SYMPOSIUM BM02

Electronic and Coupled Transport in Biology
November 26 - November 28, 2018

Symposium Organizers
Caroline Ajo-Franklin, Lawrence Berkeley National Laboratory
Renata Bilewicz, University of Warsaw
David Cahen, Weizmann Institute of Science
Pau Gorostiza, Catalan Institution for Research and Advanced Studies

* Invited Paper

SESSION BM02.01: Biomolecules as Charge Transfer Media
Session Chairs: Andrew Abell and Caroline Ajo-Franklin
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Independence East

8:15 AM *BM02.01.01
Microstructuring and Characterization of Redox-Active Polydopamine Films Jing Lin, Dominik Blaimer, Sven Daboss and Christine Kranz; Ulm University, Ulm, Germany.

Polydopamine (PDA) a synthetic eumelanin polymer is highly interesting as thin film surface modification for a multitude of applications ranging from adhesive coatings for cell immobilization[1] to biomimetic electron gates for artificial photosynthesis[2]. The polymerization of dopamine can be obtained via a chemical process at basic pH values higher than 7.4[3]. Improved control of surface morphology can be achieved via electrochemical deposition e.g. by cyclic voltammetry, leading to thin films offering various functional groups such as amines, imines and phenolic groups at conductive surfaces.

In this contribution, we report the microstructured deposition of PDA using pulsed electrochemical deposition techniques, in order to improve film uniformity and thickness. To form microspots of PDA, scanning electrochemical microscopy in direct mode[4] was used with the substrate as working electrode and the microelectrode as the counter electrode. The electron tranfer properties of the microspots were investigated in dependence on the pulse number, the distance between substrate and microelectrode, the RG value (ratio of the radius of the insulating sheath and the electrode radius) of the microelectrode and the used redox mediator. As PDA has redox-active phenolic/quinone groups, surface properties of the polymer can be electrically switched. Our group recently introduced a new type of AFM-SECM probe bearing a conductive colloid[5]. Such conductive colloidal probes will be modified with polydopamine films and first results on force spectroscopy under potential control will also be presented.

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8:45 AM *BM02.01.02
Electron Transport in Nanoscale Junctions Incorporating Peptides and Peptidomimetics Slawomir Sek; Faculty of Chemistry, Biological & Chemical Research Centre, University of Warsaw, Warsaw, Poland.

Electron transport in proteins and peptides is crucial for energy conversion in biological processes including photosynthesis, respiration and enzymatic reactions. Therefore, the important goal of the fundamental research is to provide insight into the mechanisms determining peptide-mediated electron transport. Peptides are known to adopt variability of structural motifs and when suitably designed, they can also serve as components of biosensing devices or nanoscale bioelectronic circuits. In this area of research, significant progress has been made due to the development of experimental methods, which enable fabrication of nanoscale junctions with peptide monolayers bridging two conductive electrodes. Among them, scanning probe microscopy (SPM) offers unique capability to investigate electric properties of individual molecules or molecular films.[1] Such approach involves entrapment of the assemblies of molecules between two metallic contacts established by metal support and conductive probe of SPM. When the bias voltage is applied between the contacts, the resulting current flow depends on the properties and structural features of peptide molecules forming the assembly including their length, secondary structure, dipole moment, the nature of the constituent amino acids or charge. Importnantly, SPM-based method enables control of the mechanical strain or stress of the molecular film incorporated into the junction.[2]
Among variety of structural motifs, α-helical peptides were proved to be efficient mediators of electron transport. However, their use is limited to compounds containing at least 8 amino acid residues. To overcome this problem, we have designed molecular junctions utilizing α-helicomimetic foldamers based on oligourea backbone. These particular compounds possess important features: (a) it is possible to synthesize oligoureas containing side chains of all natural amino acids; (b) the folding process of oligomers is not affected by the nature of side chains. Such characteristics make them highly robust, tunable and hence useful in the studies of electron transport processes. Additionally, only four acyclic residues are sufficient to drive complete helical turn formation. We have demonstrated that oligoureas may act as efficient electron transport mediators and the oligourea helix is more stable than the helix formed by peptides. Interestingly, electron transmission through longer analogs shows strong directional dependence, which is characteristic for diode-like behavior.

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9:15 AM BM02.01.03
Controlling the Mechanism of Charge Transport via Au-Azurin Junctions by Chemically Modulating Protein-Electrode Interactions Jerry A. Fereiro, Gilad Porat, Mudi Sheves, Israel Pecht and David Cahen; Weizmann Institute of Science, Rehovot, Israel.

A tremendous effort has been made by researchers to explore the possibility of using biomolecules, including proteins, in molecular electronics. The idea is to exploit their built-in functionalities, introduced by millions of years of evolution, for the task of electron transport However, despite great progress that was made, fundamental questions regarding the effects of relative energies, of the contacts and protein-contact coupling, as well as the nature of the internal electrostatic potential profiles are remain unclear.

We will report on the results, obtained from a systematic study of conductance, current-voltage plots and IETS measurements at low temperatures to investigate the mechanism of charge transport via different Az-Au-Az junction configurations. In all the configurations that were studied Az was covalently bound to a Au substrate on one side and chemical modifications were carried out with linker molecules to the contact that was made on the opposite side of the protein. The conductance and IETS profiles obtained from different configuration strongly suggest that by chemically fine-tuning the coupling strength to the electrodes, we can switch the tunneling mechanism ‘IN’ and ‘OUT’ of resonance. The shape of the conductance plots, intensity of the IETS spectrum and the barrier height ( ) values, obtained from fitting the I-V curves, provide the position of the frontier energy levels with respect to the electrode Fermi level, indicating that the energy levels are pushed apart upon increased coupling (fits simple MO /tight binding models). This shows that the energy-level alignment in Az-based junctions can be regulated by chemical modifications of the electrical contact to the protein. The results presented here provide a strategy suitable for altering the transport mechanism through solid state protein monolayers, by chemically modifying the interaction between the protein and the linker in protein based two-terminal device, i.e., without a gate electrode.

9:30 AM BM02.01.04
Electron Transport Through Linear Peptide Cunlan Guo; College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China.

Biomolecules display great potential for future functional molecular electronic devices, due to biomolecules’ unexpected conductance, multiple structure, unique bio-recognition and self-assembly. Peptides are suitable as one of the building blocks to bridge conductive electrodes in solid state electronic devices. To design and apply peptide junctions for solid state devices, the relations of peptide electron transport to their amino acid composition and structure need to be understood as well as the peptide electronic structures on the electrode surface. Such information may also help understanding the electron transfer processes that occur in/with proteins in biological energy conversion, sensing and signaling systems. Here, we take linear peptides as the model and construct series peptide junctions on the solid state. Combining theory and calculations, we studied the controlled ways to modulate the electrical properties of peptide junctions which display a versatile, readily available tool for future (bio)electronic applications.
Acknowledgments: The author thanks all the kind helps from the collaborators.

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9:45 AM BM02.01.05
Discovering the Structural Factors Governing Proton Transport in Self-Assembled Peptide Fibers Ohad Silberbush[1], Subhasish Roy[1] and Nurit Ashkenasy[1, 2]; [1]Ben Gurion University in the Negev, Beer Sheva, Israel; [2]Ilse Katz Institute for Nanoscale Science & Technology, Beer Sheva, Israel.

The ability to de-novo design peptides (short proteins segments) to self-assemble into functional structures has attracted an extensive attention in recent years, especially towards their implementation in biomedical and biotechnological applications. Many of the self-assembling peptide sequences include charged amino acids, making the resulting nanostructures amenable to proton conduction. Motivated by the opportunity to employ this phenomena in novel bioelectronic applications, the aim of the work I will present was to discover the structural factors that govern proton transport processes in these biomimetic structures. I will demonstrate that proton transport is enhanced significantly by the introduction of even a single charged amino acid into the sequence of a hepta-peptide that self-assembled into fibrils.[1] Moreover, I will show that acidic residues are more effective than basic ones in promoting proton-conduction of the peptide fibrils due to two orders of magnitude larger doping effect, and a threefold higher charge carrier mobility value. I will further demonstrate that both structural motif of the monomeric peptides and the secondary assembling structure have a critical impact on proton conductance of their assemblies. I will show that assemblies originating from helical structures exhibit higher conductivity than assemblies of β-sheet forming peptides with a similar sequence. Nanotube forming D, L α cyclic peptides with β-sheet structure, however, demonstrated superior conductivity to both linear assemblies. The amount of charge carriers' density was found to be structural independent and that peptide molecule configuration and self-assembled structure influence proton mobility. Finally, I will demonstrate that acidic molecules can be used for external doping of the peptides assemblies.

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10:00 AM BREAK

10:30 AM *BM02.01.06
Mechanisms of Charge Transport and Large Tunnel Magnetoresistance Across Ferritin-Based Molecular Junctions Christian A. Nijhuis; National Univ of Singapore, Singapore, Singapore.

Electron transport (ET) is important in countless biological processes including enzymatic catalysis or photosynthesis. The efficiencies of ET over long distances in biological systems can be remarkably high. Unraveling the underlying mechanisms governing long range ET across such systems is not only interesting from a fundamental point of view, but could also lead to interesting technological applications in biomolecule-based sensors or biomolecular electronics. We study ET across biomolecular junctions of ferritin which is a cage-like iron storing protein consisting of 24 subunits with an outer diameter

of 12 nm and inner diameter of 8 nm. We found that the ET mechanism is independent of the temperature when the ferritin is loaded with iron, but temperature independent when no iron is present. Junctions formed with Ni bottom-electrodes and ferritin monolayers show a tunneling magnetoresistance of 30% at room temperature. Finally, I will also discuss ET in the inverted Marcus region observed across molecular diodes; this ET mechanism may be also relevant to biological systems.

11:00 AM BM02.01.07
Large-Scale Conformational Changes Induce Tunable Electronic and Mechanical Functionality in Proteins Sibel Ebru Yalcin[1], J. Patrick O'Brien[1], Atanu Acharya[2], Yangqi Gu[3], Winston Huynh[4], Sophia M. Yi[1], Subhajyoti Chaudhuri[2], Victor Batista[2] and Nikhil S. Malvankar[1]; [1]Molecular Biophysics and Biochemistry, Yale University, New Haven, Connecticut, United States; [2]Chemistry, Yale University, New Haven, Connecticut, United States; [3]Molecular, Cellular and Developmental Biology, Yale University, New Haven, Connecticut, United States; [4]Biomedical Engineering, Yale University, New Haven, Connecticut, United States.

The ability to understand and modulate charge transport in molecules is of central importance in many basic chemical and biological processes and for the development of electronic devices. This charge transport sensitively depends on molecular conformations. Large-scale conformational changes are particularly attractive because they can serve as information carriers for switches in memory and logic devices. However, conformations affecting conductivity were previously found to remain local and < 2 Å, thus yielding at most a 10-fold change. Here we report the ability to control molecular conductivity via conformational switching at an unprecedented scale.

Although biomolecules are considered electronic insulators, *Geobacter sulfurreducens* pili protein filaments show metal-like conductivity [Malvankar et al. *Nature Nano* **6**, 573 (2011)]. However, very little is known about how to manipulate the conformation of pili in order to controllably switch conductivity. Lack of solved structures for pili, previous assumptions of homology-based models of pili filaments, and the common perception that proteins are electronic non-conductors have led to great scepticism about conductivity in these biomaterials.

To overcome these hurdles, here we directly visualize the structure of individual pili using infrared nanospectroscopy. This imaging platform has empowered us to engineer conformational changes that facilitate π-stacking of aromatic rings, enhancing both pili conductivity and stiffness. This controlled conformational change constitutes a unique combination of tunable electronic and mechanical properties in pili.

Atomic force microscopy showed that individual *Geobacter sulfurreducens* pili protein filaments undergo > 20 Å conformational change that propagates over micrometer-lengths of pili upon changing the environment or amino acid composition of pili. Infrared nanospectroscopy revealed that this conformational change is driven by an internal structural transition in pili. A suite of complementary experimental and computational methods such as X-ray diffraction, raman, fluorescence emission spectroscopy and circular dichroism further demonstrated this structural transition in pili. Molecular dynamics simulations confirmed that conformational change in pili leads to improved stacking of aromatic residues to enhance their conductivity and stiffness. Our studies thus establish nanoscopic approaches to visualize and quantify large-scale conformational changes in biomolecules and present novel strategies for tuning their structure and conductivity. The demonstrated conformation-induced conductance switching in proteins will guide the creation of a new class of programmable biomaterials with precisely controlled electronic and mechanical properties. Such tunable biomaterials will aid in the development of seamless, bidirectional interfaces between biology and electronics to transduce mechanical and chemical stimuli into electrical signals.

11:15 AM BM02.01.08
Proton Conductivity in a Thin Film of Self-Assembled Peptides Takuma Narimatsu and Yuhei Hayamizu; Tokyo Institute of Technology, Ota-ku, Japan.

Developments of bio-inspired materials have shown a remarkable progress due to their biocompatibility and environmentally-friendly functions. Proton conductivity is a one of the keys in biological function. Learning from natural proteins which have high proton conductivity, researchers have recently demonstrated high proton conductive bio-materials, such as natural protein and polysacchalide. Peptides are another candidate to promote the development of biomaterials with high proton conductivity. Due to its short amino acid sequence, we can design and synthesize arbitrary peptide sequence. The self-assembly of peptides has been intensively investigated and there are variety of peptides known to spontaneously form fibrils in solutions.
In this work, we design a series of peptides which contains simple amino acid sequence to investigate the proton conductivity of their thin films on a silicon wafer. Using a drop-casting method, we formd thin film of peptides on Si-wafers, and characterized the conductivity by electrochemical impedance spectroscopy. We found that these peptide thin film shows an over 5 mS cm^{-1} of conductivity at room temperature., and this value is higher than those of proteins reported so far. Moreovver, the conductivity depend on amino-acid residues as well as its crystallinity. This result indicates that proton conductivity could be designed by the peptide sequence.

11:30 AM BM02.01.09
Energy Transport in RNA—Fundamental Design Principles and Applications for Sensors Juan M. Artes Vivancos[2, 1], Yuanhui Li[1] and Josh Hihath[1]; [1]ECE, UC Davis, Davis, California, United States; [2]Chemistry, UMass Lowell, Lowell, Massachusetts, United States.

Energy transport is a critical process in biology, being crucial in respiration and photosynthesis.(1) Different biomolecules have evolved to be exquisitely tuned to transfer and transport energy (including excitons and charges) with astonishing efficiency. Recent literature shows multiple examples of this natural design in different biomolecules, including proteins and nucleic acids.(2) As a recent example, I will present recent results we obtained studying charge transport in nucleic acids, including DNA:RNA hybrid sequences from E. Coli.(3)

The continued discovery of new RNA modalities (non-coding, micro, enhancer, etc.) has resulted in an increased desire for detecting, sequencing, and identifying RNA segments for a variety of applications in food safety, water and environmental protection, plant and animal pathology, clinical diagnosis and research, and bio-security.

We have recently demonstrated that molecular conformation profoundly influences the conductance of nucleic acids(4) and that RNA can support long-range charge transport in specific sequences(5,6). We show that single-molecule conductance techniques can be used to extract biologically relevant information from short RNA oligonucleotides and that these measurements are sensitive to aM target concentrations, are capable of being multiplexed, and can detect targets of interest in the presence of other, possibly interfering RNA sequences.(3) We also demonstrate that the charge transport properties of RNA:DNA hybrids are sensitive to single-nucleotide polymorphisms, thus enabling differentiation between specific serotypes of Escherichia coli. Using a combination of spectroscopic and computational approaches, we determine that the conductance sensitivity primarily arises from changes the mutations have on the conformational structure of the molecules, rather than the direct chemical substitutions. This work is the first molecular conductance study of a biologically relevant sequence and opens new possibilities for developing electrically-based sensor and diagnostic platforms.

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11:45 AM BM02.01.10
Peptide Folding Influence on Electronic Properties of Bioinspired Peptide Based Materials Nurit Ashkenasy; Ben Gurion University of the Negev, Beer Sheva, Israel.

The three dimensional structure of proteins has a critical role in determining their functional behaviour in nature. As a result, proteins' misfolding is directly associated with different illnesses. The capture of these structure function relationships in self-assembled peptide nanostructures can provide a flexible handle to control their function. In this presentation, I will demonstrate the manipulation of the properties of bioelectronic materials and hybrids by the modulation of the folding of their peptidic monomeric units.
I will first demonstrate the influence of subtle changes to the peptide backbone on the electronic properties of semiconductor surfaces on which they assemble.[1] In this study, the electronic properties of GaAs functionalized with dipeptides with the same sequence (Val-Tyr) but different backbone registry were characterized. Changes both to the electron affinity and the surface potential will be demonstrated, with the magnitude of which depends on the backbone registry. In the second example I will present, specifically designed self-assembling peptides bearing natural, as well as non-natural side chains, that promote electron conduction have been used. I will demonstrate that the self-assembly medium can be used to control the specific interactions deriving the self-assembly. These interactions, as a result, influence the resulting peptide nanostructure morphology and conductivity.[2, 3] All together these examples demonstrate an exceptional flexibility in controlling the properties of peptide based bioelectronic materials.

References
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SESSION BM02.02: Electronic Interfaces
Session Chairs: Nurit Ashkenasy and Ryan Chiechi
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Independence East

1:45 PM BM02.02.01
Proton-Coupled Electron Transfer—Artificial Photosynthesis and Photoreduced Nanoparticles Sharon Hammes-Schiffer and Zachary Goldsmith; Yale University, New Haven, Connecticut, United States.

Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of energy conversion processes. This talk will focus on recent advances in the theory of PCET and applications to artificial photosynthesis and photoreduced nanoparticles. The quantum mechanical effects of the active electrons and transferring proton(s), as well as the motions of the proton donor-acceptor mode and solvent or protein environment, are included in a general theoretical formulation. This formulation enables the calculation of rate constants and kinetic isotope effects (KIEs) for comparison to experiment. A combined experimental and theoretical study of a series of substituted benzimidazole-phenol model systems inspired by the Tyr-His redox proton relay found in photosystem II provides insight into the physical principles underlying proton relays. Theory predicted a concerted two-proton transfer process associated with the electrochemical oxidation of the phenol, accompanied by a decrease in the redox potential of the phenol and a small KIE, when the benzimidazole substituents are strong proton acceptors such as primary or tertiary amines. Subsequent electrochemical, spectroelectrochemical, and KIE experiments were consistent with these predictions. More recent efforts to design a concerted three-proton transfer process associated with oxidation have also been successful. These bioinspired molecular systems demonstrate the potential use of multi-proton relays to enable the transport of protons over longer distances along specified pathways, as well as the tuning of redox potentials through this movement of positive charge. In a different direction, experiments have shown that photoreduced ZnO nanocrystals react by PCET with organic hydrogen atom acceptors such as the nitroxyl radical TEMPO. The application of PCET theory to these systems indicates that the electron transfers from the conduction band of the ZnO nanocrystal to TEMPO concertedly with proton transfer from a surface oxygen of the ZnO nanocrystal to the oxygen of TEMPO. Moreover, proton diffusion from inside the nanocrystal to reactive sites on the surface was found to explain the experimentally observed nonexponential kinetics. These applications illustrate the significant role of theory in the design of both molecular and heterogeneous catalysts to control the movement and coupling of electrons and protons.

2:00 PM *BM02.02.02
Bioelectronic Control of pH and Applications Marco Rolandi; Department of Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California, United States.

The concentration of H+ measured by pH plays an important role in many biological processes including energy conversion in mitochondria and archaea, enzymatic activity, and neuronal excitability. Using Pd/PdHx as a transducer between electronic and H+ currents we have created bioelectronic devices that are able to control H+ concentration in solution and modulate pH at different biologically relevant levels. Here, I will present recent results on how we can use this pH modulation to control enzymatic activity in bioluminescence, targeted drug delivery, and cellular function during proliferation and growth.

2:30 PM BM02.02.03
Conjugated Polymer Nanoparticles as Versatile Bioimaging Probes Anitha Ethirajan[1, 2]; [1]Hasselt University, Institute for Materials Research, Hasselt, Belgium; [2]imec Associated lab IMOMEC, Diepenbeek, Belgium.

Conjugated polymers have been extensively studied for their opto-electronic properties in the field of organic electronics. In the recent years, they have emerged as promising class of materials for bioimaging owing to their excellent optical properties. Moreover, new synthesis procedures have enabled custom-built functional conjugated polymers that facilitate the one-pot synthesis of semiconducting polymer nanoparticles (NPs) with tunable properties and interesting functionalities for use in biomedical applications.[1-4] The possibility to formulate hydrophobic conjugated polymers as water-based nanoparticle dispersions allows for the employment of these versatile materials in biological systems. In this contribution, the potential of intersting class of conjugated polymer nanoparticles (CNPs) for bioimaging will be addressed. Additionally, poly(p-phenylene vinylene) (PPV)-derivative based CNPs will be focussed due to their interesting optical properties, design flexibility for surface functionalization, and benign biological characteristics.

PEGylation strategy has been widely used for surface functionalization of nanoparticles for imparting stealth effects. In this study more profound insight into the various ways in which PEG, with different chain lengths, can affect this particular type of bioimaging probe will be highlighted.[3] Subsequently, the consequences of PEGylation on the colloidal, optical and biological characteristics uisng cell populations within the central nervous system of the bioimaging probe will be shown.

Alongside surface functionality, NP size is one of the most critical concerns for biomedical applications as it has been identified to play a key role in biological processes like cellular uptake, biodistribution and cytotoxicity. Effective internalization by cells is essential to achieve the successful application of NPs for bioimaging objectives. In addition, adjusting the size can have an influence on the optical properties of conjugated polymer NPs. In here, the potential consequences of lowering the size of functional PPV-based NPs on the optical and biological characteristics of a conjugated system specifically designed for bioimaging purposes will be shown.[4]

The obtained results valorize the potential of conjugated polymers in biomedical applications and open bright prospectives as well as unexplored pathways for these materials.

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2:45 PM BM02.02.04
Magneto-Mechanical Forces Coupled Nanostraw Electroporation System for Enhanced Intracellular Delivery During Cancer Immunotherapy Andy Kah Ping Tay and Nicholas A. Melosh; Stanford, Menlo Park, California, United States.

According to the American Cancer Society, 1.8 million new cases of cancer are expected in 2018. Despite better treatments, mortality rates of cancer like melanoma remain high. Chimeric Antigen Receptor (CAR)-T cell, with on-going clinical trials, offers a promising strategy to engineer immune T cells that recognize and kill cancer cells. Unfortunately, it is difficult to deliver genes and integrate them into the genome of T cells (~10% efficiency) for effective cancer immunotherapy.

Here, we describe a technique where we integrated magneto-mechanical modulation of cell deformability and intracellular cargo trafficking with magnetic nanoparticles (MNPs) during nanostraw electroporation (NE) to boost the transfection efficiency of Jurkat cells, a model cell line of T cells, from 12.8% to 48.0%. This method created minimal cellular stresses, as measured with intracellular calcium levels and RNAseq data, compared to other transfection techniques, leading to 2-3 folds shorter waiting time to generate high cell numbers (10^9) for therapies.

We first compared the efficiencies to deliver a fluorescent protein plasmid with viruses (lentiviruses with Ubiquitin or EF1-α promoters), biochemical polymers (Fugene, Lipofectamine), bulk electroporation (Biorad Gene Pulser, Lonza Nucleofector) and NE System (NES), and found similar efficiencies, about 10-20%, for Jurkat cells.

It was shown that biomechanical forces enhanced transfection in adherent cells. To test if this holds true for non-adherent Jurkat cells, we utilized FDA-approved starch-coated magnetic nanoparticles (MNPs) with cyto-protective effects to generate magneto-mechanical forces. Starch-coated MNPs were biocompatible, and were membrane-bound and internalized after 24 hrs of incubation.

We applied static magneto-mechanical forces to the Jurkat cells during NE and found that this boosted the transfection efficiency from 12% to 30% due to a decrease in physical distance between NES and Jurkat cells which minimized the loss of plasmid cargo.

After NE, we applied low frequency (to avoid generating heat) alternating magneto-mechanical forces through internalized MNPs to perturb the cytoskeletal network connected to the nuclear envelope. This increased intracellular cargo trafficking and opening probability of the nuclear pore complexes to enhance cargo entry into the nuclei. This modulation step further increased the transfection efficiency from 30% to 48%.

Next, by monitoring calcium stress signals and RNAseq, we found that across all the different transfection methods, NES with magneto-mechanical modulation resulted in minimal cellular stresses and treatment did not significantly lengthen cell doubling time unlike other techniques. Actin pertubation also promoted membrane resealing after electroporation.

As FDA has approved T cell isolation using magnetic beads like we did, we plan to next apply the concept of magneto-mechanical modulation to enhance T cell transfection efficiency for cancer immunotherapy.

3:00 PM BREAK

3:30 PM *BM02.02.05
Charge and Spin Transport Through Biomolecules on Electrodes David Waldeck; Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

We describe recent experiments on charge transport through peptides and through nucleic acids on electrodes. Both single-molecule molecular junction experiments and molecular monolayers on electrode surfaces are used to investigate how the charge and spin transport through molecules is affected by the

molecular properties.

4:00 PM BM02.02.06
Mitochondrial ATP Synthesis Controlled by Protonic Biotransducer Ziyi Zhand[1], Yoshihiro Ohta[2] and Takeo Miyake[1]; [1]Waseda University, Kitakyushu, Japan; [2] Tokyo University of Agriculture and Technology, Tokyo, Japan.

In nature, protons (H^+) play an important role in biological activities such as in mitochondrial ATP synthesis, which is driven by a H^+ gradient across the mitochondrial cell inner membrane, or in the activation of acid sensing ion channels in neuron cells. Bioprotonic devices directly interface with the H+ concentration (pH) to facilitate engineered interactions with these biochemical processes. Here we develop a H^+ biotransducer that changes the pH in a mitochondrial matrix the solution around mitochondria by controlling the flow of H^+ between a conductive polymer of sulfonated polyaniline and solution. We have successfully modulated the rate of ATP synthesis in mitochondria by altering the solution pH. Our H^+ biotransducer provides a new way to monitor and modulate pH dependent biological functions at the interface between the electronic devices and biological materials.

4:15 PM BM02.02.07
Enhancing Microbial Fuel Cell Power Density by Manipulating *E. coli*-Gold Interactions Through Gold-Binding Peptide Expression Justin Jahnke, Deborah Sarkes, Jessica Terrell, James Sumner and Dimitra Stratis-Cullum; US Army Research Laboratory, Adelphi, Maryland, United States.

Understanding the role of microorganism-surface interactions in charge transfer between microorganisms and electrodes remains a challenging bioelectronic problem. One approach to controlling microorganism-surface interactions is to incorporate short amino acid chains (peptides) with variable material affinity, which can be engineered into the protein sequences of outer-membrane proteins, fimbriae and other microorganism structures for extracellular presentation. Here we show that this approach to controlled surface affinity can be used to manipulate and enhance electrical power production in a typical bioelectrochemical system, a microbial fuel cell (MFC). Gold-binding motifs of various affinity were introduced into two scaffolds in *Escherichia coli*: FimH, the fimbria's tip protein, and eCPX, a modified version of outer membrane protein X (OmpX). A clear correlation is shown between the peak voltage produced during MFC operation and the affinity of a strain for a gold surface, with *E. coli* strains with high affinity to gold exhibiting up to 10 times increased power production over control strains lacking displayed peptides. The display location (e.g., coat protein vs fimbriae) affects the MFC behavior, as do changes in the peptide chemical structure. The potential extensions of this work to other biolelectrochemical devices and particular charge transfer systems will be discussed.

4:30 PM BM02.02.08
Molecularly-Precise Control of Charge Flow at the Abiotic/Biotic Interface Between Microorganisms and Nanomaterials Caroline Ajo-Franklin and Heinz Frei; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

By electrochemically coupling microbial cells with abiotic catalysts, bioelectrochemical systems can combine the distinct capabilities of living systems and non-living systems to enable bioelectronic sensing, synthesis, and gene regulation. However, the chimeric nature of these bioelectrochemical systems also poses a major scientific challenge; the pairing of microbial cells and material must avoid chemical incompatibility, i.e. toxicity, corrosion, fouling, while optimizing abiotic/biotic charge transfer. Here I describe a new approach to overcome this core challenge by demonstrating electronic coupling of a microorganism with abiotic inorganic material on the shortest possible length scale – nanometers – while chemically separating the incompatible reaction environments. We electrochemically coupled a SnO2 anode, with a microbial catalyst, Shewanella oneidensis, via a novel 2 nm-thick silica membrane with -CN and -NO2 functionalized p-oligo(phenylene vinylene) embedded molecular wires. This membrane enables electron flow at a current density from microbial catalysts to the inorganic anode, while blocking small molecule transport between oxidative and reductive environments. Thus, this new modular architecture provides a strategy to avoid chemical incompatibilities without ohmic losses and introduces a means to decouple chemical compatibility and charge transfer in bioelectrochemical systems.

4:45 PM BM02.02.09
Electronic Control of Stomata with Delivery of an Anionic Phyto-Hormone in Planta Using an Organic Electrophoretic Device Iwona Bernacka-Wojcik, Miriam Huerta, Tobias Abrahamsson, Roger Gabrielsson, Magnus Berggren, Daniel Simon and Eleni Stavrinidou; Linkoping University, Norrkoping, Sweden.

Plants comprise our primary source of food, but are also a source of oxygen, renewable energy, materials, medicines and regulators of the ecosystem. Stomata, the microscopic pores in the leaves of plants are fundamental to the plant function as they control the photosynthesis and transpiration rate. When the stomata are open the plant can exchange gasses with the environment and allow the water evaporation enabling photosynthesis and transpiration. Abscisic acid, ABA, also known as the stress hormone, plays an essential role in the signaling mechanism that triggers the stomata closure. Here we report for the first time the use of a bioelectronics device for electronic control of stomata in intact plants. The organic electronic ion pump is an electrophoretic device that allows precise delivery of ions and charged biomolecules with high spatiotemporal resolution. This device has been mainly applied in mammalian systems for therapy. For the delivery of the phyto-hormone ABA we used a new generation of the ion pump that is based on glass capillary and has an overall diameter of 60um. The small diameter of the pump allows easy insertion in leaves of intact plants through the epidermis into the internal area of the leaf. We demonstrated that the stomata close after delivery of ABA with the ion pump and that the stomata close to the pump close faster than the ones further away implying dose dependence. In addition we didn't observe any significant wound effect from the insertion of the pump signifying the potential of our method as non invasive. With our technology we can offer a new tool for fundamental understating of plant physiology but also adaptation of plants to environmental changes.

SESSION BM02.03: Charge Transfer in Bacterial Systems
Session Chairs: Renata Bilewicz and Xiaodong Chen
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Independence East

8:15 AM *BM02.03.01
Electron Transfer and Transport in Multi-Heme Proteins Jochen Blumberger; University College London, London, United Kingdom.

Certain bacteria have evolved an astonishing survival mechanisms in response to low oxygen concentrations. When cytoplasmatic O2 becomes scarce they start to grow µm-long electrically conducting cellular appendages to export electrons from the cytoplasm to extracellular space for reduction of

extracellular substrates (e.g. rocks!) in place of O2. Recently it was shown that arrays of Fe-containing multi-heme cytochromes (MHC) confer electric conductivity to those appendages, which garnered much interest for their use in ionanotechnological applications, e.g. bio-compatible field effect transistors. Here I will present recent experimental measurements probing electron transfer (ET) and electron transport (ETp) through multi-heme cytochromes (MHCs) as well as their interpretation by theory, electronic structure calculations and molecular dynamics simulation. I will discuss recent pump-probe spectroscopy results on Ru-labeled MHCs aimed at the determination of heme-heme ET rates and intrinsic electron flow in aqueous MHCs and the measurement of the I-V characteristics of dry MHCs in bioelectronic junctions (scanning tunneling microscope and protein monolayer junctions). While the ET mechanism appears to be well established for MHCs in aqueous solution, the ETp mechanism in single protein bioelectronic junction remains elusive partly due to the complexities of the electrode-protein interface and the resulting challenges for molecular modelling.

8:45 AM *BM02.03.02
Proton-Coupled Extracellular Electron Transport via Microbial Outer Membrane Flavocytochromes Yoshihide Tokunou[2], Kazuhito Hashimoto[1] and Akihiro Okamoto[1]; [1]National Institute for Materials Science, Tsukuba, Japan; [2]The University of Tokyo, Tokyo, Japan.

Bacterial electron transport to a solid substrate or electrode located extracellularly is accomplished by unidirectional electron flow via an array of more than twenty heme redox centers arranged in the outer membrane c-type cytochrome complex (OM c-Cyts). This interfacial electron transport between OM *c*-Cyts and solid substrates is termed extracellular electron transport (EET). The rate of EET is largely enhanced by self-secreted flavin molecules associated with the formation of semiquinone (Sq) state as a binding redox cofactor in the OM *c*-Cyts. However, the more negative redox potential of bound flavin Sq than the hemes in OM *c*-Cyts is energetically unfavorable for the kinetics of EET. Given the primary focus of related work in the recent past has been the electron carriers and the redox potential landscape of reaction centers, the importance of associated proton transport has not been widely investigated in EET. We,herein, show that proton transfer in the OM flavocytochromes limits the rate of EET in *Shewanella oneidensis* MR-1. Using an *in vivo*electrochemical assay, we observed a large kinetic isotope effect (KIE) following D_2O addition (< 4%), specifically when EET was the rate-determining step for the current production of lactate oxidation respiration. Replacing flavin cofactors with twelve analogous molecules, the rate of EET correlated not with their redox potential but with their pK_a at the nitrogen atom at position-5 (N(5)) in the isoalloxazine ring calculated by a quantum chemical approach. Because higher pK_a represents stronger proton acceptability in N(5), this correlation suggests that the protonation reaction at N(5) in flavin associates and limits the rate of EET. We will further discuss about the rate-determining step of proton transport coupled with the redox reaction of the bound flavin cofactor in OM *c*-Cyts, with dataset for solvent KIE with partial deletion of OM *c*-Cyts complex.

9:15 AM BM02.03.03
How Do Electrons Pass Through Multi-Heme *C*-Type Cytochromes? Kavita Garg; Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

Multi-heme cytochrome c (*CytC*) proteins are key for transporting electrons out of cells, to allow intracellular oxidation to proceed, also in the absence of O_2.[1] While the mechanism of the process is not well understood at the molecular level, these hemes may well function as "molecular wires",[2] which makes such multi-heme cytochromes of prime interest for, e.g., potential bioelectronics and bio-sensing and integrating such proteins into electronic circuits is an exciting prospect.
Figuring out ***how*** electrons pass through these proteins is a scientific challenge. We tackle this by measuring solid state electron transport (ETp) along dry multi-heme protein monolayers, a process that has similarities with, but also clear differences from ET in aqueous solution.
Earlier we studied ETp for a variety of proteins, using "dry" monolayer junctions,[3] with structurally bound H_2O retained. In such junctions the donor and acceptor, used in ET in solution,[4] are replaced by nm - mm sized metallic contacts. Electron transport is measured as current, I, as function of applied voltage, V (I-V characteristics) and temperature, T (I-V-T). Here we ETp across two multi-heme *CytC*-type proteins: the membrane-bound MtrF (deca-heme *CytC*), the globular STC (tetra-heme *CytC*) and bilayers of these proteins. Transport is measured between Au electrodes. These proteins show length-normalized conductance that is 1,000x higher than what we measured across single heme (Cytochrome C), or heme-free protein monolayers, but similar to monolayers of conjugated organics. dI/dV of the junctions were also measured using lock-in-amplification at low temperatures, to calculate the protein and protein-contact energy level landscapes, involved in electron conduction. Conductance is found to be temperature-independent (320-80K), suggesting tunneling as limiting transport mechanism. Modelling of the I-V curves was done using Simmon's model and Landauer model, results of which are consistent with that electron transport can be described as tunneling and that *protein-electrode coupling*, rather than transport in the proteins *is rate-limiting*. From the fits to the Landauer model electron transport rather than hole transport appears to dominate. To understand the involvement of heme states, results from DFT calculations of (the much smaller) STC were compared with dI/dV. We will discuss these results and put them in perspective with those obtained on other protein systems by us and others, and in light of reports on electron transfer, involving these proteins. Finally, we'll assess possibilities for use of these proteins in future bioelectronics.
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2 M. Y. El-Naggar *et al. ChemElectroChem*, 2014, **1**, 1932–1939.
3 C. D. Bostick *et al.Reports Prog. Phys.*, 2018, **81**, 026601.
4 H. B. Gray *et al. Biochim. Biophys. Acta - Bioenerg.*, 2010, **1797**, 1563–1572.

9:30 AM BM02.03.04
Core/Shell Bacterial Cables—A One-Dimensional Platform for Probing Microbial Electron Transfer Huan-Hsuan H. Hsu and Xiaocheng Jiang; Tufts University, Medford, Massachusetts, United States.

Comprehensive interpretation and interrogation of extracellular electron transfer (EET) mechanisms of electrochemically active bacteria can provide valuable information to enhance microbial fuel cells performance, which, however, are still restricted by the intrinsic complexity of natural biofilm. Here, we design core/shell bacteria-encapsulating cables as a one-dimensional model system to facilitate EET studies, where demonstrate the precise modulation of fiber diameters (from 6.9±1.1 mm to 25.1±2.4 mm) and bacteria interactions. As-formed bacterial cables exhibit that their conductivities are highly dependent on the bacteria density as well as the nature and number of intercellular interconnections. The closely contacted bacteria promote the development of high density self-assembling nanomaterials at cellular interfaces which can be directly translated to the increase of EET efficiency (16.2 mS cm^{-1}) as compared with isolated, remotely-connected bacteria samples (6.4 mS cm^{-1}). Introducing exceeding concentrations of soluble electron acceptors during cell culture, however, substantially suppresses the formation of cellular interconnections and leads to significantly reduced conductivity (2.5 mS cm^{-1}). Frequency-dependent measurements further revealed EET of EAB networks shared similar characteristics to electron hopping in conductive polymer matrix, including a DC-like mechanism in the low frequency region, and AC induced additional electron hopping when the applied frequency is above the critical frequency (10^5 Hz). The current work represents a strategically new approach for non-invasively probing EET with rationally defined micro-environment and cellular interactions across a wide range of length scales, which is expected to open up new opportunities for tackling the fundaments and implications of EET.

9:45 AM BM02.03.05

Design, Synthesis and Characterization of a Bioanode for Microbial Fuel Cells Jérémie-Luc Sanchez and Christel Laberty-Robert; Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université-Faculté de Sciences et d'Ingénierie, Paris, France.

Today the need for clean energy technologies appears urgent. Therefore, the idea of harvesting the metabolic activity of microorganisms becomes feasible. Amidst those devices microbial fuel cells focus on converting chemical energy from organic matter into electricity by gathering electrons produced by bacteria degrading these molecules. Such fuel cells may be used as renewable energy sources, but a lot of challenges need to be addressed before we can see them as an efficient, stable and profitable technology. Many approaches to tackle these problems exist. For instance, the electronic transfer between the bacterium and the electrode can be improved by working on the organism or the consortium used to degrade the organic matter. Here we rather seek to improve the material and the architecture of the electrochemical system and especially those of the bacteria-colonized anode. We start from the observations of the limitations of current carbon felt electrodes for microbial fuel cells to design a better system.
This work focuses on the conception of the bioanode of a microbial fuel cell by electrospinning. This process allows the shaping of nano to micro-scaled polymer fibers through electrically-assisted extrusion. We obtain a nonwoven mat of polymer fibers which is made conductive by the addition of anisotropic carbon-based materials. The colonization of these hybrid carbon polymer electrodes by the electroactive bacteria *Shewanella oneidensis* is conducted through diverse approaches: core-shell encapsulation or natural biofilm development. Once prepared, the anode is then integrated into a functional lab-scale fuel cell in order to evaluate its electrochemical characteristics. The impact of the colonization of these conductive electrodes on the electrochemical performances of a full bio fuel cell will be discussed.

10:00 AM BREAK

10:30 AM *BM02.03.06
Hotwired Life—What Can Bacterial Electron Conduits Teach Us About Biological Energy Conversion and Bioelectronics? Moh El-Naggar; University of Southern California, Los Angeles, California, United States.

Microorganisms have evolved exquisite electron conduits, including multiheme cytochromes, to extend their metabolic reach to external abiotic surfaces. This process, known as extracellular electron transfer (EET), is being heavily pursued for wiring microbes to electrodes in renewable energy technologies. Here we focus on biophysical measurements, electron transfer simulations, and electron cryo-tomographic studies of the multiheme cytochrome conduits that perform EET in the dissimilatory iron-reducing bacterium *Shewanella oneidensis* MR-1. We show how the electron transport rates gleaned from single molecule conductance measurements and stochastic simulations can be linked to electrochemical measurements of single cells and whole biofilms. We also describe our current understanding of the distribution and functionality of extended multiheme cytochrome networks along filamentous membrane tubes known as bacterial nanowires. To explore the role of biological electron conduits in long-distance (micrometer scale) electron transport along cellular membranes and across cells, we report *in vivo* electrochemical measurements of redox conduction through cells linking electrodes, and show that the activation energy of this process matches these obtained from electron hopping calculations through the Mtr-Omc cytochrome pathway. Since EET conduits naturally evolved for biotic-abiotic coupling, a fundamental understanding has special implications for a new generation of bioelectrochemical technologies and living electronics that that harness the advantages of microbes in detecting external signals (e.g. biosensors) or hosting synthetic genetic circuits (e.g. biocomputing).

11:00 AM *BM02.03.07
Mimicking Biological Energy Systems—From Multilayer Membrane Stacks to Molecular Electron Conduits Lars Jeuken[1], George R. Heath[1], Ee Taek Hwang[1], Valentin Radu[1], Mengqiu Li[1], Anna Stikane[1], Khizar Sheikh[1], Katherine Orchard[2], Chong-Yong Lee[2], Manuela A. Gross[2], Daisuke Hojo[3], Emma Ainsworth[4], Colin Lockwood[4], Stefan Frielingsdorf[5], Tadafumi Adschiri[3], Oliver Lenz[5], Erwin Reisner[2] and Julea N. Butt[4]; [1]School of Biomedical Sciences and Astbury Centre, University of Leeds, Leeds, United Kingdom; [2]Department of Chemistry, University of Cambridge, Cambridge, United Kingdom; [3]Advanced Institute for Material Research, Tohoku University, Miyagi, Japan; [4]Centre for Molecular and Structural Biochemistry, School of Chemistry, and School of Biological Sciences, University of East Anglia, Norwich, United Kingdom; [5]Institut für Chemie, Technische Universität Berlin, Berlin, Germany.

In nature, energy systems rely on efficient electron transfer across redox chains for charge transport across lipid membranes. Multilayered or stacked lipid membranes spatially organize and compartmentalize these energy processes, while greatly increasing the lipid membrane surface area. Here, I will present two approaches aimed to mimic these fundamental features of bioenergetics.

Long-distance charge separation in photosynthesis was mimicked by coupling dye-sensitized TiO_2 nanocrystals and CdS quantum dots to two decaheme protein, MtrC and OmcA from *Shewanella oneidensis* MR-1, where the decahemes form a ~7 nm long molecular wire between the light harvesting nanoparticle (NP) and the underlying anode. The system is assembled by forming a densely-packed decaheme film on an ultra-flat gold electrode, followed by the adsorption of monolayer of NP. The step-by-step construction of the decaheme/NP system is monitored with (photo)electrochemistry, quartz-crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM). When using TiO_2 nanocrystals, dye-sensitized with a phosphonated bipyridine Ru(II) dye, photocurrents are observed that are dependent on the redox state of the decaheme, confirming that electrons are transferred from the TiO_2 nanocrystals to the surface *via* the decaheme conduit. In other words, TiO_2/decaheme wires function as hybrid photodiodes in which the decaheme traps the conduction-band electrons from TiO_2before transferring them to the electrode. To the best of our knowledge, the TiO_2 nanocrystal/decaheme system is the first demonstration of a photobioelectrochemical system that uses a redox protein to mimic charge separation found in biological photosystems.

Stacked lipid membrane system were mimicked by using poly-L-lysine to electrostatically assemble multilayers of negatively charged lipid membranes on gold electrodes. When membrane enzymes are incorporated, either an ubiquinol oxidase (cytochrome bo_3 from *Escherichia coli*) or an oxygen tolerant hydrogenase (the membrane-bound hydrogenase from *Ralstonia eutropha*), cyclic voltammetry (CV) reveals a linear increase in biocatalytic activity with each additional membrane layer (oxygen reduction or hydrogen oxidation, respectively). Electron transfer between the enzymes and the electrode is mediated by the quinone pool that is present in the lipid phase. We deduce by atomic force microscopy, CV and fluorescence microscopy that quinones are able to diffuse between the stacked lipid membrane layers via defect sites where the lipid membranes are interconnected. This assembly is akin to that of interconnected thylakoid membranes or the folded cristae of mitochondria and have significant potential for mimicry in biotechnology applications such as energy production or biosensing.

11:30 AM BM02.03.08
Biological Electron Transfer Over Centimeter Distances in Cable Bacteria Rob Cornelissen[1], Raghavendran T. Eachambadi[1], Robin Bonné[1], Silvia Hidalgo Martinez[2, 3], Ji-Ling Hou[1], Jeanine S. Geelhoed[2], Jan D'Haen[4], Henricus T. Boschker[2, 3], Roland Valcke[5], Bart Cleuren[6], Jean V. Manca[1] and Filip J. Meysman[2, 3]; [1]X-LAB, Hasselt University, Hasselt, Belgium; [2]Department of Biology, University of Antwerp, Antwerp, Belgium; [3]Department of Biotechnology, Delft University of Technology, Delft, Belgium; [4]Institute for Materials Research, Hasselt University, Diepenbeek, Belgium; [5]Molecular and Physical Plant Physiology, Hasselt University, Hasselt, Belgium; [6]Theoretical Physics, Hasselt University, Hasselt, Belgium.

Biological electron transfer is generally thought to occur over nanometer to micrometer-scale distances, as is the case in cellular respiration or extracellular electron transport via conductive nanowires in metal-reducing bacteria. Yet, various lines of evidence suggest that the recently discovered multicellular cable bacteria[1] can induce biological electron transfer over centimeter-scale distances[2,3] – three orders of magnitude longer than previously observed. However, up until now, no direct quantification of an electrical current flow through a cable bacterium filament has been reported.

In this contribution we present some recent insights and advances on the characterization of the electron transport and the conductive structures in cable bacteria. Using SEM, TEM and AFM, we examined in detail the cell envelope of cable bacteria filaments. A fiber network residing in the periplasmic space was discovered, which we propose to be universally present in different species of cable bacteria. The fibers are running in parallel to the longitudinal axis of the filaments. Using amperometric measurements on custom-built electrodes, we successfully measured the conductivity of single intact cable bacteria filaments as well as isolated periplasmic sheaths that contain the fibers. These results demonstrate that the periplasmic fibers are indeed responsible for long-distance electron transport in cable bacteria.

Understanding the conductive structures of the cable bacteria and the associated mechanism of long-distance electron transfer will not only help to understand the role of cable bacteria in their natural environment, but could also enable the development of new applications in bioelectronics.

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11:45 AM BM02.03.09
Electrochemical Investigation of Extracellular Electron Transport Through *Pseudomonas aeruginosa* Biofilms Leonard Tender[1], Matthew Yates[1], Scott Saunders[2] and Dianne Newman[2]; [1]Center for Bio/Molecular Science and Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; [2]Biology and Biological Engineering, Caltech, Pasadena, California, United States.

Electroactive microorganisms (EM) can utilize a non-corroding electrode as an inexhaustible electron acceptor or donor for respiration and/or metabolism. During the past 6 years we have applied electrochemical gating measurements (EGM) using interdigitated microelectrode arrays (IDA) to study multi-cell-length long-distance extracellular electron transport (LD-EET) through electrode- grown EM biofilms. For all biofilms we have examined thus far, EGM reveals that the biofilms act as redox conductors, whereby LD-EET occurs via electron transfer reactions among immobilized extracellular redox cofactors. Here, we apply EGM to study LD-EET occurring in the pure-culture *Pseudomonas aeruginosa* biofilm (PAB). *P. aeruginosa*secretes phenazines, small redox molecules, which among other things, export electrons resulting from respiration by oxygen-limited cells residing deep in PAB. It is conventionally thought that this occurs by physical diffusion of phenazines out of PAB. Our results indicate however that an appreciable amount become immobilized within PAB, imparting redox conductivity to the biofilm. Moreover, PAB appears to have different affinities for the different phenazines – with pyocyanin (PYO) contributing most to LD-EET. A model is presented in which PYO exhibits bounded diffusion analogous to certain redox polymers. *P. aeruginosa* is an opportunistic pathogen which forms biofilms in the lungs. The results presented have implications for improved treatment strategies.

SESSION BM02.04: Light and Oxygen Mediated Charge Transport
Session Chairs: Pau Gorostiza and Eleni Stavrinidou
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Independence East

1:30 PM *BM02.04.01
Self-Assembly and Electron Transport of Photosystem I in Tunneling Junctions and Soft Photovoltaic Devices Ryan Chiechi[1, 2], Andreas Herrmann[2], Xinkai Qiu[1, 2], Olga Castaneda Ocampo[1, 2], Mark Loznik[2], Henry de Vries[1, 2] and Pavlo Gordiichuk[2]; [1]Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands; [2]Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

Photosystem I (PSI) is a trimeric protein complex capable of converting light into spatially separated electron/hole pairs. In Nature, this process is used to convert light-energy into chemical-energy to drive photosynthesis. Ex vivo, the electron/hole pairs can be injected directly into electrodes and/or redox couples, turning PSI complexes into nanoscale photovoltaic devices with an internal quantum efficiency of unity. Because PSI is a membrane protein, the complexes are flat and the edges are non-polar, facilitating self-assembly on (electrode) surfaces. However, they assemble with an equal probability of the two possible orientations of the electron transport chain, meaning they will inject holes and electrons with equal probability, resulting in zero photocurrent. We successfully biased this orientation by functionalizing the surfaces of electrodes with either hydrogen-bond donors or ionic groups to exploit the slight differences in the nature of the polarity of the two faces of PSI to demonstrate thin-film, solid-state bio-photovolatic devices.
The focus of this talk will be examining the mechanism of charge-transport through self-assembled monolayers of complexes of PSI with and without orientational bias. We find that, in all cases, non-resonant tunneling is remarkably efficient even though tunneling electrons do not interact strongly with the electron transport chain. Rather, the effect of built-in electric field generated by the alpha helices in the periphery of the complexes dominates transport. Using the insights gained from these studies, we used phage display to find linker units capable of biasing the self-assembly of complexes of PSI completely in one direction. We then inserted nano-structured electrodes into microfluidic chips made by soft lithography. When the electrodes are properly functionalized, PSI self-assembles on them resulting in soft, stretchable photovoltaic devices in a single fabrication step. We followed the performance of the devices over time, showing that they are capable of self-regeneration via the circulation of active PSI through the devices in operando.

2:00 PM *BM02.04.02
Oxidative Stress is Tightly Regulated by Cytochrome *c* Phosphorylation and Respirasome Factors in Mitochondria Alejandra Guerra-Castellano, Antonio Díaz-Moreno, Gonzalo Pérez-Mejías, Carlos A. Elena-Real, Katiuska González-Arzola, Sofia M. García-Mauriño, Miguel A. De la Rosa and Irene Diaz-Moreno; Institute for Chemical Research - cicCartuja, Seville, Spain.

Respiratory cytochrome *c* has been found to be phosphorylated at tyrosine 48 or 97 in the post-ischemic brain upon neuroprotective insulin treatment, but how such post-translational modification affects mitochondrial metabolism is unclear. Here, we report the structural features and functional behavior of phosphomimetic cytochrome *c* mutants, which were generated by site-specific incorporation at position 48 or 97 of *p*-carboxymethyl-L-phenylalanine (*p*CMF) using the evolved tRNA synthetase method. We found that the point mutations do not alter the overall folding and heme environment of cytochrome *c*, but significantly affect the whole oxidative phosphorylation process. In fact, the electron donation rate of the Y97*p*CMF mutant heme

protein to cytochrome *c* oxidase, or complex IV, within respiratory supercomplexes was higher than that of the wild-type species, in agreement with the observed decrease in reactive oxygen species (ROS) production. Direct contact of cytochrome *c* with the respiratory supercomplex factor HIGD1A (hypoxia inducible domain family member 1A) is herein first reported, with the Y97*p*CMF mutant heme protein exhibiting a lower affinity than the wild-type species. Interestingly, phosphomimetic cytochrome *c* also exhibited a lower caspase-3 activation activity. Altogether, these findings yield a better understanding of the molecular basis for mitochondrial metabolism in acute diseases, such as brain ischemia, and could thus allow the use of phosphomimetic cytochrome *c* as a neuroprotector with therapeutic applications.

2:30 PM *BM02.04.03
A Novel Biological *p-n* Junction for Modulating the Proton Transport in Bacteriorhodopsin Yan Xiang[2, 1]; [1]Southen New Hampshire University, Manchester, New Hampshire, United States; [2]Beihang University, Beijing, China.

Hampered by the absence of evidence and theoretical model of biological semiconductor, the unidirectional electron transport via the p-n junction structure between functional proteins and abiotic materials remains a challenge for bioelectronics. *Bacteriorhodopsin (bR), a representative transmembrane protein, has demonstrated exceptional optoelectronic* effects in bR/semiconductor hybrid materials and offers a possible pathway for addressing this challenge. In the present work, bR is found to be an *n*-type semiconductor with an indirect electron transition. Thereby, we successfully explain the mutual cohesion and unidirectional interfacial electron transport between bR and *p*-type semiconductor, specifically, the enhanced yet stable photocurrent, in regard to optoelectronics and the acceleration of the bR photocycle, via a distinctive bio-*p-n* junction mechanism. We believe the concept of protein based *p-n* junction will underscore research on bioelectric applications for bR and its homologues.

2:45 PM BREAK

3:15 PM BM02.04.04
New Insights on the Electrical Resistive Switching Behavior of Eumelanin—Toward Memory Application Devices Manuel Reali and Abdelaziz M. Gouda; Engineering Physics, Polytechnique Montréal, Montréal, Quebec, Canada.

Eumelanin is a black biopigment present in flora and fauna [1]. It features fascinating properties such as radical scavenging, metal chelation, photoprotection, broadband optical absorption and hydration-dependent electrical conductivity [2]. Remarkable research efforts have been devoted to unravel its optical and electrical properties to integrate eumelanin in optoelectronic and energy storage devices [3].
A debate whether eumelanin is an amorphous semiconductor (ASc) or a mixed ionic-electronic conductor (MIEc) is open among the scientific community. The discovery of a resistive switching behavior in eumelanin pellets [4] along with theoretical simulations that predict the existence of mid-gap states in eumelanin have been considered primary evidence for the ASc model [5]. Recently, it has been proposed that adsorbed water would activate a comproportionation equilibrium between redox active eumelanin moieties, favouring a de Grotthuss-like charge transport [6]. Even though the MIE conduction model excludes the ASc model, the causes of the resistive switching are not well understood.
In this work, we fabricated wet and dry *Sepia* eumelanin pellets (hydrated at different percentages of relative humidity (%RH) or processed in Ar glove box), sandwiched in coin cell configuration, using Cu and stainless-steel electrodes. Hydrated samples show a reproducible resistive switching over many cycles with an on/off ratio of ca 10^{-1}-10^{-4}. Dry samples switch only during the first cycles, with an exponential I-V behavior. SEM images of Cu electrodes taken after the electrical characterization of wet samples reveal CuO_x dendritic structures. These dendrimers could bridge the two electrodes. The I-V electrical response of dry samples could be interpreted as evidence of an electronic transport in bulk eumelanin thus supporting the ASc model. Understanding the mechanisms of the resistive switching behavior and shedding light on the electrical properties of eumelanin under different hydration conditions is critical to demonstrate eumelanin-based memory devices.

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3:30 PM BM02.04.05
Photonic Nanoparticles as Molecular Sensors Holly Clingan, Vladimiro Mujica and Antonio Garcia; Arizona State University, Tempe, Arizona, United States.

The interactions between bovine serum albumin (BSA) and gold colloids was examined using ultraviolet (UV) and visible light absorption spectroscopy measurements to determine the surface coverage and binding activity. The binding of BSA to citrate-coated gold nanoparticles (AuNP) suggests an electrostatic interaction mechanism. Surface coverage on the colloids is based on the concentration of BSA. The measurements of the surface plasmon resonance (SPR) show that BSA and citrate-coated AuNP achieve stabilization and surface coverage at or above the isoelectric point (~4.7), and that the optical response of the system corresponds to a change in intensity only of the SPR. The data supports a non-covalent and non-spontaneous binding mechanism of gold colloids and shows a maximum surface coverage that is dependent on concentration.

3:45 PM BM02.04.06
Label-Free Detection of Conformational Changes in DNA Nanotweezers with Microwave Microfluidics Angela C. Stelson[1], Minghui Liu[2], Charles A. Little[1], Christian J. Long[1], Nathan D. Orloff[1], Nicholas Stephanopoulos[2] and James C. Booth[1]; [1]National Institute of Standards and Technology, Boulder, Colorado, United States; [2]School of Molecular Sciences, Arizona State University, Tempe, Arizona, United States.

Detection of conformational changes in biomolecular assemblies provides critical information into biological and self-assembly processes. State-of-the-art *in situ* biomolecular conformation detection techniques rely on fluorescent labels or protein-specific binding agents to signal conformational changes. Here, we present an on-chip, label-free technique to detect conformational changes in a DNA nanomechanical ‘tweezer’ structure using microwave microfluidics. We measured the electromagnetic properties of suspended DNA tweezer solutions from 50 kHz to 110 GHz and directly detected two distinct conformations of the structures. We developed a physical model to describe the electrical properties of the tweezers, and correlated model

parameters to conformational changes. The strongest indicators for conformational changes in DNA tweezers were the ionic conductivity and shifts in the magnitude of the cooperative water relaxation. Microwave microfluidics detection of conformational changes is a generalizable, non-destructive technique that requires only nanoliter sample volumes, making it attractive for high-throughput measurements.

4:00 PM BM02.04.07
Nanoscale Mapping of the Fundamental Building Blocks of the Brain Deblina Sarkar[1], Asmamaw Wassie[1], Kiryl Piatkevich[1], Tyler Tarr[2], Aihui Tang[2], Thomas Blanpied[2] and Edward Boyden[1]; [1]Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; [2]University of Maryland, Baltimore, Maryland, United States.

Understanding in 3-D how molecules are configured throughout neurons, and how neurons are configured in circuits, may not only enable the discovery of new targets and technologies for treating neural diseases, but could help reveal fundamental principles of neural computation. Since biomolecules are nanoscale, however, and configured with nanoscale precision, this has remained difficult to study. For example, with electron microscopy, fantastic spatial resolution is possible, but it is difficult to identify the biomolecules in a protein complex. On the other hand, with optical microscopes the spatial resolution is limited to 300 nm due to the diffraction of light waves. Optical super-resolution techniques that overcome this limit face challenges in 3D scalability and require expensive hardware and/or are slow to image large scale specimens, which limits their application.

We recently discovered that it was possible to beat the diffraction limit through physical magnification of biological specimens, by embedding them in dense, swellable polyelectrolyte gels (Science (2015) 347(6221):543-548). The original process, which we called expansion microscopy (ExM), achieved a 4.5x linear expansion (i.e., a 300 nm diffraction limited lens would now have a resolution of 300 / 4.5 ≈ 60 nm). We also showed that, by iterating the polymerization and expansion process (iExM), we could achieve higher expansion factors (4.5 x 4.5 ~20x, enabling a resolution of 300/20 ~15 nm; Nature Methods (2017) 14, 593–599). However, iExM required us to discard the original biomolecules, replacing them with a polymer-anchored DNA oligo. This results in limited resolution due to the fact that the antibody must be administered first, and thus the size of the antibody becomes the key factor limiting resolution.

Here, we report a new form of iterative expansion microscopy which addresses these problems – enabling the preservation of biomolecules throughout the entire process, and also allowing for antibodies and other probes to be delivered at the end of the process, greatly improving resolution. Our new method, which we call iterated direct ExM (idExM), enables high expansion factors (20x to 100x) to be achieved, and may lead to resolution on the scale of individual biomolecules.

IdExM overcomes the limit of all previous super-resolution techniques, where the effective resolution is limited by the size of the labels (eg. primary and secondary antibodies which are about 20-30 nm in total size). This may, in principle, result in resolutions of 1 nm or less. IdExM also de-crowds biomolecules through iterative expansion, allowing access of antibodies to epitopes that may not otherwise be accessible for viewing by existing super-resolution methods. Using this technology, we revealed for the first time, detailed synaptic architectures in intact brain circuits, which influences the transport of neurotransmitters accross the synapse as well as nanoscale organization of transcriptomes.

4:15 PM BM02.04.08
Biohybrids from Organic Semiconductors and Photosynthetic Bacteria Gianluca M. Farinola[1], Francesco Milano[2], Roberta Ragni[1], Marco Lo Presti[1], Simona la Gatta[1], Angela Agostiano[1, 2] and Massimo Trotta[2]; [1]University degli Studi-Bari Aldo Moro, Bari, Italy; [2]Dipartimento di Chimica Università degli Studi di Bari "Aldo Moro", Bari, Italy, CNR IPCF UOS BARI , Bari, Italy.

The Reaction Center (RC) is the photoenzyme used by photosynthetic bacteria, such as the purple Rhodobacter Sphaeroides R26, to convert solar energy into charge separated states with efficiency close to 100% [1]. Upon its isolation from the living bacterium, the RC retains stability and enzymatic activity in surfactant aqueous media and is envisaged as a promising biological system to generate new photoactive materials for bioelectronics [2].
However, the applicability of RC in bioelectronic devices is strictly related to (a) finding suitable deposition methods enabling controlled orientation of the protein on conducting or semiconducting interfaces and (b) employing chemical strategies to enhance the protein light absorption in the visible region. A successful approach to extend the RC visible absorption is covalently binding tailored organic molecules that harvest white light and efficiently transfer it to the protein [3, 4]. A variety of molecular fluorophores acting as efficient antennas will be presented, highlighting their role in the enhancement of biohybrids' photoconversion efficiencies. The lecture will also discuss strategies to efficiently affix the RC on organic semiconductors layers in photoconversion devices and to embed the RC in polymeric thin films at the electrodes [5].
Design and construction of smart supramolecular architectures by the multiple combination of different enzymes assembled with tailored linkers will be also presented as a proof of the concept that supramolecular bioinspired machineries based on the functioning of the bacterial RC photoenzyme can be developed for solar energy conversion.

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4:30 PM BM02.04.09
Coupling Electron and Proton Transfer—The Lesson From the Photosynthetic Reaction Center Massimo Trotta[1], Francesco Milano[1], Roberta Ragni[2] and Gianluca M. Farinola[2]; [1]Istituto per i Processi Chimico Fisici, Consiglio Nazionale delle Ricerche, Bari, Italy; [2]Department of Chemistry, Università degli Studi di Bari Aldo Moro, Bari, Italy.

Photosynthetic reaction centers from photosynthetic bacteria are integral membrane proteins able to transform the electromagnetic radiation associated to solar light in a biological hole-electron couple amenable for being used in a number of possible applications. The hole-electron couple formed upon light

absorption is characterised by a long-living property: the charge-separated state can survive from 100 milliseconds to 3 seconds, depending on the environmental conditions[1].
One of the key issues for this extent lifetime of the dipole within the scaffolding of the protein is that the formation of the charge-separated state draws protons from the aqueous solution within the inner part of the protein, eventually modulating the redox chemistry of the final electron acceptor[2, 3].The role of the proton uptake from the photoenzymes during its functioning will be addressed along with some possible consequences on the applicative use the Reaction Center as organic-biological biohybrid[4-9]

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4:45 PM BM02.04.10
Intracellular Au Nanocluster Photosensitized Bacteria for Solar Fuel Production Hao Zhang[1] and Peidong Yang[1, 2]; [1]Department of Chemistry, University of California, Berkeley, Berkeley, California, United States; [2]Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The demand for renewable and sustainable fuel has prompted the rapid development of advanced nanotechnologies to effectively harness the copious flux of solar power. Although the solar-to-energy efficiencies of inorganic semiconductor devices can easily surpass 20%, the transduction of solar energy into specific organics remains a bottleneck for abiotic catalysts. The construction of photosynthetic biohybrid systems (PBSs) aims to link preassembled biosynthetic pathways with inorganic light absorbers. This strategy inherits both the high light-harvesting efficiency and the superior catalytic performance from solid-state semiconductors and whole-cell microorganisms, respectively. Recently, we have demonstrated a version of membrane-bound CdS nanoparticle on nonphotosynthetic bacterium, *Moorella thermoacetica* for artificial photosynthesis. To eliminate potential mass and energy losses during transporting electrons across cell membranes, the spatial conjugation between inorganic material and microorganism could be designed in cytoplasm. Here, we introduce an intracellular, biocompatible light absorber, namely gold nanoclusters (Au NCs), to circumvent the sluggish kinetics of electron transfer for existing PBSs. Translocation of these Au NCs into nonphotosynthetic bacteria enabled photosynthesis of acetic acid from CO_2. Besides, Au NCs also serve as reactive oxygen species (ROS) inhibitors to maintain high bacterium viability. Taking the dual advantages of light absorption and biocompatibility, this new generation of PBS can efficiently harvest sunlight and transfer photo-generated electrons to cellular metabolism, realizing CO_2 fixation continuously over several days. Moreover, intracellular PBS represents a promising platform to investigate the charge transfer, and leads to a deeper understanding of the burgeoning complex nexus of inorganic materials and biological systems.

SESSION BM02.05: Charge Transport in Peptides and Proteins
Session Chairs: David Cahen and Xiaodong Chen
Wednesday Morning, November 28, 2018
Sheraton, 2nd Floor, Independence East

8:15 AM *BM02.05.01
Charge Transport Investigation Through Supramolecular Peptides/Proteins Junctions Using STM-BJ Technique Wenjing Hong, Haining Zheng, Xiaoyan Zhuang and Baishan Fang; Chemical and biochemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Collaborative Innovation Center of Chemistry for Energy Materials, Xiamen University, Xiamen, Xiamen, China.

The charge transport investigation through peptides and proteins offers an unique opportunity to study the supramolecular interaction, information transmission, and even bio-catalytic process in biological systems, however the single-molecule experimental measurement of charge transport through peptides and proteins remained as experimental challenges due to the difficulties in the binding of peptides/proteins on electrodes and also the extraction of low current signals through the single peptides/proteins junction. On the other hand, the calculations predicted that the conductance of peptides junctions exhibited low conductance, while the experimental measurement provides relatively high conductance, then what is the dominated conduction channel through the single peptide/protein?
Here we studied the charge transport properties through a series of peptide-supramolecular interactions, including hydrogen bonds and π-π stacking, and we measured the supramolecular charge transport between two peptides anchored on two separated gold electrodes using scanning tunneling microscopy break junction (STM-BJ) technique. The combined molecular dynamic simulations further revealed the conformation evolution of supramolecular peptides junctions. It is found that the supramolecular interaction between the peptides offer the conduction channel, and the charge transport through the supramolecular process could be further tuned by the environments.
As perspective, we further applied the technique to investigate the charge transport through an enzyme, oxidoreductase, and our preliminary results suggested that the charge transport process are correlated to the bio-catalytic process, which offer an unique testbed to look into the bio-catalysis from the single-molecule level.

8:45 AM *BM02.05.02
Polymeric and Biopolymeric Matrices for Proton Conduction and Ion-to-Electron Transduction Paul Meredith[1], Bernard Mostert[2], Margarita

Sheliakina[3] and Adam Micolich[4]; [1]Department of Physics, Swansea University, Swansea, United Kingdom; [2]Chemistry Department, Swansea University, Swansea, United Kingdom; [3]School of Mathematics and Physics, The University of Queensland, Brisbane, Queensland, Australia; [4]School of Physics, University of New South Wales, Sydney, New South Wales, Australia.

Transducing between ion and electron currents is a key challenge underpinning the emerging field of bioelectronics [1]. In general, ions (including protons) are the dominant signal carrying entities in biology, and modern electronics relies on semiconductors where the carriers are electrons and holes. Solid state ionic conductors (SSICs), whilst not rare, are somewhat few and far between – so-called ionic glasses such as silver iodide or sodium alumina being classic and early examples. Of more relevance to bioelectronic applications are polymeric-SSICs and there are several well-known examples such as DuPont's Nafion (a proton transport membrane). Polymeric matrices such as polyethylene oxide can also conduct ions when suitably 'doped' (or solvated depending upon your nomenclature) with for example, water or lithium perchlorate [2]. Finally, several biopolymeric matrices such as melanin and proteins [1, 2, 3] show respectable proton conductivities when hydrated.
In my talk I will present several examples of polymeric and biopolymeric SSIC materials and exemplify the 'conduction physics' at play. I will also describe recent progress in utilising these materials as transducing elements in hybrid and all-organic transistors which represent prototype bioelectronic logic elements [4, 5].

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9:15 AM BM02.05.03
Mechanism of Metal-Like Transport In Bacterial Pili Protein Nanofilaments Sophia M. Yi[1, 2, 9], Yangqi Gu[2, 3, 9], Jens Neu[4], J. Patrick O'Brien[1, 2], Dennis Vu[1, 2], Winston Huynh[2, 5], Sibel Ebru Yalcin[6, 9], Tamas Varga[6], Hao Jiang[7], Qiangfei Xia[7], Geyou Ao[8, 10], Ming Zheng[8], Victor Batista[4], Charles A. Schmuttenmaier[4] and Nikhil S. Malvankar[1, 2]; [1]Department of Molecular Biophysics and Biochemistry, Yale University, West Haven, Connecticut, United States; [2]Microbial Sciences Institute, Yale University, New Haven, Connecticut, United States; [3]Department of Molecular, Cellular and Developmental Biology, Yale University, New Haven, Connecticut, United States; [4]Department of Chemistry, Yale University, New Haven, Connecticut, United States; [5]Department of Biomedical Engineering, Yale University, New Haven, Connecticut, United States; [6]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, United States; [7]Department of Electrical and Computer Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States; [8]Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; [9]Present Address, Department of Molecular Biophysics & Biochemistry, Microbial Sciences Institute, Yale University, New Haven, Connecticut, United States; [10]Present Address, Department of Chemical and Biomedical Engineering, Cleveland State University, Cleveland, Ohio, United States.

Electron transfer is central to all life processes. Every living cell must get rid of a large number of electrons left behind in metabolism when nutrients convert into energy. Electron transfer in proteins occurs through either tunneling or hopping a few nanometers via inorganic cofactors. However, the common soil bacteria Geobacter sulfurreducens transfer electrons over hundreds of micrometers, to insoluble electron acceptors or syntrophic partner species. These bacteria use surface appendages called pili for extracellular electron transport, allowing them to survive in environments that lack membrane-permeable electron acceptors such as oxygen. Near room temperature, the conductivity of wild-type pili exhibits temperature dependence similar to that of metallic polymers, which recently was confirmed independently. However, the composition and structure of pili as well as the mechanism of pili conductivity has remained unclear.

I will present our recent structural, molecular and biophysical studies to identify the mechanism of metallic-like conductivity in pili. We elucidate the physical mechanism of electron transport by measuring the electrical and optical conductivity of pili from multiple mutant strains as a function of molecular length, temperature, frequency, pH and stacking. We demonstrate that intrinsic conductivity of individual pili can be accurately described by nearest-neighbor, tight-binding model as predicted theoretically for quasi-one-dimensional materials. To determine the molecular architecture responsible for conductivity, we are using a suite of complementary experimental and computational methods such as molecular dynamics, x-ray diffraction and near-atomic resolution cryo-electron microscopy. Our studies suggest a pi stacking-like interaction in pili, that can cause intermolecular electron delocalization, conferring metallic conductivity to pili. Furthermore, increasing p-stacking in pili improves their crystallinity, yielding a longer mean free path for electrons, and stronger electronic coupling in pili which is 1000 times higher than other proteins or DNA. Pili thus represent a new class of electronically functional proteins that can transport electrons at rates and distances unprecedented in biology. These findings will help development of genetically programmable biomolecular materials with tunable functionality through precise control of their electronic and protein structure.

9:30 AM BM02.05.04
Long Range Electron and Ion Conduction Across Protein-Based Free-Standing Thin Films Nadav Amdursky; Schulich Faculty of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel.

Biological charge transfer processes are mostly based on the controlled diffusion of charges (electrons, protons, ions) across specific pathways within proteins over distances of <100 nm. Rather recently, long electron transfer has been found in bacterial wires for distances of few μm's, which is probably also mediated by proteins. With this biological inspiration, we report here on the formation of free-standing films that were formed from the serum albumin protein, which were bioinspired functionalized to exhibit efficient electron transport on the centimeter length scales. Furthermore, we show that the protein-based films can be functionalized in a different way for the formation of efficient ionomers with measured ionic conduction of >5 mS/cm at room temperature. Our formed films have attractive mechanical properties, with a high elastic modulus of ~160 MPa, but at the same time they are highly stretchable, capable of stretching more than 4 times their length. They have high resistance to harsh organic solvents and acids, they are very easy to form, and have a very low price tag with materials cost of around a $1/cm^2. We believe that our newly formed films can be used as a universal scientific test bed for exploring protein-based long range conduction, and even can find themselves in various applications, from biomedical ones all the way to membranes for fuel cells.

9:45 AM BREAK

10:15 AM BM02.05.05
***Ab Initio* Study of the Electronic Structure of an Entire Blue-Copper Protein** Carlos Romero Muñiz[1, 2], Maria Ortega[1], Guilherme Vilhena[1, 3], Juan Carlos Cuevas[1, 2], Rubén Pérez[1, 2] and Linda Angela Zotti[1, 2]; [1]Universidad Autónoma de Madrid, Madrid, Spain; [2]Condensed Matter Physics Center

(IFIMAC), Madrid, Spain; [3]University of Basel, Basel, Switzerland.

We present a combined theoretical study of density functional theory and molecular dynamics simulations of a copper-binding protein azurin from Pseudomonas aeruginosa and some selected mutants. Contrary to previous studies where only the copper complex and its surroundings were considered, we here analyzed, for the first time, the whole structure of the protein. We found that the peripheral part actually also plays an important role in the electronic structure at energies close to the Fermi level [1]. Furthermore, our results are in good agreement with recent experiments [2]. We also explored the role of thermal fluctuations and how they affect both the geometrical conformation and the electronic structure.

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10:30 AM BM02.05.06
Transistor Configuration Yields Energy Level Control in Protein Electronics Ben Kayser, Jerry A. Fereiro, Cunlan Guo, Sidney Cohen, Israel Pecht, Mudi Sheves and David Cahen; Weizmann Institute of Science, Rehovot, Israel.

A great effort has been made in recent years to incorporate proteins as functional components in electronic junctions [1]. A number of studies report the surprising efficiency of electron transport (ETp) in proteins, as well as temperature-independent conductance over distances of up to ~ 10 nm, calling into question the applicability of known ETp mechanisms to these systems. From molecular and organic electronics we know that the positions of the molecule's frontier energy levels, relative to the electrodes' Fermi level (E_F), play a key role in charge transport. In protein electronics, very little is known about these energy levels; to make things worse, the leading "normal" method to determine these levels, photoemission spectroscopy has not yet been applied successfully to protein monolayers.

Gating measurements provide an ideal platform to study energy levels by means of modulating the positions of the frontier orbitals, relative to those of the electrodes. However, geometric considerations make implementing a gate in protein-based junctions challenging, primarily due to the difficulty in binding proteins inside nano-gaps.

Here we report a new method that does allow for gating of proteins, and in a highly reproducible manner, to provide an energy level description of ETp in Azurin (a blue copper, bacterial electron-transfer protein). Drain and gate gold (Au) electrodes are separated by ~ 80 nm, on a SiO_2 substrate (fabricated by electron-beam lithography), with an AFM tip acting as the source. Source-drain current-voltage measurements at different gate bias, and gate-bias sweeps at low source-drain bias, show reversible gate-induced conductance in Azurin. Current onset was observed only at positive V_G, indicating that transport in Azurin is dominated via the tail of the LUMO. The importance of Cu(II) in Azurin for ETp was tested by comparing measurements with Apo-Azurin, i.e., Cu- depleted Azurin. The results emphasize the contribution of the Cu(II) ions towards energy alignment for efficient ETp.

Comparing gating measurements performed with an Au and a Pt AFM tip as source, shows that a lower V_G is required to induce a current onset in Azurin with Au than with Pt tips. Furthermore, the difference in measured work function of Au and Pt electrodes, served as reference to calibrate V_G with the energy level shift in eV. Thus, we evaluate *quantitatively* the energetic distance from the Fermi level to the LUMO tail. Calibrating the energy in this way has not previously been done and opens new opportunities to study the energetics involved in protein-based electronic devices. In our case, the tail of the LUMO was found to only be an energetic distance of ~ 100 meV from the E_F of the electrodes, possibly explaining the high efficiency ETp that has been reported in Azurin previously.

[1] Bostick, et al., Protein bioelectronics: a review of what we do and do not know. *Reports on Progress in Physics* **2018**, *81*, 026601.

10:45 AM BM02.05.07
Electrochemical and Spectroscopic Study of Peptide-Templated Eumelanin Pigments Zhen Tian and Young Jo Kim; Department of Chemical Engineering, University of New Hampshire, Durham, New Hampshire, United States.

Eumelanin, as a subset of melanins is a type of biological pigments and is widely present in living organisms. Eumelanins are synthesized in the melanocytes by templated autoxidative polymerization using 5,6-dihydroxyindole carboxylic acid (DHICA) and 5,6-dihydroxyindole (DHI). Molecular subunits are formed into oligomeric macromolecules that p-stacked into microstructures. Despite the chemical similarity of subunits, it is challenging to reproduce eumelanins in a synthetic way due to the absence of templates. Research herein focuses on synthesizing biologically-derived melanins with various topographies and examine structure-property relationship. Microscopic structures of melanins are controlled by the templates made of tripeptides sequences. Three types of peptides including aspartic acid (D), phenylalanine (F), and tyrosine (Y) are self-assembled with various sequences to form distinct templates, which can formulate melanins into fibrous or sheet-like microstructures. These class of melanin electrodes with tunable microstructures would serve as the next generation biodegradable charge storage materials that can power various types of biomedical electronics devices. Microstructures are characterized using scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area measurement. Electrochemical performance of electrodes are examined by cyclic voltammetry and chronopotentiometry within aqueous electrolytes containing either Na+ or Mg2+. Structural changes along with chemical signatures are analyzed by fourier transform infrared and raman spectroscopy after coordinating with cations.

11:00 AM DISCUSSION SESSION

SESSION BM02.06: Materials and Systems for Bio-Inspired and Bio-Compatible Electronics
Session Chairs: Irene Diaz-Moreno and Wenjing Hong
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Independence East

1:30 PM *BM02.06.01
Peptides as Bio-Inspired Electronic Materials and Sensing Motifs Andrew Abell[1, 2], John Horsley[1, 2] and Jingxian Yu[1, 2]; [1]University of Adelaide, Adelaide, New South Wales, Australia; [2]Centre for Nanoscale BioPhotonics, Adelaide, South Australia, Australia.

Bio-inspired molecular electronics is a particularly intriguing paradigm, as charge transfer in proteins/peptides, for example, plays a crucial role in energy storage and conversion processes in all living organisms. However, the structure and conformation of even the simplest protein is complex, and as such, model synthetic peptides containing well-defined geometry and pre-determined functionality, present as ideal platforms to mimic nature for the elucidation of fundamental biological processes, while also advancing the design and development of single-peptide electronic components and other devices.
We present studies on intramolecular electron transfer in synthetic peptides of well-defined helical conformation and also ill-defined geometry, using electrochemical techniques and constrained density functional theory simulations. Two definitive electron transfer pathways are apparent, the nature of which is dependent on secondary structure. Electrochemical results indicate that peptides constrained by either Huisgen cycloaddition, ring-closing metathesis or lactam-bridge exhibit remarkable positive formal potential shifts (> 460 mV) and significant electron transfer rate constant drops (up to 15-fold), which represent two distinct electronic 'on/off' states. The additional backbone rigidity imparted by the side-bridge constraints leads to an increased reorganization energy barrier to restrict the torsional motions necessary for facile intramolecular electron transfer along the backbone. A clear mechanistic transition from hopping to superexchange, stemming from side-bridge gating, is apparent. The electronic properties of peptides can be fine-tuned through both structural and chemical manipulation, to reveal an interplay between backbone rigidity and electron rich side-chains on electron transfer. The side-bridge constraints provide an additional electron transport pathway, to provide two distinct forms of quantum interferometers. The effects of destructive quantum interference occur essentially through the backbone and the additional tunnelling pathway provided by the side-bridge in the constrained β-strand peptide, as evidenced by a correlation between electrochemical measurements and molecular junction conductance simulations for both linear and constrained β-strand peptides. In contrast, an interplay between quantum interference effects and vibrational fluctuations is revealed in the linear and constrained helical peptides.
Collectively, these findings not only augment our fundamental knowledge of charge transfer dynamics and kinetics in peptides, but also open up new avenues to design and develop functional bio-inspired electronic devices, such as on/off switches and quantum interferometers, for practical applications in molecular electronics. These studies also provide an opportunity to develop peptide-based sensors for detecting biological Zn^{2+} and also protein-protein interactions, aspects of which will also be discussed.

2:00 PM *BM02.06.02
Mechano-Adaptable Electrodes for *In Vivo* Electrophysiological Interfacing Xiaodong Chen; Nanyang Technological University, Singapore, Singapore.

Polymeric microelectrode arrays are emerging as a new generation of biointegrated microelectrodes to transduce original electrochemical signals in living tissues to external electrical circuits, and vice versa. So far, the challenge of stretchable polymeric microelectrode arrays lies in the competition between high stretchability and good electrode–substrate adhesion. The larger the stretchability, the easier the delamination of electrodes from the substrate due to the mismatch in their Young's modulus. Here, I will present our recent work on designing mechano-adaptable electrodes and their application for conformally recording the electrocorticograph signals from rats.

2:30 PM BREAK

3:30 PM *BM02.06.03
Dynamic Materials Inspired by Cephalopods Alon Gorodetsky; University of California, Irvine, Irvine, California, United States.

Cephalopods, e.g. squid, octopuses, and cuttlefish, have captivated the imagination of both the general public and scientists for more than a century due to their visually stunning camouflage displays, sophisticated nervous systems, and complex behavioral patterns.[1] Given their unique capabilities and characteristics, it is not surprising that these marine invertebrates have emerged as exciting models for novel materials and systems. Within this context, our laboratory has developed various cephalopod-derived and cephalopod-inspired materials with unique functionalities.[2-4] Our findings hold implications for next-generation adaptive camouflage devices, sensitive bioelectronic platforms, and advanced renewable energy technologies.

References
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[3] D. D. Ordinario *et al.*, Bulk protonic conductivity in a cephalopod structural protein. *Nat. Chem.* **6**, 596–602 (2014).
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4:00 PM *BM02.06.04
Single Molecule Detection of Markers with a Label-Free Bio-Electronic Sensor Luisa Torsi[1], Eleonora Macchia[1], Kyriaki Manoli[1], Brigitte Holtzed[1], Cinzia Di Franco[2], Matteo Ghittorelli[3], Fabrizio Torricelli[3], Domenico Alberga[2], Giuseppe F. Mangiatordi[2], Gerardo Palazzo[1] and Gaetano Scamarcio[2]; [1]Chemistry, Università degli Studi di Bari Aldo Moro, Bari, Italy; [2]Università degli Studi di Bari Aldo Moro, Bari, Italy; [3]Università degli Studi di Brescia, Brescia, Italy.

Label-free single-molecule detection has been achieved so far by funnelling a large number of ligands into a sequence of single-binding events with few recognition elements host on nanometric transducers. Such approaches are inherently unable to sense a cue in a bulk milieu. Conceptualizing cells' ability to sense at the physical limit by means of highly-packed recognition elements, a millimetric sized field-effect-transistor is used to detect a single molecule. To this end, the gate is bio-functionalized with a self-assembled-monolayer of trillions of capturing anti-Immunoglobulin-G and is endowed with a hydrogen-bonding network enabling cooperative-interactions. The selective and label-free single-molecule IgG detection is strikingly demonstrated in diluted saliva while 15 IgGs are assayed in whole serum. The suggested sensing mechanism triggered by the affinity binding event, involves a work-function change that is assumed to propagate in the gating-field through the electrostatic hydrogen-bonding network. The proposed immunoassay platform is general and can revolutionize the current approach to protein detection.

4:30 PM BM02.06.05
Fast Dissolving Transient Electronics Incorporating Peptide Insulator Seok Daniel Namgung[1], Min-Kyu Song[1], Taehoon Sung[1], Jaehun Lee[2], Misong Ju[2], Ki Tae Nam[2] and Jang-Yeon Kwon[1]; [1]School of Integrated Technology, Yonsei University, Incheon, Korea (the Republic of); [2]Department of Material Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Transient electronics has been suggested as one of the formats of human implantable devices, since the device disappearing within human body at programmed time may reduce risk of immune response or inflammation caused by remaining rigid electronic components. There have been many demonstrated applications including biosensors, circuits, memories, RF antennas and etc, in which silicon dioxide (SiO_2) has been frequently used as an insulator. However, SiO_2 still has limit on slow dissolution rate and it may cause inflammation at the targeted organ. Toxicity issue, also, can arise because insulator is the largest part of device, and the absolute amount of insulator might exceed appropriate range, as a device is expanded to circuit application. From this context, we suggest specific tyrosine-based peptide sequence, Tyr-Tyr-Ala-Ala-Cys-Ala-Tyr-Tyr (YYACAYY), as an insulator component, since it has high biodegradability, intrinsic biocompatibility, and previously shown high dielectric constant.
In this report, we fabricated biocompatible and biodegradable thin film transistors (TFTs) consisting of tungsten (W) conductor, zinc oxide (ZnO) semiconductor and peptide insulator. The device structure is bottom gate top contact, in which 100 nm-thick W and 30 nm-thick ZnO are patterned using shadow mask, and 400 nm-thick YYACAYY peptide that is dissolved in trifluoroacetic acid(TFA) is spin-coated. The device shows field effect mobility of ~21.80 $cm^2V^{-1}s^{-1}$ and ON/OFF current ratio of ~10^5, which are comparable to SiO_2 based TFT. The device further dissolves at 37 ºC in bio-fluids such as deionized water, phosphate-buffered saline (PBS, pH~7.4) and bovine serum, and it is optically observed that all the device components dissolve within 12 hours, which is faster than that of SiO_2 based TFT. The fast dissolution is attributed to peptide film, and dissolution rate of the film at 37 ºC in deionized water is ~1300 Å/m, which is ~20,000 times faster than that of e-beam deposited SiO_2 that is previously reported. Mechanism on dissolution of peptide film is inspected through X-ray Photoelectron Spectroscopy (XPS) analysis and destruction of overall device interfaces incorporating peptide film is investigated through cross-sectional Transmission Electron Microscopy (TEM) analysis.
In conclusion, peptide insulator is newly suggested toward transient electronics as an alternative of SiO_2 insulator, in which the peptide shows advantages on high degradability, biocompatibility and high dielectric constant. Biocompatible and biodegradable TFT incorporating peptide film is further demonstrated and shows moderate device performance and fast dissolving property. This strategy to select fast dissolving material at human implantable device may significantly reduce the risk of inflammation within human body.

4:45 PM BM02.06.06
Exploring Fast Proton Transfer Events Associated with Lateral Proton Diffusion on the Surface of Membranes Nadav Amdursky; Schulich Faculty of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel.

Proton diffusion across biological membranes is a fundamental process in many biological systems, and much experimental and theoretical effort have been employed for deciphering it. Here we report on a new spectroscopic probe, which can be tightly tethered to the membrane, for following fast (ns) proton transfer events on the surface of membranes. Our probe is composed of a photoacid that serve as our light-induced proton source for the initiation of the proton diffusion process. We use our probe to follow this diffusion, and its pH-dependence, on the surface of lipid vesicles composed of either a zwitterionic headgroup, a negative headgroup, a headgroup that is composed only from the negative phosphate group or a positive headgroup without the phosphate group. We reveal that the kinetic parameters of proton diffusion are highly sensitive to the nature of the lipid headgroup, from a fast lateral diffusion at some membranes to the escape of protons from surface to bulk (and vice-versa) at others. By referring to existing theoretical models for the diffusion process of protons on the surface of membranes we found that while some of our results confirm the quasi-equilibrium model, other results are in line with the non-equilibrium model.anes for fuel cells.