Surface Science
Room 104D - Session SS-ThM

Chirality and Enantioselectivity on Surfaces; Ionic Liquid Interfaces

Moderator: Eddy Tysoe, University of Wisconsin-Milwaukee

8:00am **SS-ThM1 Self-assembly and Dynamics for Chiral Conformational Switches on Surfaces Studied by UHV-STM***, **Trolle Linderoth**,* Aarhus University, Denmark **INVITED**

Chiral self-assembled structures formed from organic molecules adsorbed on surfaces can be studied at high resolution by Scanning Tunneling Microscopy under Ultra-High Vacuum conditions. Through collaboration between UHV-STM experiments and organic synthesis, we have investigated how molecular conformational flexibility can lead to new chiral effects in the form of chiral switching, chiral accommodation and chiral induction, allowing transfer of chirality from the molecular to the supra-molecular level [1-5]. To generalize these principles, we have recently developed a new system of 3-bit binary conformational switches (Oligo-Naphthalene Ethynylenes) [6, 7] and in particular quantified their dynamic conformational switching and collective effects in ordering using time-resolved STM movies.

[1] Weigelt, S.; Busse. C.; Petersen, L.; Rauls, E.; Hammer, B.; Gothelf, K.V.; Besenbacher, F.; Linderoth, T.R. Nature Materials, **2006**, **5** 11.

[2] Bombis, C.; Weigelt, S.; Knudsen, M. M.; Nørgaard, M.; Busse, C.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. ACS NANO **2010***4*, 297.

[3] Knudsen, M.; Kalashnyk, N.; Masini, F.; Cramer, J.; Lægsgaard, E.: Besenbacher, F.; Linderoth, T. R.; Gothelf, K. .V. Journ. Am. Chem. Soc. **2011**, *133*, 4896.

[4] Masini, F.; Kalashnyk, N.; Knudsen, M. M.; Cramer, J. R.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. Journ. Am. Chem. Soc. **2011,***133* 13910.

[5] Nuermaimaiti, A.; Bombis, C.; Knudsen, M. M.,; Cramer, J.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. ACS Nano **2014,***8*, 8074.

[6] Cramer, J. R.; Ning, Y.; Shen, C.; Nuermaimaiti, A.; Besenbacher, F.: Linderoth, T. R.; Gothelf, K.V. Eur. J. Org. Chem. **2013** 2813.

[7] Ning, Y.; Cramer, J. R.; Nuermaimaiti, A.; Svane, K.; Yu, M.; Lægsgaard, E.; Besenbacher, F.; Xue, Q.-K. ; Ma, X.; Hammer, B.; Gothelf, K. V.; Linderoth, T. R. J. Chem. Phys. **2015***142*, 101922.

8:40am **SS-ThM3 Chiral Recognition among Non-planar Aromatic Hydrocarbons on Metal Surfaces***, A. Mairena,* Empa, Swiss Federal Laboratories for Materials Science and Technology*; M. Parschau, **Karl-Heinz Ernst**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Molecular recognition among chiral molecules on surfaces is of paramount importance in biomineralization, enantioselective heterogeneous catalysis, and for the separation of chiral molecules into their enantiomers via crystallization or chromatography. Understanding the principles of molecular recognition in general, however, is a difficult task and calls for investigation of appropriate model systems. One popular approach is thereby studying intermolecular interactions on well-defined solid surfaces, which allows in particular the use of scanning tunneling microscopy (STM). We present an elucidation of chiral recognition of helical and bowl-shaped hydrocarbons in monolayers and in multilayers. For penthalicene, a unique coexistence of 2D conglomerate and racemate is observed on a copper surface. Chiral bias in form of small enantiomeric excess leads to single enantiomorphism in multilayered samples of racemic heptahelicene.[1] Only the majority enantiomer is allowed to exist in the bottom layer, whereas the top layer consists exclusively of the minority enantiomer, i.e., enantioselective de-wetting occurs.

Pentagonal substituted chiral buckybowls form 2D racemate crystals, but chiral hemifullerene restructures a copper surface such that special chiral kinks become stabilized by the enantiomers.[2]

1 M. Parschau, K.-H. Ernst, *Angew. Chem. Int. Ed.* **2015**, *54*, 14422.

2 W. Xiao, K.-H. Ernst et al., *Nature Chemistry***2016**, in press.

9:00am **SS-ThM4 Competing Forces in Chiral Surface Chemistry: Enantiospecificity versus Enantiomer Disproportionation***, **Andrew Gellman**, Y. Yun,* Carnegie Mellon University

{The enantiospecific adsorption of chiral molecules on chiral surfaces is dictated by two competing forces the enantiospecificity of adsorption energetics and the propensity of enantiomers to disproportionate into homochiral (conglomerate) or heterochiral (racemate) clusters. These phenomena have been studied by measuring the surface enantiomeric excess, ee_s, of mixtures of chiral amino acids adsorbed on Cu surfaces and in equilibrium with gas phase mixtures of varying enantiomeric excess, ee_g. Alanine adsorption on Cu$\{3,1,17\}^{R\&S}$ surfaces is non-enantiospecific, $ee_s = ee_g$, because alanine enantiomers do not interact with either the surface or one another enantiospecifically. Aspartic acid adsorbs enantiospecifically on the Cu$\{3,1,17\}^{R\&S}$ surfaces; ee_snot= ee_g, even during exposure to a racemic mixture in the gas phase, ee_g=0. Exposure of the achiral Cu{111} surface to non-racemic aspartic acid, ee_g not= 0, results in local amplification of enantiomeric excess, $|ee_s| > |ee_g|$, as a result of homochiral disproportionation. Finally, in spite of the fact that the Cu$\{653\}^{R\&S}$ surfaces are chiral, the adsorption of aspartic acid mixture is dominated by homochiral disproportionation of adsorbed enantiomers rather than enantiospecific adsorbate-surface interactions, $|ee_s| > |ee_g|$. All of these types of behavior are captured by a Langmuir-like adsorption isotherm that also describes competition between enantiospecific adsorption and both homochiral (conglomerate) and heterochiral (racemate) clustering of adsorbed molecules.}

9:20am **SS-ThM5 Probing Individual Binding Sites around Individual Chiral Molecules on a Metal Surface: Chemisorption and Non-Covalent Bonding in Heterogeneous Asymmetric Hydrogenation***, **Peter McBreen**,* Laval University, Canada*; B. Hammer,* Aarhus University, Denmark*; M. Goves,* Aarhus University*; J.-C. Lemay, Y. Dong,* Laval University, Canada

There is rapid progress in the design and application of chirally-modified metal particles for heterogeneous catalytic enantioselective reactions. Modification is achieved by adsorbing chiral molecules to create asymmetric active sites. Great advances are being made in *operando* studies, surface science studies and theoretical studies of such systems. We will describe combined experimental and theoretical work related to the enantioselective hydrogenation of activated ketones on chirally-modified Pt(111). We will present results from combined variable temperature STM and optB88-vdW DFT studies of individual bimolecular docking complexes formed between enantiopure 1-(1-naphthyl)ethylamine, and related molecules, and representative prochiral substrates. The experiments reveal sub-molecularly resolved site-specific and stereospecific data. Single chemisorbed enanantiomers simultaneously present several chiral pockets, each displaying a specific prochiral ratio for a given substrate molecule. A hierarchy of chemisorption and intermolecular interactions is found to control prochiral selection at each pocket. Fine-tuning the structure of the modifier reveals how sensitive the stereochemical outcome is to even minor molecular changes. Time-lapsed STM measurements of individual substrate molecules sampling a set of chiral pockets provide new insight on stereocontrol, and on reaction paths and barriers at individual binding sites.

9:40am **SS-ThM6 Enhanced Hydrogenation Activity and Diastereomeric Inter-actions of Methyl Pyruvate Co-adsorbed with R-1-(1-Naphthylethylamine) on Pd(111)***, **Mausumi Mahapatra**, W.T. Tysoe,* University of Wisconsin-Milwaukee

The diastereomeric interactions and reactivity of co-adsorbed methyl pyruvate (MP) and *R*-1-(1-naphthyl)ethylamine (NEA) are studied on a Pd(111) model single crystal catalyst using temperature-programmed desorption (TPD) and scanning tunneling microscopy (STM) with the aim of identifying the nature of the interactions and understanding the observed enhancement in hydrogenation activity of MP to methyl lactate on NEA-modified surfaces. The enhancement in hydrogenation activity of chirally modified sites is critical in designing heterogeneous enantioselective catalysts by mitigating the effect of unmodified racemic sites. TPD experiments of coadsorbed MP and hydrogen or deuterium on Pd(111) reveal that NEA accelerates the rates of both MP hydrogenation and H/D exchange. The measured STM images of docking complexes on Pd(111) are classified according to the angles between the long axes of MP and the naphthyl ring of NEA, which fall into well-defined ranges of 10 ± 5, 45 ± 5 and 70 ± 5º. Docking structures are modeled using first-principles density functional theory (DFT) calculations that include van der Waals interactions, and STM image simulations. Excellent agreement is found both between the shapes of the calculated and simulated images and their theoretical and experimental dihedral angle distributions, thereby confirming the validity of the calculations. Diastereomeric interactions between NEA and MP occur predominantly by binding of the carbon-carbon double bond of the *enol* tautomer of MP to the surface, while simultaneously optimizing C=O····H_2N hydrogen-bonding interactions. The combination of chiral-NEA driven diastereomeric docking with a tautomeric preference enhances the hydrogenation activity since C=C bonds hydrogenate more easily than C=O bonds. This model provides a rationale for the catalytic observations.

11:00am **SS-ThM10 Structural Transitions of Ionic Liquids at Nanoconfined Interfaces***, **Rosa M. Espinosa-Marzal,*** University of Illinois at Urbana-Champaign **INVITED**

Ionic liquids (ILs) have remarkable properties including vanishingly low vapor-pressures, are non-flammable, and have wide thermal and electrochemical stability windows that make them ideal for several applications, including electrolytes in supercapacitors and lubricants. Our interest is to understand the interfacial behavior of ILs under nanoconfinement. Several studies have demonstrated the layered structure of ILs in nanoconfinement. The confined ions resist being " squeezed out" when surfaces are compressed, with the result that an IL film remains between the surfaces up to high pressures, thus preventing direct contact between the surfaces, also under shear, which can aid in reducing friction.

Laboratory studies have mainly focused on atomically flat and chemically homogeneous substrates, i.e. on ideal surfaces, to understand fundamental mechanisms. In our current work we are exploring the influence of nanoscale heterogeneities on ionic-liquid interfacial properties. Such heterogeneities can be composed of contamination, roughness or chemical surface groups. The strong molecular interactions still facilitate self-assembly of ILs on the surfaces, but they reveal new aspects of the IL behavior. We address diverse fundamental questions about the interfacial IL structure and the response to shear in the presence of heterogeneities. Further, these studies are of relevance to extend studies performed on ideal systems to real applications.

11:40am **SS-ThM12 Ionic Liquid Ordering at a Model Electrode Interface: 1-butyl-3-methylimidazolium Tetrafluoroborate, [C4C1Im][BF4], Interaction with the Anatase TiO2 (101) Surface***, **Michael Wagstaffe,*** University of Manchester, UK

Ionic liquids are room temperature molten salts comprised entirely of cations and anions. They have an array of unique physico-chemical properties that have led to their use in a wide variety of electrochemical systems.[1] These include actuators, corrosion inhibitors, energy storage for batteries, supercapacitors, displays and as the electrolyte in photovoltaic devices. Both the function and performance of devices employing ionic liquids are dependent on how the ionic liquid behaves at phase boundaries, interfaces and near interfacial areas. Previous studies have shown that ionic liquids have a tendency to self organize at the IL/solid interface.[2] Such ordering has been shown to reduce the barrier to charge injection when ionic liquids are used in oxide solar cells.[3] As such, the ordering and chemistry of ionic liquids at the anatase TiO_2(101) surface is of some interest since this is the dominant surface in mesoporous TiO_2 films used in dye sensitized solar cells.

Although there is a growing body of work on the surface chemistry of bulk ionic liquids studied by photoelectron spectroscopy, studies of their interaction with solid surfaces are still relatively rare. On this basis, in an attempt to address the gap in the work, we adopted a surface science approach in which we utilized a combination of X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. From this we were able to successfully determine the orientation of the cation on the surface of anatase(101), at both high and low coverage, and also the manner in which it adsorbs. Additionally, a surface induced degradation reaction of the anion was observed at room temperature.

[1] K. R. J. Lovelock *et al.Chem. Rev.*, 2010, **110**, 5158–90.

[2] E. Binetti *et al.J. Phys. Chem. C*, 2013, **117**, 12923–12929.

[3] B. R. Lee *et al. J. Mater. Chem.*, 2011, **21**, 2051.

12:00pm **SS-ThM13 In-Situ Photocurrent Measurements in Liquid-Phase Molecular Layer Deposition (LP-MLD)***, **Shi Bai,*** Tokyo University of Technology, Japan

[Introduction] A solution of the loss of heat by using black dye in a dye-sensitization solar cell is expending the width of the light absorbing wavelength by growing multi-dye with narrow wavelength to reduce the loss of heat. So, we supply and make the molecules grow according to the reaction between the molecules, and apply the multi-dye layer film by using Liquid-Phase Molecular Layer Deposition. By way of LP-MLD, the multi-dye layer forms on the surface of ZnO, and we test the expansion effect of the photocurrent spectrum width.

[Growth of multi-dye layer film]First, adsorb the p-type dye(Rose Bengal)molecules p1 on the surface. Because there is no reaction between the same molecules, and they don't combine each other. So the first layer is completed on the surface of the substrate which the surface is filled with p1.Second, remove the p1 by IPA(isopropyl alcohol), then supply the n1,molecules of n-type dye(Brilliant Green).p1 and n1 react and they combined. The same as step 1,the p1 layer is filled with n1,then the second layer is completed. Step 3 is using p-type dye(Eosin Y) molecules again. Repeat these steps, adsorb the molecules in the array as designed, and complete the multi-dye molecule layer film.

[Measurement of the photocurrent in LP-MLD]LP-MLD is a technology using the combination power between molecules of p-type dye and molecule of n-type dye to make a layer. Use IPA as the solvent to make a solution with the concentration of 1.6 x 10^{-2}mol/L. Set the substrate in a cell,inject the cell with IPA until the cell is full of it. Then inject the solution of p1 to make the dye molecules adsorbed by the substrate. After 20 minutes, in order to remove p1 solution in the cell, inject the cell with IPA again. After putting the laser on the substrate and measuring the photocurrent, repeat the process with other dye solution. Base on the measurement, the expansion effect of the photocurrent spectrum width was deduced.

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