

Thursday Morning, November 1, 2012

Surface Science

Room: 22 - Session SS-ThM

Molecular Films: Chirality & Electronic Features

Moderator: A.J. Gellman, Carnegie Mellon University, S.L. Tait, Indiana University - Bloomington

8:00am **SS-ThM1 Smooth and Transparent Organic Surfaces showing Exceptional Dynamic Dewetting Behavior Toward Nonpolar Liquids ~ Oleophobicity is Independent on Length of Perfluoroalkyl Groups ~**, A. Hozumi, J. Park, D.F. Cheng, B. Masheder, C. Urata, AIST, Japan

Perfluorinated compounds such as perfluoroalkylsilanes (FASs) and related materials have been widely employed in a wide variety of engineering fields by taking advantages of their excellent hydrophobic/oleophobic properties. However, their chemical and physical effects on human health and the environment have been lately viewed with suspicion. In particular, the use of long-chain perfluorinated chemicals (LCPFCs) is going to phase out by the end of 2015. An alternative hydrophobic/oleophobic treatment method not requiring LCPFCs has been strongly demanded.

In this study, we report smooth and transparent organic surfaces showing unusual dynamic dewetting behavior toward nonpolar liquids. We prepared two different surfaces on glass slides: one, organic surfaces consisting of self-assembled monolayers (SAMs) of FASs with different chain length [CF₃(CF₂)_nCH₂CH₂Si(OR)₃, n = 0, 3, 5, 7, R=CH₃ or C₂H₅], and the other, organic surfaces derived from a mixture of FASs and tetramethoxysilane (TMOS). Oleophobicity on the former surfaces was markedly depended on the length of perfluoroalkyl chains, but the latter exhibited excellent dynamic oleophobicity toward various kinds of nonpolar liquids, independent of the length of the perfluoroalkyl chains. Due to the addition of TMOS, condensed silica species most likely acted as spacer moieties such that an appropriate distance now separated the perfluoroalkyl chains allowing them to rotate freely and confer liquid-like properties on the surface [1,2]. This leads to the exceptional dynamic dewetting behavior toward various nonpolar liquids.

[1] A. Hozumi and T. J. McCarthy, *Langmuir*, 26 (2010) 2567-2573.

[2] D. F. Cheng, C. Urata, M. Yagihashi and A. Hozumi, *Angew. Chem. Int. Ed.*, 51 (2012) 2956-2959.

8:20am **SS-ThM2 Enantioselective Separation on Chiral Au Nanoparticles**, N. Shukla, N. Khosla, N. Ondeck, A.J. Gellman, Carnegie Mellon University

Adsorption of chiral compounds on chiral surfaces is the initial step in enantioselective processes such as separations and catalysis. There has been a significant effort over the past decade aimed at the preparation of chiral nanoparticles based on metallic cores modified by chiral ligands. In principle, these can serve as the basis for enantioselective chemical processing. In this work we demonstrate a simple measurement of enantioselective adsorption on chiral metal nanoparticles using a method that can yield quantitative measures of the enantiospecific adsorption equilibrium constants [1].

The surfaces of chemically synthesized Au nanoparticles have been modified with D- or L-cysteine to render them chiral and enantioselective for adsorption of chiral molecules. Their enantioselective interaction with chiral compounds has been probed by optical rotation measurements when exposed to racemic propylene oxide. The ability of optical rotation to detect enantiospecific adsorption arises from the fact that the specific rotation of polarized light by R- and S-propylene oxide is enhanced by interaction Au nanoparticles. This effect is related to previous observations of enhanced circular dichroism by Au nanoparticles modified by chiral adsorbates. More importantly, chiral Au nanoparticles modified with either D- or L-cysteine selectively adsorb one enantiomer of propylene oxide from a solution of racemic propylene oxide, thus leaving an enantiomeric excess in the solution phase. Au nanoparticles modified with L-cysteine (D-cysteine) selectively adsorb the R-propylene oxide (S-propylene oxide). A simple model has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-PO adsorption on the chiral Au nanoparticles.

[1] N. Shukla, M.A. Bartel, A.J. Gellman "Enantioselective separation on chiral Au nanoparticles" *Journal of the American Chemical Society*, 132(25), (2010), 8575-8580

8:40am **SS-ThM3 2012 AVS Peter Mark Award Lecture: Effects of Chirality in Electron Tunneling, Molecular Excitation and Rotation**, C.H. Sykes*, Tufts University **INVITED**

Industrially, the selective conversion of prochiral reagents to chiral products is a crucial step in the production of a variety of asymmetric pharmaceuticals. While this feat is accomplished using either chiral catalysts or crystallization, many external influences have been shown to be capable of inducing such symmetry breaking including circularly polarized light, spin-polarized electrons, and combinations of unpolarized light and magnetic fields. Pioneering studies have made great strides towards explaining these various interactions, however many of the fundamental mechanisms by which chirality is transferred at the molecular-level are not yet fully understood. It is also a great challenge to design experimental setups with which to study these phenomena in a quantitative and reproducible manner. We report a simple thioether system in which symmetry breaking can be both induced and measured in situ at the single-molecule level. We demonstrate that electrical excitation of a prochiral molecule on an achiral surface produces large enantiomeric excesses in the chiral adsorbed state of up to 40%, whereas thermal annealing produces racemic mixtures as expected. These effects arise from a previously unreported phenomenon that standard polycrystalline metal scanning probe tips can possess intrinsic chirality.

Thioethers also constitute a simple, robust system with which to study molecular rotation as a function of temperature, electron energy, applied fields, and proximity of neighboring molecules. In order for molecules to be used as components in molecular machines, methods are required to couple individual molecules to external energy sources and to selectively excite motion in a given direction. Studying the rotation of molecules bound to surfaces offers the advantage that a single layer can be assembled, monitored and manipulated using the tools of surface science. We report that a butyl methyl sulfide (BuSMe) molecule adsorbed on a copper surface can be operated as a single-molecule electric motor. Electrons from a scanning tunneling microscope are used to drive directional motion of the BuSMe molecule in a two terminal setup. Moreover, the temperature and electron flux can be adjusted to allow each rotational event to be monitored at the molecular-scale in real time. The direction and rate of the rotation are related to the chiralities of the molecule and the tip of the microscope (which serves as the electrode), which again illustrates the importance of the symmetry of the metal contacts in atomic-scale electrical devices.

9:20am **SS-ThM5 Single-Site Studies of Chirality Transfer Complexes on Chirally Modified Pt(111)**, J.-C. Lemay, P.H. McBreen, V. Demers-Carpentier, G. Goubert, Y. Dong, Université Laval, Canada, B. Hammer, A.M.H. Rasmussen, L. Ferrighi, Aarhus University, Denmark, F. Masini, Université Laval, Canada

Stereoselective catalytic sites on achiral metallic surfaces may be prepared by adsorbing optically active compounds described as chiral modifiers. A fundamental understanding of the stereodirecting forces in such systems is necessary to develop more efficient enantioselective catalysts. We will present data for chirality transfer complexes formed by the chiral modifier (R)-(+)-1-(1-naphthyl)ethylamine ((R)-NEA) and pro-chiral α -phenylketone and α -ketoester substrates on Pt(111). Time-lapsed scanning tunneling microscopy allowed us to isolate individual chiral modifier/substrate complexes. The structure of the diastereomeric complexes were separately determined using DFT calculations. The extremely good convergence between the calculated structures and visual STM data, as well as supporting surface spectroscopy data, shows that prochiral steering on chirally modified Pt(111) can be followed with submolecular resolution at the reaction temperature (room temperature), thus enabling conformational, regiospecific and enantiospecific characterisation. The study reveals the contributions of steric repulsion, non-covalent attractive interactions and site-specific chemisorption to stereoinduction. We will conclude with a short description of the targeted design of new chiral modifiers.

9:40am **SS-ThM6 Chirality in Flatland: 2D Crystallization, Single-Molecule Dynamics and Unidirectional Rotors**, K.-H. Ernst, EMPA, Switzerland

A promising approach to study chiral molecular recognition is studying two-dimensional (2D) crystallization phenomena on well-defined surfaces via scanning tunneling microscopy (STM). We present studies on different

* Peter Mark Memorial Award Winner

two-dimensional chiral systems and discuss their tendency to undergo enantiomeric separation. A special surface enantiomorphism is observed via STM after adsorption of the enantiomers of a helical aromatic hydrocarbon on Cu(111). Instead of crystallization into homochiral 2D domains on the surface, racemic enantiomorphs are observed. In this situation, a small excess of one enantiomer is sufficient to create domains possessing single handedness throughout the entire surface layer. The induction of homochirality by chiral doping has also been observed for succinic acid and achiral (*R,S*)-tartaric acid. Our findings are explained by cooperative interactions between many chiral units, similar to the mechanism of chiral amplification observed in helical polymers and coined as "Sergeants-and-soldiers" principle. Another recently observed phenomenon is single enantiomorphism due to chiral conflict. Depending on the handedness of a chiral adduct to a racemic situation suppresses one enantiomorph during crystal growth, but supports the other by forming a quasiracemic solid solution. Finally, we present chirality aspects in single molecule surface dynamics, including conversion of adsorbate handedness and linear, unidirectional propulsion of a molecular car with chiral "wheels".

10:40am **SS-ThM9 Functional Molecular Layers for Energy Applications**, *R.J. Hamers*, University of Wisconsin-Madison **INVITED** Electrode materials for renewable energy applications are largely based on materials such as metal oxides and various forms of carbon because of their intrinsically high stability. However, the properties can be markedly enhanced through the integration of "smart" molecular functionalities. We have been investigating the development and application of new chemistry for fabricating novel types of electrochemically and photoelectrochemically active molecular structures on surfaces of metal oxides and on thin-film diamond. One area of interest has been the use of "click" chemistry as a versatile approach to functionalizing surfaces with redox-active molecules that can be used either as potential catalysts or as light-harvesting molecules. By using complementary functionalization on two different nanostructured oxides, it is also possible to make chemically-assembled oxide-oxide heterojunctions, such as TiO₂/SnO₂. In these cases the formation of a heterojunction can provide a built-in potential to enhance charge transfer at the interface.

A key question in these studies has been understanding how the presence of alkyl chain, ranging from ~4 atoms to ~12 atoms, impacts the electron transfer. While most previous work on molecular layers has been performed on densely packed layer on coinage metals such as gold and silver, when molecular layers are tethered to covalent materials such as diamond or metal oxides, the resulting layers have a high degree of disorder due to the mismatch between the native packing of the alkyl chains and the distribution of available surface sites. We have investigated the electron-transfer properties at these functionalized interfaces and find that the electron transfer rates are surprisingly high and only weakly dependent on the length of the alkyl chain, which we explain as a result of the increased conformational disorder. Our data suggest that the "best" molecular layers for electron-transfer applications are those that have a controlled degree of conformational disorder. We demonstrate these effects using recent measurements of electroactive Ru(bpy)-based complexes on diamond and on metal oxides.

11:20am **SS-ThM11 Atomic Study for P-type Doping Process of CuPc Molecules with STM**, *J.H. Park, K. Tyler, C.T. William, A.C. Kummel*, University of California San Diego

Metal phthalocyanines (MPc) have been widely employed as channel materials in organic thin film transistor (OTFT) for chemical vapor sensing, due to their novel gas adsorption properties. Theoretically, MPc molecules act electron donors during reaction with oxidative analytes and are the basis of their chemical sensing. However, this sensing reaction has not been understood fully. This study presents molecular scale observation of NO adsorption onto CuPc monolayers using ultra-high vacuum (UHV) scanning tunneling microscopy (STM). CuPc monolayers were deposited on Au (111) surfaces by organic molecular beam epitaxy in ultra-high vacuum (UHV) and subsequently dosed at 150 K substrate temperature with NO (5% : diluted by He of 95 %) via a supersonic molecular beam source (MBS). After dosing NO for 1 min, STM images reveal small NO chemisorption sites on the CuPc metal centers and ~4 % of CuPc molecules are reacted with NO. Un-reacted central Cu²⁺ ion of CuPc appears as dark hole in both of empty and filled states STM images. Conversely, after chemisorption of NO, the topographic appearance of core metal ion is modified into a bright spot, while the 4-leaf pattern of ring still remain. As dosing duration increases to 10 min, the coverage of NO chemisorption sites increases to ~7 %. However this coverage increase is sublinear and further dosing does not increase the coverage consistent with a chemisorption induced change in electronic structure. In order to study the electronic structure of NO chemisorption onto CuPc molecules, scanning tunneling spectroscopy (STS) data was also obtained. Unreacted CuPc has a Fermi level (E_F) almost in the middle of the band gap. However, after NO

chemisorption, this central E_F shifts to the highest occupied molecular orbital (HOMO) and this transition indicates CuPc molecules is doped to 'p-type' by NO. This 'doping' process of NO is in good agreement with previously published theoretical predictions and is consistent with the high sensitivity of CuPc film to strong oxidants in CuPc OTFT chemical sensors.

11:40am **SS-ThM12 Formation of 2D Superstructure with Wide Band-gap n-type Behavior**, *T.K. Shimizu, J. Jung*, RIKEN, Japan, *T. Otani*, University of Tokyo, Japan, *Y.-K. Han*, Korea Basic Science Institute, *M. Kawai*, University of Tokyo, Japan, *Y. Kim*, RIKEN, Japan

A two-dimensional superstructure of molecules with high electron affinity was successfully formed on Au(111), and it indicated wide band-gap n-type behavior. The molecule used was fluorinated fullerene (C60F36). Although there exist three isomers (C3, C1, and T) in our molecular source, scanning tunneling microscopy (STM) images and density functional theory (DFT) calculations suggested that the molecules in the well-ordered region consisted of only the C3 isomer. Its LUMO distribution governs the adsorption orientation due to partial electron transfer from Au to the molecule. The intermolecular C-F...p electrostatic interactions determines the lateral orientation of C60F36 molecules.

[Ref] Shimizu et al., ACS Nano 6, 2679-2685 (2012).

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