2). Recently, gallium nanoparticles have emerged as an alternative for antimicrobial agent and other uses. Thus, the major goal of this study is to test if using gallium nitride nanoparticles (GaNP) and two surface-modified derivatives (hydroxyl and carboxylate) can modulate or affect the kinetic and size formation of the IAPP oligomerization. Our results for the oligomerization process of IAPP in the presence of GaNP shows a typical nucleation process. However, we notice that increasing the concentration of GaNP does not change the lag phase delay but lowers the maximum fluorescence intensity of the sigmoidal response. In relation to the second project, the interaction of HSA as a gold nanoparticle protector has been previously studied and it has been demonstrated, using fluorescence measurements, that the single tryptophan in HSA transfers energy to the gold nanoparticle. In an attempt to study this type of interactions, modified nanoparticles were synthetized using beta-cyclodextrin and 2-hydroxypropil-beta-cyclodextrin. The objective of introducing cyclodextrin is to modulate the protein corona formation. A fluorescence quenching effect of the single tryptophan in HSA is observed as the concentration of the modified gold nanoparticles increases. Subsequent addition of potassium iodide (KI) induces more quenching. Our results suggest that in presence of the modified nanoparticles the HSA shows distinctive conformational changes in the presence of AuNP and KI.

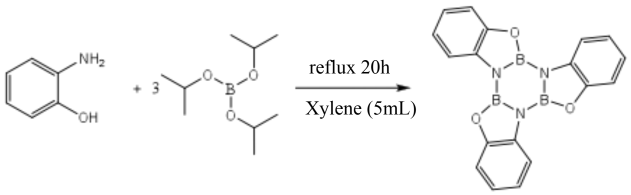
P-1: Synthesis of the organic borazine derived from 2-aminophenol using sodium borohydride and boron trifluoride-etherate, Yareslie Cruz, Melvin De Jesús & Margarita Ortiz, UPR-Humacao

The basic borazine molecule has a planar hexagonal structure of six alternating boron nitrogen atoms that was initially used as fuel additives and rocket fuels, but more recently, its polymeric material is used in semi conductive boron nitride (BN) ceramics. However, borazines containing organic fragment are less well-known. The development of a facile method for the synthesis of the borazine derived from 2-aminophenol with suitable boron reagents is of interest in our group to study the physical and chemical properties of these novel compounds. Initially, we proceeded by mixing sodium borohydride and 2-aminophenol in dry THF under N_2 atmosphere, and BF_3-OEt_2 was slowly added via syringe. The reaction mixture was heated to reflux for 3 h and washed with hot dioxane. The crude product, isolated by filtration under a nitrogen atmosphere and dried under vacuum, was obtained as a light brown solid in a 93% yield. The product was analyzed by IR, and ^{1}H and ^{11}B NMR. The characteristic signal for the borazine ring appeared at ~20.0 ppm in the ^{11}B NMR. The decomposition point was 215 ^{o}C, like the reported melting point of the desired borazine. We plan to continue exploring the best purification conditions to obtain this borazine in a pure form to study its physical properties for future applications in electronic devices.

P-2: Synthesis and characterization of borazines derived from 2-aminophenol and norephedrine using borane and trimethylborate, Leeza M. Santiago-Millán, Melvin De Jesús & Margarita Ortiz, UPR-Humacao

Organic borazines are cyclic compounds composed of a hexagonal ring of alternating boron and nitrogen atoms, which recently have been of great interest in materials sciences. Polycyclic borazine with three adjacent 1,3,2-oxazaborolidine rings were previously synthesized by our group using the reaction of the 1,2-amino alcohols with borane-DMS at room temperature and subsequent trimerization of the oxazaborolidine intermediate by heating the mixture under N_2. However, the synthesis of the borazine derived from the 1,2-aminophenol by this method was not successful, and a mixture of products was observed by ^{1}H, ^{13}C and ^{11}B NMR, and IR. The borazine derived from (1*S*, 2*R*)-norephedrine (dried under high vacuum at 45-50^{o} C for 3h) was successfully carried out by the reaction of norephedrine in diethyl ether with distilled trimethyl borate, followed by trimerization of the dimethoxy borate intermediate by gradually heating the mixture at 150 ^{o}C for 4 h under nitrogen. Analysis of the dimethoxy borate intermediate and the borazine product by ^{1}H, ^{13}C and ^{11}B NMR, and IR confirmed the structure of the desired compounds. Accordingly, we are now exploring new approaches to obtain other important borazines in a pure and facile way. The photophysical and conductivity properties of the synthetized pure polycyclic borazines are of great interest and will be studied in the future.

P-3: **Synthesis and Characterization of the Borazine derived from 2-Aminophenol and Triisopropylborate**, Jonathan Ramos Agosto, Melvin De Jesús-Flores & Margarita Ortiz-Marciales, UPR-Humacao



Borazines are compounds with six-membered ring structure of alternating boron and nitrogen atoms. The multi-functionality and thermal stability properties of these compounds made them useful as semiconducting materials. The borazine derived from o-aminophenol was prepared by the reaction with BH_3-DMS and BH_3-THF by our previous methodology. Then, due to the explosive danger of these reagents, we have been exploring new methods for the synthesis of borazines using triisopropylborate under a variety of conditions. The desired crude borazine was obtained, although with some impurities. After attempted purification, the compound was characterized by IR and NMR spectroscopic methods. We will continue improving these method to obtain a practical synthesis of this and other borazines in a pure form. Using novel chemistry and environmentally benign boron compounds, these borazine will offer possible applications and inventions of advanced functional materials.

P-4: **p-n Junction Diodes Fabricated using Poly(3-hexythiophen-2,5-dyil) (P3HT) Thin Films and Nanofibers**, Shamir Maldonado-Rivera & Nicholas J. Pinto, UPR-Humacao.

Poly (3-hexylthiophene-2,5-dyil) (P3HT) is a p-type semiconducting polymer which is commonly used in electronic devices. A p-n junction diode is an essential electronic device in all power supplies used to charge cellular telephones. Using a n-doped silicon substrate together with thin films or nanofibers of P3HT, we have fabricated and characterized p-n junction diodes. P3HT thin films were prepared via drop casting a 2 wt % P3HT solution in chloroform, while P3HT nanofibers were fabricated using the electrospinning technique. The diodes were electrically characterized in air and in vacuum, with and without ultraviolet (UV) exposure. The diodes fabricated using thin films had a higher rectification ratio and lower turn on voltage compared to those fabricated using nanofibers. Exposure to UV resulted in a higher rectification ratio, and the changes were not reversible. The thin film diode was successfully tested as a half wave rectifier, and the rectification efficiency was 14%. The diodes fabricated therefore have the potential to be used as a rectifier and a UV sensor, rendering it multifunctional.

P-5: Electro-spun PEDOT-PSS nano-ribbon transistor using ion-gel gate dielectric, Deliris Ortiz & Nicholas J. Pinto, UPR-Humacao

Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) PEDOT:PSS is a p-doped conducting polymer. Using the electrospinning technique, we have fabricated nano-ribbons of this polymer and deposited them on pre-patterned doped Si/SiO_2 wafers. Using the doped Si substrate as the back gate electrode and the SiO_2 as the dielectric insulator, the ribbon was characterized in a 3-terminal transistor configuration. No change in the channel current was observed for back gate bias under these conditions. We also used an ion-gel gate dielectric by placing a drop of the ion-gel over the ribbon and inserting a Au wire into the drop. By applying a bias to this contact (top gate), we were able to modulate the current through the ribbon at low voltages. The device operated like a field effect/electrochemical transistor, characteristic of a p-doped semiconductor with an on/off ratio of 730, threshold voltage of 0.8V, mobility of 5.5 cm^2/V-s, and a zero gate bias conductivity of 4 S/cm. The large specific capacitance of the ion-gel (as compared to SiO_2) and the formation of an electric double layer at the semiconductor/ion-gel interface was responsible for its operation below 2V. The device was also successfully tested at 100Hz making it useful in low frequency applications.

P-6: Green Preparation of Graphene Oxide and Carbon Nanospheres for Gas Sensing Applications, José L. Pérez-Gordillo[1], Ahmad Matar[2], Anamaris Meléndez[2], Nicholas Pinto[2] & Idalia Ramos[2], [1]Petra Mercado High School, [2]UPR-Humacao

Reduced Graphene Oxide (r-GO) thin films and Carbon nanospheres (CNS) are important for electronic, energy storage, environmental and medical applications. Both r-GO and CNS have been prepared by hydrothermal carbonization of sucrose and subsequent reduction by thermal annealing. This method of preparation is greener, simpler and more economical than conventional ones such as Hummer's method. The materials are electrically conductive and respond to the presence and removal of methanol (CH_3OH), ethanol (C_2H_6O), and 1-Propanol (C_3H_8O) gas. For both materials, the sensitivity of the sensors decreases when the size of the alcohol molecules increases. The CNS sensor shows higher sensitivities that the r-GO and the potential to discriminate between alcohol molecules.

P-7: Temperature-dependent charge transport in carbon-based polymer composites, Cesar A Nieves-Sanabria, Luis M. Martínez, Anamaris Meléndez, Margarita Ortiz, Idalia Ramos, & Nicholas Pinto, UPR-Humacao

Carbon spheres (CS) were prepared via hydrothermal method using an aqueous solution of sucrose and heated at 400°C. The spheres were thermally annealed in N_2 at 800°C to eliminate functional groups on the surface of the CS. Annealing increases the carbon content and decreases the oxygen content and leads to an increase in conductivity. Electron transport as function of temperature was studied using an insulating (polyethylene oxide-PEO) and a conducting (polyaniline-PANiES) polymer. A conductivity maxima was observed in the CS/PEO composite but was absent in the CS/PANiES composite. While tunneling and thermal activation are responsible for electron transport in CS/PEO, variable range hopping is a more appropriate mechanism in CS/PANiES composites.

P-8: Preparation of carbon foams from sucrose, Orlando Carromero, Anamaris Meléndez & Idalia Ramos, UPR-Humacao

Low-density carbon foams were prepared by hydrothermal carbonization of a sucrose solution in DI water, and subsequent annealing in a nitrogen atmosphere. The foams are free standing and can be cut into different shapes. Scanning Electron Microscopy (SEM) analysis shows the formation of foams composed of interconnected carbon micro-spheres with average diameters of 2.3 micro-m. Electrical characterization shows that the foams are highly conductive. We will also present results of foams prepared by adding naphtalene to the sucrose solution. Future work includes measuring the electrochemical performance of the carbon foams and their applications in supercapacitors.

P-9: The study of the oligomerization process of IAPP in presence of modified Gallium nanoparticles, Ambar S. Delgado-Carrión & Rolando Oyola, UPR-Humacao

Islet Amyloid Polypeptide (IAPP) also known as Amylin, is a peptide naturally made and co-secreted with insulin from the pancreatic beta cell of the human body. As a normal function, IAPP can control the activity of other peptides and it also helps with the sugar level regulation. When the misfolding of IAPP takes place, insoluble fibril aggregates that are toxic to the pancreatic beta cells form, and induce a decline on the insulin secretion (diabetes type 2). One of the many possible pathways to decrease the IAPP oligomeric formation, is the use of beta-sheet inhibitors. The major goal of this study is to test if using gallium nitride nanoparticles (GaNP) and two surfaces-modified derivatives (hydroxyl and carboxylate) can modulate or affect the kinetic and size formation of the amylin oligomerization. To fulfill this goal, we use several experimental techniques including fluorescence and UV-Vis. The results for the oligomerization process of IAPP show a typical nucleation process, sigmoidal response. However, we notice that increasing the concentration of GaNP does not change the lag phase delay but lowers the maximum fluorescence intensity of the sigmoidal response. For future work, several spectroscopic techniques will be performed to analyze the morphology of the amylin oligomers in solution.

P-10: Protein/ Peptide Interactions with Gold Nanoparticles, Lilliana I Ortiz- Rodriguez, Ambar Delgado & Rolando Oyola, UPR-Humacao

The interaction of gold nanoparticles with proteins has been a topic of interest to the biophysics community in the last few years. It is well known that corona formation is the major structural motif upon interaction of HSA with gold nanoparticles. Also, it has been shown, that the single tryptophan in HSA transfers energy to the gold nanoclusters. In an attempt to better understand protein/ nanoparticle interaction, modified gold nanoparticles were synthetized using beta-cyclodextrin (AuBCD) and 2-hydroxypropil-beta-cyclodextrin (AuHPCD) as capping agents. In order to fulfill this purpose, Trp fluorescence was used as a probe of protein/nanoparticle interactions. Both, HPCD and BCD molecules have hydrophobic center to which the hydrophobic sites in HSA can bind and induce conformational changes. The intensity of the fluorescence emission of the single Trp in HSA decreases as the concentration of the modified gold nanoparticles increases. Additionally, potassium iodide (KI) was used as a quencher at different temperatures. The data suggests that in presence of the modified gold nanoparticles the HSA has one conformation, but when KI is added, conformational changes occur. Further studies are required to better understand and characterize the accompanying conformational changes in the HSA/AuCDs complex assumed by these preliminary results of the interaction of the AuCDs nanoparticles and the KI.

P-11: Laser scanning confocal microscope as a tool for ligand density and protein binding estimation in affinity membranes, Junellie L. Cruz-Lebrón[1], Sean Yeldell[2], José O. Sotero-Esteva[1], Vihba Bansal[3], Ivan Dmoshowski[2] & Ezio Fasoli[1], [1]UPR-Humacao, [2]PENN, [3]UPR-Cayey

Affinity membrane purification is an advantageous technique which allows separation of analytes through binding between an affinity ligand linked to a membranes and the target molecules. The quantitative analysis of the ligand density and protein binding using a laser scanning confocal microscope (LSCM), is pursued in this research. LSCM is an instrument of choice for imaging solid phases with a fluorescent probe. Affinity membranes for the purification of serine proteases family were prepared in the following way: Commercially available cellulose acetate membranes were regenerated and chemically modified with a 5-atom spacer arm, epichlorihydrin. The spacer arm was further functionalized with para-aminobenzamidine (pABA), an affinity ligand for serine proteases. In order to visualize and quantify protein binding and ligand density in modified affinity membrane by LSCM the membranes were dyed with Rhodamine B, (ex. 545nm, em. 580 nm) which allows the visualization of membrane structure and porosity. The affinity ligands (PABA) were fluorescently labeled by a chemical reaction with glyoxal and Fluorene-2-carboxaldehyde (ex 488 nm em 530 nm). *Substilisin carlsberg* from *Bacillus licheniformis*, was fluorescently labeled with Fluorescein isothiocyanate (ex. 480 em. 520 nm) and used as model protein to study protein binding on chemically modified affinity membranes. Different images using LSCM were taken on membrane carrying different ligand density, and protein concentration. Analysis of images was done using an algorithm which allows through pixel counting to determine: the degree of membrane functionalized with the affinity ligand and the amount of protein bound to the ligand.

P-12: Confocal Laser Scanning Microscopy Image Analysis Using Python and Matplotlib, Joshua Cruz-Cintrón[1] & José Sotero-Esteva[2], [1]Petra Mercado High School, [2]UPR-Humacao

Confocal laser scanning microscopy (CLSM) is used for the examination of fluorescent material samples. The focused point on the material is excited by a laser. In theory, the microscope's mechanism only absorbs light emitted from that focus point using a pinhole near the Photomultiplier (PMT) to filter it. However, when the laser is applied, areas outside the focus point still emit some low intensity light. This out-of-focus light is a problem for quantification and can lead to imprecise conclusions. The digital images could be analyzed through a programming script written in Python in order to produce intensity graphs for different layers of the image. The script can filter intensities using an adjustable threshold, the intensity threshold is raised until all out-of-focus light is removed. The script is used on a sequence of images taken from samples of cellulose membranes covered in 4-Aminobenzoic acid (pABA), both chemically treated to emit light. The membranes of cellulose act as a filter for the pABA and it is necessary to quantify the amount of coinciding cellulose and pABA to understand its effectiveness. The script separates the cellulose and pABA into two layers. Intensity is adjusted for each layer per image. Digital diagrams show which pixels of the image are above the threshold of each layer and combined. The combined layers are compared to the original image with the out-of-focus light. The result is an image that does not show out-of-focus light, a more precise quantification of the colocalization of the pABA and cellulose can be made.

P-13: Fluorescent assay for determination of ligand density in para aminobenzamidine affinity membranes

Christian J. Ortiz-Hernández[1], Adaliz Torres[2], Vibha Bansal[3] & Ezio Fasoli[1], [1]UPR-Humacao, [2]Petra Mercado High School, [3]UPR-Cayey

The purification of therapeutic proteins from complex mixtures such as cell culture broth is a challenging and expensive task due to the long time required and the high costs of chromatography purification systems. Affinity membrane-based purification represents a viable alternative and it is being pursued in this project. Cellulose Acetate membranes can be deacetylated and chemically modified with epichlorohydrin leading to the introduction of a 5-atoms long spacer arm (linker) on the membranes. The spacer arm end group can be further functionalized with para-aminobenzamidine (PABA), an affinity ligand selective for serine proteases. In previous works we demonstrated that the obtained affinity membranes are able to selectively bind and purify serine proteases such as Subtilisin Carlsberg and Urokinase type Plasminogen Activators. We also showed how ligand density is a critical parameter to account in the optimization of the purification process. In this project, we developed a fluorescent assay for the estimation of ligand density (PABA) on cellulose membrane surface. The fluorescent probe 2-aryl-4-arylidene-2-imidazolin-5–one was synthetized starting from benzamidine, glyoxal, and benzaldhyde, and charactherized by ^{1}HNMR. The fluorophore has a maxium exctication at 385 nm and and a maxium emission at 455 nm. In order to measure the ligand density of PABA on cellulose membranes a standard curve was obtained submerging unmodified cellulose membranes in solution containing increasing concentration of fluorescent probe. The obtained curve was used to measure the ligand density on the chemically modified membranes.

P-14: Effects of pore size on protein binding capacity of affinity membranes, Adriana N. Santiago-Ruiz[1], Christian Ortiz[2], Rolando Oyola[2] & Ezio Fasoli[2], Vibha Bansal[1], [1]UPR-Cayey, [2]UPR-Humacao

Membrane discs have emerged as an attractive alternatives to micro bead based chromatography columns. Pharmaceutical companies typically rely on traditional packed chromatography columns for downstream processing. But 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. Membrane based processes can eventually translate into time- and cost-effective tools. The goal of this project is thus to develop affinity membranes for protein capture from biological mixtures. To accomplish this, commercially available cellulose acetate membranes were chemically modified to allow them to specifically and selectively bind the protein of interest. The model protein chosen for these studies was *Subtilisin Carlsberg*, a serine protease. Using the model previously developed in our laboratory, a five-atom long spacer arm was attached to the regenerated cellulose membrane, followed by the linking of para-aminobenzamidine as the terminal group. The amidine group, in this case, will serve as the affinity ligand for the target protein. Preliminary studies showed a successful capture of the protein from a pure protein solution using these affinity membranes. As a second step, cellulose actetate membranes of different pore sizes were purchased (0.2 – 7.0 microns) and modified similarly with para-aminobenzamidine. An accurate quantification of the para-aminobenzamidine is needed to evaluate the protein binding capacity of the membranes. Glyoxal method based on the formation of a fluorescent derivative of para-aminobenzamidine was thus adapted and optimized for amidine quantification in solid phase on membrane surface. The fluorescent probe 2-aryl-4-arylidene-2-imidazolin-5–one was synthesized starting from benzamidine, glyoxal, and benzaldhyde, and characterized by ^{1}HNMR. The probe showed an absorbance maxima at 405 nm and an emission maxima at 450 nm in water. When adsorbed on cellulose membrane, the adsorption spectra shifted to 330 nm while the emission maxima stayed at 450 nm. With this method, the ligand (amidine) concentrations on membranes of different pore sizes (0.2, 0.45, 0.8, 1.2, and 3.0 μm) were determined to be in the range of 25-50 mM. No clear correlation was seen between the ligand concentration and pore size. Experiments are being performed now to determine the protein binding capacities of these membranes and understand the role of pore size in it. This study is important because pore sizes are known to be important determinants of the separation efficiency of membranes.

P-15: Characterization and analysis of bamboo cellulose nanocrystals,

Nicole Ramos-Solis, Carolyn Carradero & Josee Vedrine, UPR-Humacao

In this work, we extracted and characterized cellulose nanocrystals from Bambusa vulgaris Schrad. ex Wendl Bamboo, a type of Bamboo found in Puerto Rico. Bambusa vulgaris Schrad. ex Wendl is known as a common type of bamboo that can easily grow in tropical areas. To extract the CNCs we used a four-step process composed of alkaline, bleaching, hydrolysis and dialysis. The alkaline treatment is based on the addition of sodium hydroxide (NaOH) to remove cellulosic and non-cellulosic components inside the bamboo, leaving only the cellulose fibers. The bleaching treatment is to brighten microfibrilar structures. Additionally, hydrolysis is achieved using sulfuric acid (H_2SO_4) solution to remove the phenolic compounds and chromophoric molecules in lignin and to degrade hemicellulose & lignin components within bamboo fibers that will eventually release cellulose nanocrystals. In our final step, we collect the nanocrystals through dialysis and then lyophilized to obtain solid samples. For characterization we used XRD, AFM, IR and SEM/EDS analysis tools. We also performed Zeta Potential analysis to measure the magnitude of the electrostatic or charge repulsion/attraction between dispersed cellulose nanocrystal particles and used a Flow Coater System, and LB to align CNCs. We compare our results commercial soft-wood pulp CNCs, which verifies that our bamboo CNCs is pure cellulose. The LB demonstrated that CNCs can be aligned to create organized monolayer nanostructures on surface for specified nanoscale interactions with macromolecules.

P-16: Ligand mediated interaction between hard metal nanoparticles and cellulose polymer fibers, Jorge L. Berrios-Rivera & Víctor Pantojas, UPR-Cayey

In this research project, the interaction between metal nanoparticles and cellulose polymer fiber, mediated through a ligand is investigated. Cellulose acetate nanofibers were electrospun followed by deacetylation. The fibers were then treated with sodium chloroacetate to functionalize the surface with a sodium carbixymethyl ligand. The anionic cellulose fibers exposed to a $CoCl_2$ solution and a simple wet reduction using $NaBH_4$ as a reducing agent. SEM images of the nanocomposites confirmed changes in surface morphology of the functionalized cellulose nanofibers. The attachment of the Co metal was confirmed by SEM-EDS analysis. The weight percentage of metal in the nanocomposites was found to be 47.77wt% (lower magnification) and 10.89wt% (higher magnification) for the 0.1M solution, while the 0.05M solution showed weight percentages of 13.23wt% (lower magnification) and 16.53wt% (higher magnification). Based on these results, we believe that the metal has incorporated on the nanofibers in the form of nanoparticles. Future work will be focused on more throughout analysis to determine whether the metal was integrated as nanoparticles, as well as the optimization of metal loading on these cellulose nanofibers.

P-17: Study of nanoscale adhesion of different metal nanoparticles on the surface of cellulose nanocrystals, Milagros M. Rivera-Cruz & Víctor Pantojas, UPR-Cayey

The objective of this research project was to study the difference in adhesion forces between different metalic nanoparticles and the surface of a thin film composed of cellulose nanocrystals/glicerol by functionalizing the surface of the film with a sodium acetate ligand. Samples treated with copper and nickel salts were analyzed to obtain the amount of metal attached to the surface. The surface treatment included an organic synthesis procedure to deprotonate, protonate, heat and reduce with the objective of obtaining as a final product a coordinated metal bonded to the cellulose nanocrystal. Samples were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Our results indicate that the metals attached to the thin film surface. In some samples contamination was observed, which we think is due to inefficient or insufficient washing steps in the procedure. Process steps were corrected in order to eliminate contamination. Samples with copper metal showed less contamination. The amount of metal that adheres to the surface varies with position in the sample and with the concentration of the metallic salt solution used for the surface treatment. The thin film surface has a rough morphology as observed by SEM. Future studies will focus on the crystal structure of the cellulose nanocrystals thin films and how this affects the adherence of the metal through the surface.

P-18: Shearing of an Organic Polymer Film for Improved Solar Cell Devices, Luis A. Ortiz-Flores, Gabriel Calderón-Ortiz & Josee Vedrine-Pauleús, UPR-Humacao

Fabrication of large area solar cells on printable and flexible substrates using organic photovoltaic (OPV) devices is a developing field, and understanding their functional chemistry and nanoscale-engineered properties is coupled to increasing device efficiency. In our research work, we align the thin polymer film surface to study absorption and transmission properties that can enhance the nanoscale-engineered properties relevant to improving sunlight conversion efficiency. Our interest is to analyze the behavior of shear aligned polymers, such as P3HT fibrils within a network of PCBM matrix. We hypothesize that this cell fabrication process will facilitate the flow of current through the active layer to increase devices efficiency. We will use characterization tools such optical microscopy, AFM/SEM, UV-Vis, and XRD and spectroscopies to analyze basic thin film properties.

P-19: Purification, characterization and synthetic applications of an esterase from a moderately halophilic microorganism, Mahmoud Matar, Steven J. Toro, José Sánchez, Ángel Miranda Iris Flores & Ezio Fasoli, UPR-Humacao

The use of esterases in organic synthesis is of immense significance because of the low environmental impact of this methodology as well as the ability of these enzymes to catalyze synthesis of chiral alcohols, esters, and acids with high chemo-, regio-, and stereo-selectivity. Despite many enzyme-catalyzed reactions having been employed at industrial level, the complete shift from traditional chemical approach to more green biotechnological alternatives (biocatalysis) has been hampered by the instability of esterases when exposed to harsh conditions such as non-aqueous media or high temperature. In this project we studied a new esterase from a moderately halophilic microorganism isolated from the microbial mats in the salterns of Cabo Rojo, (PR). The enzyme was semi-purified from microbial cultures and studied for activity and stability under different experimental conditions (presence of organic solvents or ionic liquids, high temperature and extreme pH). Results show that the enzyme has an optimum activity at: pH 9.5, 45°C, 9% (w/v) NaCl and maintains its activity after 24 hours of incubation, in a broad range of organic solvent/water mixtures at different ratios (15%, 30% and 50% (v/v)). These results are in accordance with other studies in which the presence of organic solvents seems to stabilize the protein's folded structure by acting as salt mimicking agents in solvent/water mixture. We further studied the chemo-, regio-, and stereo- selectivity of the esterase towards several substrates of synthetic interest. Kinetic resolution of esters of secondary chiral alcohols with different chain lengths, steric hindrance, and electron acceptor/donor groups was evaluated using HPLC equipped with chiral columns. Moderate to high enantioselectivity was observed. This data suggests that the new esterase isolated from moderately halophilic microorganism has a good stability in a broad range of experimental conditions and can catalyze the hydrolysis of different chiral esters in an enantioselective manner.

P-20: Electrochemical Studies of Ferrocene Compounds, Francisco Velázquez-Alvarez, Jorge Castillo-Ramírez & Mirna Claudio-Rivera, UPR-Humacao

The cyclic voltammetry of ferrocene derivatives containing aldehyde, alcohol and other functional groups has been studied in acetonitrile with the supporting electrolyte TBATFB. The organometallic compounds have shown a one electron reversible process. In the future we will study their potential application as biosensors.

NOTES

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Cover and art design:
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