Nucleic Acids at Surfaces Topical Conference
Room 2014 - Session DN-MoA

Nucleic Acids at Surfaces II

Moderator: L.J. Gamble, University of Washington

2:00pm **DN-MoA1 Counter Ion Free DNA Monolayers - Is It Possible?**, ***A. Vilan***, *D. Peled, S. Guha Ray, S. Daube, H. Cohen, R. Naaman,* Weizmann Institute of Science, Israel

It is a common knowledge that the phosphate groups of DNA are negatively charged and hence balanced by counter ions. However, using XPS we find very small amounts of cations (e.g., Na, Mg) in compact DNA monolayers self-assembled on gold, with no net charge accumulation. This remarkable observation is studied for single and double strand DNA prepared from different buffer solutions. The counter ion concentration is found to systematically decrease under improving monolayer quality, suggesting that the system gains energy by replacing the original counter ions with protons. Discussion of the experimental evidences and possible implications to naturally packed DNA properties will be given. @FootnoteText@ This research was partially supported by the Grand Center.

2:20pm **DN-MoA2 Transport of DNA in Porous Silicon-Based Microarrays by an External Potential Gradient**, ***R. Yamaguchi***, *K. Ishibashi, K. Miyamoto, Y. Kimura, M. Niwano,* Tohoku University, Japan

We have previously proposed a porous Si (por-Si) DNA microarray in which DNA hybridization can be detected on por-Si layers by infrared (IR) microspetroscopy. Since por-Si has a quite large effective surface area, we can immobilize a great number of DNA molecules in a small surface area on the array surface, which facilitate high-sensitive detection of DNA hybridization on a small area. In our previous work, we showed that DNA hybridization can be monitored through infrared absorption spectral profiles in the region of the base vibration modes. However, the disadvantage of our method is that it takes several hours to put DNA molecules into the por-Si nanopores. In this study, therefore, we have investigated a method of transporting DNA molecules through the nanopores by an externally applied potential. We utilized a tiny solution cell which is separated into two compartments by a plate of por-Si microarray. One of the compartments was filled with single stranded DNA solution, and the other was filled with pure water. We applied electrical potential between the two compartments. As a result, we found that in the presence of an external potential, DNA molecules quickly moved through the por-Si nanopores, and DNA molecules were condensed in the por-Si layers with high efficiency. This suggests that the efficiency of DNA hybridization can be improved by applying an external potential gradient to the DNA microarray.

2:40pm **DN-MoA3 The Charging Response of DNA Brushes**, ***R. Levicky***, Polytechnic University*; G. Shen, N. Tercero, P. Gong,* Columbia University

Monolayers of polynucleic acids at solid-liquid interfaces are widely encountered in biological research and medical diagnostics, and also provide versatile experimental models for elucidating the interfacial behavior of charged polymers. When a time varying potential is applied across a layer of end-tethered DNA chains, between the underlying solid support and bulk solution, the resultant capacitive charging currents provide information on layer organization as well as means for monitoring binding of analyte species in diagnostic applications. Experimental data on the capacitance of DNA monolayers have been obtained over a range of ionic strengths and chain coverages, and interpreted in terms of monolayer organization using concepts from polymer science and a modified Gouy-Chapman theory of double layer capacitance. Retention of counterions by the monolayers manifests as a decreased susceptibility of the capacitance to the external salt environment. Moreover, the charging response exhibits signatures of structural reorganization whereby the DNA strands stretch or relax with changes in solution ionic strength. A method for non-destructive electrochemical quantification of strand coverage, based on shifts in the reduction potential of redox-active counterions associated with the monolayer, was also developed. The shifts are partially an outcome of electrical work needed to bring additional counterions into the monolayer, against a concentration gradient, in order to preserve monolayer electroneutrality when its counterions are reduced.

3:00pm **DN-MoA4 Electrostatic Forces at the Liquid-Solid Interface: Biochips**, ***B.M. Pettitt***, University of Houston

Interfaces between disparate phases of matter offer large electrostatic field and density gradients changing the local free energy surface and therefore form a challenging set of problems in current chemical physics. Experiments on DNA microarrays have revealed substantial differences in hybridization thermodynamics between DNA free in solution and surface tethered DNA. We have developed a mean field model of the Coulomb effects in 2-D DNA arrays to understand the binding isotherms and thermal denaturation of the double helix. We find that the electrostatic repulsion of the assayed nucleic acid from the array of DNA probes dominates the binding thermodynamics and thus causes a Coulomb induced blockage of the hybridization. The results explain the effects observed in DNA microarrays: dramatic decrease of the hybridization efficiency and the thermal denaturation curve broadening as the probe surface density grows. We demonstrate application of the theory for evaluation and optimization of the sensitivity, specificity and the dynamic range of DNA array devices.

3:20pm **DN-MoA5 DNA Conformation on Surfaces Measured by Fluorescence Self-Interference**, ***B.B. Goldberg***, *L. Moiseev, C.R. Cantor, A.K. Swan, M.S. Unlu,* Boston University **INVITED**

The conformation of DNA molecules tethered to the surface of a microarray may significantly affect the efficiency of hybridization. Although a number of methods have been applied to determine the structure of the DNA layer, they are not particularly sensitive to variations in the shape of DNA molecules. Here we describe the application of a novel interferometric technique called Spectral Self-Interference Fluorescence Microscopy (SSFM) to the precise measurement of the average location of a fluorescent label in a DNA layer relative to the surface and thus determine specific information on the conformation of the surface-bound DNA molecules. Using SSFM we have estimated the shape of coiled single-stranded DNA, the average tilt of double-stranded DNA of different lengths, and estimated the amount of hybridization. The data provide important new proofs of concept for the capabilities of novel optical surface analytical methods of the molecular disposition of DNA on surfaces. The determination of DNA conformations on surfaces and hybridization behavior provide information required to move DNA interfacial applications forward and thus impact emerging clinical and biotechnological fields.

4:00pm **DN-MoA7 Investigation of the Electronic Structure of Ribonucleic Acid Homo Polymer Electronic Structure, Ionization Energy and Charge Injection Barriers to Inorganic Materials**, ***J.P. Magulick***, *Y. Yi, M.M. Beerbom, R. Schlaf,* University of South Florida

We employed electrospray thin film deposition in concert with photoemission spectroscopy (PES) to investigate the electronic structure of ribonucleic acid (RNA) homo polymers, and their interfaces to inorganic materials such as highly oriented pyrolytic graphite (HOPG) and Au. In these measurements RNA homopolymers were injected directly from solution into a high vacuum chamber attached via in-situ transfer to a photoelectron sprectroscopy chamber. This enabled the preparation of clean RNA thin films in multi-step deposition sequences starting out at initial sub-monolayer thicknesses to investigate the details of interface formation. The final multi-layer thickness of the films gave insight into the bulk electronic structure. After each deposition step the samples were characterized with PES without breaking the vacuum. Our results indicate distinctly different ionization energies and charge injection barriers between purines and pyrimidines. Purine homopolymers have an ionization energy of about 6-7 eV while pyrimidine homopolymers exceed 8 eV. In order to further investigate these differences, we also investigated the electronic structure of the isolated backbone, and the individual nucleobases using the same experimental protocol. These results gave insight into the.

4:20pm **DN-MoA8 Electrical Manipulation of DNA on Metal Substrates: Electric Interactions, Molecular Dynamics, and Implications of Hydrodynamic Flow**, ***U. Rant***, Walter Schottky Institute, Tech. Univ. Munich, Germany*; K. Arinaga,* Walter Schottky Institute, Germany & Fujitsu Labs Ltd., Japan*; C. Hautmann, S. Scherer, E. Pringsheim,* Walter Schottky Institute, Tech. Univ. Munich, Germany*; S. Fujita, N. Yokoyama,* Fujitsu Labs Ltd., Japan*; M. Tornow, G. Abstreiter,* Walter Schottky Institute, Tech. Univ. Munich, Germany

We present experimental investigations addressing the response of surface-tethered oligonucleotides to electric fields at the metal/solution interface. By applying AC potentials to the supporting gold substrates, the

DNA layer conformation can be efficiently modulated using driving frequencies ranging up to the kHz regime. Simultaneously, optical energy-transfer methods are employed to monitor the layer structure in-situ and in real-time. We discuss electric interactions between the charged substrate and the DNA and elucidate how the manipulation efficiency is determined by the electrode bias and electrolyte screening effects. Time-resolved measurements reveal intriguing molecular dynamics of nucleic acids in surface-confined fields and are compared to hydrodynamic simulations. In addition, we show the implications of lateral hydrodynamic flow on the DNA layer structure. The presented results are expected to be generally representative for charged polymers exposed to short-ranged electric fields at surfaces, and, moreover, are of significant importance for the design of a novel type of actively controlled biosensors based on switchable DNA layers.

4:40pm **DN-MoA9 Achieving Reliable Microarray Analysis Results Using Competitive Hybridization***, **A. Chagovetz**, L. Williams, J. Bishop, S. Blair,* University of Utah

As microarrays migrate from detection of dissimilar analytes to the detection of analytes that have only a single to a few base mismatches, surface hybridization may become competitive. We have simulated competitive hybridization using a finite element analysis model. Our results show that observed dynamic range between the complement and its competitors increases with temperature because of enhanced dissociation of the mismatch target, assuming thermodynamic equilibrium is not reached. Additionally, competitive hybridization can be enhanced by decreasing the immobilized probe concentration on the surface of the substrate. Using the two observations above we propose two different analysis methods for hybridization experiments, one which applies to end-point analysis and the other which is for real-time analysis. The first method uses a labeled multianalyte sample, while the second method is a novel label-less detection mechanism for multianalyte samples. By introducing a label target that is known to be of a lower affinity than the targets to be investigated we can watch the dissociation of the lower affinity species and predict the concentration of the complement. This is verified experimentally using a microscale array of individually controlled heating elements. The heater array was developed at Sandia National Laboratories, using surface micromachining technology.

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