

Wednesday Morning, October 17, 2007

Surface Science

Room: 611 - Session SS2+EM+TF-WeM

SAMs and Organic Films I

Moderator: H. Fairbrother, Johns Hopkins University

8:00am **SS2+EM+TF-WeM1 Scanning Tunneling Microscopy Growth Study of a Columnar Liquid Crystalline Hexaazatriphenylene Derivative on Au(111)**, *S.D. Ha*, Princeton University, *Q. Zhang*, *S. Barlow*, *S.R. Marder*, Georgia Institute of Technology, *A. Kahn*, Princeton University

The growth of a discotic liquid crystal derivative of tris(thieno)hexaazatriphenylene (THAP) is studied with scanning tunneling microscopy (STM). An electron transport material with relatively high electron affinity (4.59eV), THAP is expected to form columnar stacks in a thick bulk film. It is shown with STM that on Au(111), the first four monolayers of THAP molecules order in such columnar mesophases. The first monolayer forms a square $10.1\text{\AA} \times 10.1\text{\AA}$ unit cell with one molecule per cell. However, this is much smaller than expected, and it may be due to buckling caused by the substrate interaction or in-plane molecule-molecule interaction. The second monolayer, at partial coverage, grows commensurate to the first monolayer in a rectangular herringbone with two molecules per $15.7\text{\AA} \times 14.0\text{\AA}$ unit cell. The molecules tilt in order to conform to the packing of the first layer and the interlayer interaction controls the molecular orientation. Yet upon full coverage of the second monolayer, the intralayer interaction prevails and the molecules reorganize into a hexagonal close-packed (HCP) structure without obvious tilt. The unit cell is rhomboidal with dimensions $21.0\text{\AA} \times 22.2\text{\AA}$ and one molecule per cell. Moreover, the rotational orientation of the molecules forms a herringbone pattern, with alternating rows of the HCP structure switching between two opposite orientations. As for the third and fourth monolayers, STM images indicate that they have HCP geometry with the same dimensions as the second layer. Given the tendency of molecules similar to THAP to stack into columns, it is likely that because the third and fourth layers have the same in-plane structure as the second layer, they are commensurate to the latter. Thus, on Au(111), THAP readily grows in the expected columnar liquid crystal fashion directly from the interface layer, and the columns are hexagonal close-packed with negligible molecular tilt.

8:20am **SS2+EM+TF-WeM2 UHV-STM Studies of DNA Bases on Au(111)**, *W. Xu*, *R. Otero*, *M. Schock*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark, *R. Kelly*, *L. Kantorovich*, King's College London, UK, *F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

The self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has recently attracted much attention as on one hand, such studies provide invaluable insight into fundamental interactions between these molecules. On the other hand, NA base molecules and DNA molecules are particularly interesting as promising building blocks for the bottom-up fabrication of functional supramolecular nanostructures on surfaces within the emerging area of nanotechnology. From a biological point of view, the self-assembly processes in DNA and RNA molecules are controlled by i) cross-strand interactions between NA base molecules, which are dominated by hydrogen bonds (H-bonds), ii) stacking interactions between NA base molecules along the strand, and iii) the interactions of NA base molecules with water molecules and metal ions, such as Na^+ , K^+ . Among these interactions, the hydrogen bonding between NA base molecules plays a crucial role in determining the conformation and biochemical properties of DNA and RNA molecules. Hence, it is important and interesting to study the fundamental interactions between NA base molecules at the single molecule level to reveal the exact physicochemical nature of the biological systems. Here we will show our recent experimental progress on four individual NA base molecules (guanine, adenine, cytosine, thymine) that are adsorbed on Au(111) surface under Ultrahigh Vacuum (UHV) conditions. We demonstrate by variable-temperature scanning tunnelling microscopy (VT-STM) experiments that guanine and adenine form 2D island with well-ordered structures through hydrogen bonds, and the so-called guanine quartet structure is found to be stabilized by the cooperative hydrogen bonds. Interestingly, cytosine only forms disordered 1D filamentary structure by fast cooling the sample, whose behavior could be described as a 2D organic glass. Thymine in the first stage (low surface coverage) also forms 1D filamentary structure steered by hydrogen bonds. However, when the surface coverage is increased, the filaments could merge into 2D well-

ordered islands by van der Waals (vdW) interactions. Moreover, we have also investigated that the thymine 2D island can be broken back into the 1D hydrogen bonded filaments by STM manipulation, which further confirm that we are able to directly probe the hierarchy of bond-strengths involved in the surface self-assembly of multifunctional organic molecules with highly anisotropic interactions.

8:40am **SS2+EM+TF-WeM3 Understanding Molecular Exchange on Surfaces: Controlling and Elucidating the Mechanism of 1-Adamantathiolate Monolayer Displacement**, *H.M. Saavedra*, *T.J. Mullen*, *C.M. Barbu*, The Pennsylvania State University, *A.A. Dameron*, University of Colorado, *V.H. Crespi*, *P.S. Weiss*, The Pennsylvania State University

We have investigated the solution-phase displacement kinetics of 1-adamantanethiolate self-assembled monolayers on Au{111} by n-dodecanethiol molecules using infrared spectroscopy, scanning tunneling microscopy, x-ray photoelectron spectroscopy and electrochemical desorption. The displacement reaction can be described by the fast insertion of n-dodecanethiolate at defects in the original 1-adamantanethiolate monolayer, which nucleates island growth and is followed by eventual slow ordering of the n-dodecanethiolate domains. Langmuir-based kinetics, which describe alkanethiolate adsorption on bare Au{111}, fail to describe this displacement reaction. Instead, a Johnson-Mehl-Avrami-Kolmogorov model of perimeter-dependent island growth yields good agreement with kinetic data obtained over a hundred-fold variation in n-dodecanethiol concentration. Analysis on a model-free basis suggests that displacement is a scale-free process within this concentration regime. The crucial role of the adsorbate lattice, along with the thermodynamic driving forces, rationalizes the rapid and complete displacement of 1-adamantanethiolate monolayers and explains why other monolayers reach kinetic traps that result in slow and incomplete displacement.

9:00am **SS2+EM+TF-WeM4 Thermal Treatment of Glutamic Acid Etched Ni Nanoclusters on Au{111} Leads to the Formation of 1-D Metal Organic Co-Ordination Networks**, *A.G. Trant*, *T.E. Jones*, *C.J. Baddeley*, University of St Andrews, UK

The adsorption of glutamic acid onto 2-D Ni clusters on Au{111} has been investigated using reflection absorption infrared spectroscopy (RAIRS) and scanning tunnelling microscopy (STM). Adsorption at 300 K leads to two distinct adsorbate species which we conclude are zwitterionic species adsorbed either at Ni-like sites in the centre of the clusters or at interfacial sites at the edges of clusters. Adsorption of (S)-glutamic acid causes the complete destruction of clusters of initial diameter <3 nm. We conclude that the Ni islands have been corroded resulting in the formation of a Ni salt - presumably nickel (II) glutamate. On annealing to 350 K, chains of 1-D molecular features are observed in STM experiments. We discuss the possible composition and structure of this salt and conclude that the chains most likely consist of nickel (II) pyroglutamate. Metal pyroglutamate salts are known to be produced by heating glutamate salts. The intermolecular bonding and azimuthal alignment of the 1-D chains are discussed. We also report the formation of analogous networks from Ni + (R)-glutamic acid and discuss the influence of stereochemistry on the structure of the networks.

9:20am **SS2+EM+TF-WeM5 Crossover from Site-Sensitive to Site-Insensitive Adsorption of the Fullerene Derivative PCBM on Au(111) due to Hydrogen-Bond Formation**, *D. Ecija*, *R. Otero*, Univ. Autonoma de Madrid, Spain, *L. Sanchez*, Univ. Complutense de Madrid, Spain, *J.M. Gallego*, Inst. de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *Y. Wang*, *M. Alcami*, *F. Martin*, Univ. Autonoma de Madrid, Spain, *N. Martin*, Univ. Complutense de Madrid, Spain, *R. Miranda*, Univ. Autonoma de Madrid, Spain

The 2D arrangement of organic adsorbates at solid surfaces results from a combination of non-covalent intermolecular forces with molecule-substrate interactions. It is generally thought that molecule-substrate interactions determine adsorption geometry and conformation in first place, while intermolecular interactions affect the subsequent self-assembly of the adsorbates. Only when the molecules can form strong directional bonds, like hydrogen bonds or coordination bonds, and the corrugation of the adsorption potential energy is small, the supramolecular structure is dominated by intermolecular interactions. On the other end of the spectrum, vicinal or heterogeneous surfaces show a strong selectivity in the adsorption site of the adsorbates, leading to a final morphology which is almost exclusively substrate-controlled (templated growth). Usually, the role of molecule-substrate interactions on self-assembly is discussed at the single-molecule level, but this is strictly speaking just an approximation, since the formation of intermolecular bonds might modify the adsorption geometry

and thus molecule-substrate interactions. For systems showing site-selective adsorption, the modification of the adsorption geometry upon intermolecular bond formation might result in the removal of the site-selectivity. By means of variable-temperature Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) calculations, here we investigate the crossover from site-selective to site-insensitive adsorption of PCBM, a C₆₀ derivative, on the herringbone-reconstructed Au(111) surface as a function of the coverage. Whereas at low coverages PCBM self-assembly is dictated almost exclusively by the substrate-related preference for nucleating at the fcc sites of the reconstruction, with a selectivity close to 100%, at higher coverages intermolecular interactions take over the substrate influence, giving rise to PCBM islands that extend through fcc, hcp and dislocations of the herringbone reconstruction. Comparison with theoretical calculations offers the following picture of this crossover: at high-enough coverages hydrogen bonds between double rows are formed that modify the adsorption geometry of PCBM molecules, which in turn removes site-selectivity. The phenomenon of intermolecular interaction-driven modification of the adsorption geometry might thus be crucial to optimize the templating effect of surface nano-scale patterns on adsorbed organic overlayers.

9:40am **SS2+EM+TF-WeM6 Nanostructured Binary Molecular Films: Lessons from ACA:C₆₀ Mixtures**, *J.E. Reutt-Robey*, University of Maryland, *B. Xu*, Yanshan University, China, *C.G. Tao*, University of Maryland, *D.B. Dougherty*, National Institute of Standards and Technology, *W. Jin*, University of Maryland

Multi-component aromatic molecular films are of increasing interest in photovoltaic technologies and other organic electronic applications. Binary organic films offer the potential to tailor film structure on the nanoscale to optimize device performance through phase selection, domain size, distribution and orientation. A basic understanding of the factors that control structure in binary molecular films is thus important to advance these materials technologies. We report STM-studies of structure evolution in model donor-acceptor systems, such as ACA:C₆₀ and Pentacene:C₆₀. Films prepared by sequential physical vapor deposition onto Ag(111) substrates under UHV are monitored directly with an integrated UHV-STM. We demonstrate how ACA:C₆₀ film growth conditions can be adjusted to selectively fabricate films that range from phase-separated hexagonal -C₆₀ and chain-phase [4 0, 2]-ACA domains to intermixed co-crystalline chiral domains comprised of C₆₀-terminated ACA pinwheels. Films produced with arbitrary composition generally lead to complex multi-phase structures. Predeposited ACA films with single phase structures provide the most effective pathway to single phases of intermixed structures. For example, the intermixed chiral phase is only accessible from the 2-D ACA molecular gas, whereas extended C₆₀ chain structures may be accessed only from the dimer-phase [12 2, 6 5]-ACA domains. We apply lessons from the ACA:C₆₀ system to Pentacene:C₆₀ mixtures, utilizing the 2-D pentacene gas to access an intermixed honeycomb Pentacene:C₆₀ phase.

10:40am **SS2+EM+TF-WeM9 Detection of Gaseous Nitric Oxide Using X-ray Photoelectron Spectroscopy**, *M. Dubey*, *J. Schwartz*, *S.L. Bernasek*, Princeton University

Detection of gaseous nitric oxide (NO) in biological systems has attracted significant attention since the identification of NO as the endothelial-derived relaxing factor (EDRF).¹ NO also acts as a signal molecule in the nervous system, and is associated with the presence of infection and Alzheimer's and other diseases. Apart from biological systems, NO is a main product released on the pyrolysis of nitro-organic explosives. For these reasons, much work has been done in the field of NO detection, and the need for a sensitive detector is evident. In this study, we report a direct and a highly sensitive technique to detect gaseous NO using X-ray Photoelectron Spectroscopy (XPS). The binding of NO by heme proteins is well understood,² and we have utilized it for detection. We have developed a reliable method to grow Self-Assembled Monolayers (SAMs) of alkylphosphonic acids on oxide surfaces.³ This platform is used to covalently attach a uniform layer of an iron heme-like molecule, which was synthesized separately. Differential charging in XPS has been used to ascertain the uniformity of the organic film.⁴ The N1s signal from the heme ligand was measured by XPS before and after exposure to NO. Before NO binds to the iron, a single nitrogen peak is present, attributed to the nitrogens of the porphyrin ring. After reaction with NO, a new, distinct peak was observed in the high resolution N1s spectrum. This peak is at a higher binding energy (approx 5.5 eV), and is attributed to the NO bound to the iron. An estimate of the bound NO was calculated using XPS and QCM to be about 40 picomoles.

¹ R. M. J. Palmer, A. G. Ferrige, S. Moncada, *Nature*, 1987, 327, 524.

² K. R. Rodgers, *Curr Opin Chem Biol*, 1999, 3, 158.

³ E. L. Hanson, J. Schwartz, B. Nickel, M. Koch, M. F. Danisman, *J. Am. Chem. Soc.*, 2003, 125, 16074.

⁴ M. Dubey, I. Gouzman, S. L. Bernasek, J. Schwartz, *Langmuir*, 2006, 10, 4649.

11:00am **SS2+EM+TF-WeM10 An In Situ EC-STM Study of the Restructuring of Self-Assembled Monolayers upon Metal Deposition**, *C. Silien*, *M. Buck*, University of St Andrews, UK

The combination of electrochemistry and self-assembled monolayers offers interesting opportunities for nanotechnology due to high resolution defined by patterned SAMs and simplicity and scalability afforded by electrochemistry. However, control of processes such as electrochemical metal deposition on the nanometer length scale requires exact knowledge of the mutual influence of a SAM structure and electrochemical processes. Aiming for an understanding at the molecular level we report an investigation of the underpotential deposition of copper on Au(111) electrodes modified by ω -(4'-methyl-biphenyl-4-yl)-alkanethiols (H₂C-(C₆H₄)-(C₆H₄)-(CH₂)_nSH, BPn). As reported recently, this class of molecules gives rise to pronounced structural variations with length n of the alkane spacer and, for n = even, exhibits polymorphism.^{1,2} Furthermore they can be prepared to an exceptionally high structural perfection. These properties make SAMs of BPn thiols an attractive basis for further tailoring of properties of functionalized electrodes and the electrochemical generation of nanometer-scaled structures. A decisive step in SAM controlled electrometallisation is the deposition of the first layer of metal which takes place in the underpotential region. Its understanding is of crucial importance as this layer forms at the SAM-substrate interface and, therefore, affects the properties of the system. Our in situ STM investigations of the underpotential deposition reveal, firstly, pronounced differences between BPn SAMs and alkane thiols and, secondly, a pronounced influence of the length of the alkane spacer in the BPn SAMs, i.e., whether n = odd or even. The molecular resolution achieved in this study combined with time resolved monitoring of the events occurring in the course of the copper deposition allows us to highlight the relationship between the SAM structure and its influence on the generation of nanometer scaled structures by electrochemical metal deposition.

¹ Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Wilton-Ely, J. D. E. T.; Zharnikov, M.; Wöll, C. *J. Am. Chem. Soc.* 2006, 128, 13868.

² Cyganik, P.; Buck, M.; Azzam, W.; Wöll, C. *J. Phys. Chem. B* 2004, 108, 4989.

11:20am **SS2+EM+TF-WeM11 Irradiation-Promoted Exchange Reaction: A New Approach to the Fabrication of Heterogeneous Self-Assembled Monolayers and Chemical Lithography**, *N. Ballav*, *T. Weidner*, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can undergo an exchange reaction with the molecules capable of building a SAM on the same substrate upon the immersion into the respective solution. However, for most systems, the exchange reaction is very slow and incomplete at normal conditions, taking from days to weeks and occurring to a limited extent only. Using several different model systems, we show that the rate and extent of the exchange reaction can be significantly enhanced and even precisely tuned by either electron irradiation with a small dose or exposure to UV light. We assume that both electron and UV irradiation result in the appearance of structural and chemical defects in the target SAM, which promote the molecular exchange. The effect of irradiation and the parameters of the exchange reaction were monitored in detail and correlated with each other using several complementary experimental techniques. The developed approach, irradiation-promoted exchange reaction, can be considered as a platform for the preparation of heterogeneous mixed SAMs. Also, in combination with e-beam or UV-lithography, this method can be used for the fabrication of chemical patterns, including gradient ones. In this regard, the approach is similar to conventional photography: a desired pattern is initially written by electron or UV beam and later "developed" upon its immersion into the solution of a molecular substituent. There are no principal limitations for the form of the fabricated features while the characteristic length scale can be varied in a broad range from centimetres to several tens of nanometers.

11:40am **SS2+EM+TF-WeM12 Calcium Adsorption on Regioregular Poly(3-hexylthiophene): Synchrotron Radiation Photoemission and Microcalorimetric Studies**, *J.F. Zhu*, *W. Zhao*, *W.H. Zhang*, University of Science and Technology of China, *J. Farmer*, *C.T. Campbell*, University of Washington

The adsorption of Ca on the regioregular poly(3-hexylthiophene) (rr-P3HT) thin film surfaces at 300 K has been studied using synchrotron radiation photoemission spectroscopy, adsorption microcalorimetry and atomic beam/surface scattering. The polymer films were spin-coated on the Si wafers with typical thickness of > 100 nm and were free of oxygen contamination as clarified by both X-ray photoelectron spectroscopy and Auger electron spectroscopy. Synchrotron radiation photoemission spectroscopy provides precise experimental information on the alteration of the Ca/polymer interfacial energy level line-up and the chemical nature at this interface. The deposition of calcium on the rr-P3HT film at room temperature induced a decrease of the work function, indicating Ca donates electron density to the polymer substrate. Moreover, Ca adsorption led to the depression of the bands of the rr-P3HT. The strength of interaction

between Ca and the rr-P3HT is probed by both microcalorimetric heats of adsorption and sticking probability measurements.

12:00pm **SS2+EM+TF-WeM13 Supramolecular Coordination Networks at Surfaces: Self-selection and Error Correction in Multi-ligand Nanopore Arrays.** *S.L. Tait, A. Langner, N. Lin*, Max Planck Institute for Solid State Research, Germany, *C. Rajadurai, M. Ruben*, Research Center Karlsruhe, Germany, *K. Kern*, Max Planck Institute for Solid State Research, Germany and Ecole Polytechnique Fédérale de Lausanne, Switzerland

Supramolecular self-assembly of organic ligands and metal centers is a topic of growing interest for efficient molecular-scale patterning of surfaces. Molecular networks can be designed to self-organize in regular, 2D nanopore lattices, whose dimensions and properties can be controlled by selection of the organic ligands. This approach offers a natural alternative to current nano-fabrication methods, allowing atomic and molecular building blocks to organize themselves into useful nanostructures, and is a model system for supramolecular and biomolecular assembly in general. We present recent results of self-assembled supramolecular networks on the Cu(100) surface, which demonstrate multi-ligand construction of 2D arrays of compartments with tunable shape and size. These binary combinations of complementary ligands represent a significant step in complexity over previous studies. Of technological interest is the capability for modular replacement of either of the two ligands to produce a range of nanopore lattice sizes and shapes in a very predictable and programmable way. Of more fundamental interest in these systems is molecular level resolution imaging using scanning tunneling microscopy, which allows an unprecedented perspective of fundamental steps to supramolecular assembly, such as structural error correction achieved by efficient molecule self-selection. Non-covalent metal—organic coordination provides room temperature stability and high structural ordering through directional and selective interactions, but also allows for bonding reversibility, enabling error correction during assembly. By selection of molecular building blocks with specific properties, we can "program" these systems to pattern a surface with homogenous networks of specific size, structure, and physical and chemical properties. The ability to tailor the size and functionality of nanometer-scale arrays produced by molecular self-assembly represents a unique opportunity for molecular recognition, heterogeneous catalysis, thin film growth, and other fields.

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