

Surface Science

Room: Santa Ana - Session SS2-TuM

Aromatic Molecular Films

Moderator: C. Wöll, Karlsruhe Institute of Technology, Germany

8:00am **SS2-TuM1 Relating Aromatic Molecule Structure to Film Structure/Property Relationships**, *J.E. Anthony*, University of Kentucky **INVITED**

The ease with which small-molecule organic semiconductors can be functionalized allows a single chromophore framework to be tuned for use in a myriad of electronic applications. Careful selection of substituents allows tuning of both solubility and crystal packing, allowing optimum structures for both film morphology and charge transport to be dialed in by careful structure-property studies. Additional substituents on the chromophore can be added to improve stability, shift phase transitions, or change the dominant carrier type for the material. Using 4, 5 and 6 fused-ring acenes and heteroacenes as the chromophore, our straightforward functionalization approach has created organic materials for use in high-performance organic transistors and organic solar cells. The crystal-packing arrangements for these two types of devices are dramatically different. This talk will examine how materials with two-dimensional pi-stacking arrangements yield high-performance transistors, and how subtle tuning of the substituents can further improve performance and alter solubility. In the optimum case, hole mobility as high as $5 \text{ cm}^2 / \text{Vs}$ was observed from a dip-cast film. Structure-property relationships in organic transistors are also explored in high-quality single crystals, showing how changes in crystalline order changes the intrinsic carrier properties of a homologous series of materials. In the case of bulk heterojunction organic solar cells, substitution of the acene chromophore with small electron-withdrawing groups yielded effective acceptors in blends with polythiophene donors. In this case, materials with strong pi-stacking interactions yielded the poorest-performing solar cells. In contrast, materials with weak, 1-dimensional pi-stacking interactions yielded the best performance, with power conversion efficiencies greater than 1.5% in these fullerene-free blends.

8:40am **SS2-TuM3 Optimal Electron Doping of a C_{60} Monolayer on Cu(111) via Interface Reconstruction**, *W.W. Pai*, National Taiwan Univ., *H.T. Jeng*, Academia Sinica, Taiwan, *C.-M. Cheng*, National Synchrotron Radiation Research Center, Taiwan, *C.-H. Lin*, National Taiwan Univ., *X.D. Xiao*, *A.D. Zhao*, *X.Q. Zhang*, Hong Kong Univ. of Sci. and Tech., *G. Xu*, *X.Q. Shi*, *M.A. Van Hove*, City Univ. of Hong Kong, *C.-S. Hsue*, National Tsing Hua Univ., Taiwan, *K.-D. Tsuei*, National Synchrotron Radiation Research Center, Taiwan

We demonstrate the charge state of C_{60} on a Cu(111) surface can be made optimal, i.e., forming C_{60}^{3-} as required for superconductivity in bulk alkali-doped C_{60} , purely through interface reconstruction rather than with foreign dopants [1]. We link the origin of the C_{60}^{3-} charge state to a reconstructed interface with ordered (4×4) 7-atom vacancy holes in the surface. In contrast, C_{60} adsorbed on unreconstructed Cu(111) receives a much smaller amount of electrons. Specifically, we used multiple techniques of scanning tunneling microscopy and spectroscopy (STM/STS), angle-resolved and angle-integrated photoemission spectroscopy (AR-, AI-PES), ab initio calculations, and low-energy electron diffraction I-V analysis (LEED I-V) to convincingly establish the C_{60}^{3-} charge state and the reconstructed interface model. With STM, in-situ monitoring of C_{60} growth at $\sim 400 \text{ K}$ revealed that each C_{60} removes 7 atoms. STS showed the LUMO band sits nearly at the Fermi energy when the interface is reconstructed, or $\sim 0.8 \text{ eV}$ above the Fermi energy at unreconstructed interface. AI-PES indicated the initial charge state of C_{60} over reconstructed interface is already close to C_{60}^{3-} because very few extra K atoms are needed to reach maximal LUMO spectra intensity. AR-PES showed two hole-like bands crossing Γ bar that account for most of the charge transfer, and a shallow electron-like band near Γ bar. An extensive LEED I-V analysis using a total fitting range of $\sim 3500 \text{ eV}$ and 33 independent beams resolved the preferred structure model as the unfaulted fcc 7-atom monolayer vacancy model. We obtained a very good Pendry factor of ~ 0.27 . Finally, although the C_{60} has an optimal doping level for bulk superconductivity, we did not observe surface superconductivity down to $\sim 5 \text{ K}$. Our result adds a new dimension in understanding functional molecular thin films; it illustrates a definitive interface structure-doping effect that affects the electronic properties of molecule-electrode contact.

[1] Woei Wu Pai et al., *Phys. Rev. Lett.* **104**, 036103 (2010)

9:00am **SS2-TuM4 Pattern Formation of Arenes and their Derivates on Cu(111)**, *D.Z. Sun*, *D.H. Kim*, *Z.H. Cheng*, *Y.M. Zhu*, *W.H. Lu*, *M. Luo*, University of California at Riverside, *S. Hong*, *T.S. Rahman*, University of Central Florida, *L. Bartels*, University of California at Riverside

Intermolecular force plays an important role in self-assembly and surface pattern formation. Unsubstituted arenes, such as anthracene, attach to a metallic substrate predominantly through van der Waals interaction leading to substrate binding that is less sensitive to the precise adsorption configuration and allows a range of ordered surface patterns. In contrast, substitution of the arenes can lead to strong intermolecular forces within the film and amplified substituent-substrate interactions that strictly define the adsorption configuration and film pattern. In this contribution we present the pattern formation of anthracene on Cu(111) and show how addition of thiol and carbonyl groups can vary the resultant surface pattern. For each case we investigate the chemical and physical interaction underlying the pattern formation using a combination of variable temperature scanning tunneling microscopy (STM) imaging and density functional theory (DFT) simulation.

9:20am **SS2-TuM5 Step Edge Barriers and Island Nucleation in Organic Thin Film Growth**, *C.K. Teichert*, *A. Hlawacek*, *S.B. Lorbek*, *P.C. Puschnig*, *D. Nabok*, *C.E. Ambrosch-Draxl*, University of Leoben, Austria, *P.F. Frank*, *T.G. Potocar*, *A.H. Winkler*, Graz University of Technology, Austria

Crystalline films of conjugated organic semiconductors offer attractive potential for optoelectronic and electronic applications on flexible substrates. Due to the complexity and anisotropy of the molecular building blocks, novel growth mechanisms can occur as is demonstrated for the growth of the rod-like oligophenylene molecule paraxiphenyl (6P) on mica surfaces. On clean mica(001), the self-organization of crystallites into one-dimensional chains is observed on a wetting layer where the 6P molecules lie flat with their long molecular axis parallel to the surface [1].

Here, we demonstrate by atomic force microscopy that on an ion bombarded mica surface, the formation of terraced mounds composed by almost upright standing molecules is observed. In inorganic growth systems such a mound morphology is frequently due to a kinetic effect, the so-called Ehrlich-Schwoebel barrier for step-edge crossing [2]. Quantitative analysis of the mound morphology together with transition state theory calculations revealed the existence of molecule bending during step edge crossing and level dependent step edge barriers [3]. A lower barrier due to a larger molecular tilt angle (with respect to the surface normal) in the first layer results in the completion of one monolayer before mound formation starts. This is convincingly demonstrated by transverse shear microscopy measurements.

By temperature and rate dependent growth experiments we also determined the size of the critical nucleus to be significantly larger than one. These findings are again complemented by force-field calculations revealing the size of an energetically stable island of upright standing molecules.

Our analysis shows that procedures developed and verified for inorganic systems [2] can be successfully applied to organic thin film growth. However, we have also demonstrated that the complexity and anisotropy of the molecular building blocks lead to additional effects [3] that are not observed in atomic inorganic growth systems.

[1] C. Teichert, G. Hlawacek, A. Andreev, H. Sitter, P. Frank, A. Winkler, N.S. Sariciftci, *Appl. Phys. A* **82** (2006) 665.

[2] T. Michely and J. Krug; *Islands, Mounds and Atoms* (Springer, Berlin 2004).

[3] G. Hlawacek, P. Puschnig, P. Frank, A. Winkler, C. Ambrosch-Draxl, C. Teichert, *Science* **321** (2008) 108.

This work has been funded by Austrian Science Fund (FWF) within NFN "Organic Thin Films" Projects S9707 + S9714 as well as P19197.

9:40am **SS2-TuM6 Filamentous C_{60} Structures at C_{60} -ZnPc Interfaces**, *L. Tskipuri*, *W. Jin*, *Q. Liu*, *J. Weeks*, University of Maryland, *D.B. Dougherty*, North Carolina State University, *S.W. Robey*, NIST, *J.E. Reutt-Robey*, University of Maryland

Since the introduction of the bulk heterostructure concept, efficiencies of organic photovoltaic devices have improved markedly. This has spurred intense interest in controlling chemical morphologies to achieve more efficient charge separation. Unfortunately, there is surprisingly little guidance on how to achieve vertical nanophase separation in small-molecule materials. Basic studies of interface formation and nanophase separation in molecular materials are needed to understand how local chemical forces direct chemical morphology.

We present STM investigations of interface-formation and nanophase separation in binary films of zinc phthalocyanine (ZnPc) and C60 on Ag(111) and Au(111) supports. Physical vapor deposition provides exquisite control of the growth kinetics, allowing access to both metastable and thermodynamic phases. We demonstrate the controlled formation of ZnPc:C601-D and 2-D interfaces with distinctive molecular orientations and packing densities. Of particular interest is the formation of filamentous C60 structures at the ZnPc surface. C60 chains of single-molecular width wander the ZnPc substrate without registration to the underlying ZnPc template, islanding into a disordered chain phase. (Similar structures are also observed on Pn and 6-T surfaces.) These structures are reminiscent of dipole fluids (albeit of single molecular widths!) We present detailed measurements and analysis of C60 wandering chain formation on ZnPc/Ag(111) and ZnPc/Au(111) substrates. We then explore the physical origin of these structures through simulations with a model potential that incorporates short-range C60–C60 attraction and a long-range dipolar repulsion. From simulations of realized structures, we estimate the effective dipole needed for chain formation. We account for unexpected magnitude through the combined influences of the charge-transfer (interface) moment and the induced moment in these highly polarizable materials.

*This work has been supported by the UMD MRSEC (DMR 0520471) and NSF Surface and Analytical Chemistry(CHE0750203)

10:40am **SS2-TuM9 Manipulating Island Density and Shape in Organic Thin Film Growth: the Nucleation of Perfluoropentacene on Self-Assembled Monolayers**, *T.V. Desai, A.R. Woll, J.R. Engstrom*, Cornell University

We have examined the nucleation and growth of perfluoropentacene (PFP) on SiO₂ and on a variety of surfaces possessing different terminating self-assembled-monolayers (SAMs) using *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy (AFM). The SAMs ranged from very low surface energy hydrophobic surfaces (perfluorooctyltrichlorosilane, FOTS), to higher surface energy hydrophilic surfaces (3-methacryloxypropyltrichlorosilane, MAOPTS). From real time x-ray scattering we find that the growth of PFP, while crystalline, becomes very 3D after completion of the first 1-2 monolayers, independent of the substrate surface termination. Concerning growth in the submonolayer regime, we find that nucleation is homogeneous, and that the absolute density of islands depends strongly on the surface termination, while the relative change of the island density with increasing growth rate is essentially independent of the underlying SAM. From the latter we find that a critical island size of ~ 3 molecules can describe all the data. On the other hand, the dependence of the island density on termination implicates a significant change in the diffusivity of PFP with the identity of the SAM, with values differing by over 2 orders of magnitude. The shape of the islands also depends on the surface termination, but somewhat unexpectedly—the islands are most compact and faceted on surfaces where the diffusivity of isolated PFP molecules is the smallest. The shapes of the islands on these surfaces can be interpreted by arguments based on equilibrium, where polygonal islands expose low energy facets. These results demonstrate the sensitivity of the initial stages of nucleation to the nature and identity of the underlying substrate.

11:00am **SS2-TuM10 Surface Structure Directed Chemistry: A Scanning Tunneling Microscopy Study of Chemically Reactive Self-Assembled Monolayers**, *D.H. Dahanayaka*, The University of Oklahoma, *R.D. Abrahams*, University of Maryland, *A. Singh, L.P. Jackson, L.A. Bumm, R.L. Halterman*, The University of Oklahoma

Self-assembled monolayers (SAMs) are flexible substrates for surface chemistry. A wide variety of SAM-surface functionalities can be prepared using alkanethiols with different terminal functional groups. Typically this requires a different alkanethiol for each. Another strategy uses a single alkanethiol to create a reactive surface which can be chemically modified post self-assembly. We are exploring azido-functional monolayers, which are reactive under mild conditions. The best known reaction is the copper catalyzed catalytic 1,3-dipolar cycloaddition with terminal alkynes. This approach has already been demonstrated for general surface chemical modification. We demonstrate molecularly-resolved STM imaging of these SAMs before and after the reaction. The surface structure affects the local reactivity and can be used to direct the reaction at the nanometer scale.

This work has been supported by NSF CAREER grant No. CHE- 0239803, NSF MRSEC No. DMR-0080054, and NSF No. DMR-0805233.

11:20am **SS2-TuM11 Molecular Organization and Odd-Even Effects in in Perfluoro-terphenyl-Based Monomolecular Films**, *F. Chesneau*, Universität Heidelberg, Germany, *B. Schüpbach*, Universität Frankfurt, Germany, *K. Szalagowska-Kunstman*, Jagiellonian University, Poland, *N. Ballav*, Universität Heidelberg, Germany, *P. Cyganik*, Jagiellonian University, Poland, *A. Terfort*, Universität Frankfurt, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) formed by perfluoro-terphenyl-substituted alkanethiols (PFTP-ATs) with variable length of the aliphatic linker (either 2 or 3 methylene units) were prepared on (111) Au and Ag and characterized by a combination of several complementary spectroscopic and microscopic techniques. A specific feature of these systems is the helical conformation of the PFTP moieties, which, along with the high electronegativity of fluorine, distinguishes them from the analogous non-fluorinated systems and makes them attractive for different applications. The SAMs were found to be well-defined, highly ordered, and densely packed, which suggests a perfect correlation between the orientations and, in particular, twists of the PFTP helices in the adjacent molecules. Significantly, the SAM exhibited pronounced odd-even effects, i.e. a dependence of the molecular orientation and packing density on the length of the aliphatic linker in the target molecules, with parity of *n* being the decisive parameter and the direction of the effects on Au opposite to that on Ag. The presence of the odd-even effects in the FTPn system brings new aspects into the discussion about the origin and mechanism of these phenomena. Specifically, the helical conformation of the FTP moieties in the dense phase excludes a variation of the intramolecular torsion and molecular twist as the mechanism behind the odd-even effects.

11:40am **SS2-TuM12 From Selective Adsorption to Substrate Reconstruction: A Scanning Tunneling Microscopy Study of 4'-nitro-1,1'-biphenyl-4-thiol Self-Assembled Monolayers on Au(111)**, *H. Muzik*,

L. Kankate, A. Turchanin, A. Götzhäuser, University of Bielefeld, Germany
Self-assembled monolayers (SAMs) of 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) on gold surfaces are extensively used for applications in chemical nanolithography and fabrication of chemically functionalized ultrathin (down to 1 nm) nanomembranes. However, the structure of NBPT SAMs has not yet been investigated in detail. Here we present the first scanning tunneling microscopy (STM) study of NBPT SAMs on the Au(111) surface. NBPT SAMs were prepared both in solvent and by vapor deposition in vacuum. We show by complementary STM and X-ray photoelectron spectroscopy (XPS) measurements that NBPT SAMs exhibits a complex polymorphic phase behavior which strongly correlates with the surface density of NBPT molecules. We have found that at low NBPT coverage, the molecules selectively adsorb outside the bridging regions of the herringbone reconstructed Au(111) surface, whereas at high coverage intermolecular interactions lead to a reorganization of the Au(111) substrate. These findings can be very relevant for the tuning of nanomaterials and devices fabricated by chemical nanolithography from NBPT SAMs and give new insights in the molecular self-assembly of aromatic thiols on gold surfaces.

[1] A. Turchanin, A. Tinazli, M. El-Desawy, H. Großmann, M. Schnietz, H. H. Solak, R. Tampé, and A. Götzhäuser: Molecular self-assembly, chemical lithography, and biochemical tweezers: A path for the fabrication of functional nanometer-scale protein arrays: *Adv. Mater.* 20, 471-477 (2008).

[2] L. Kankate, A. Turchanin, and A. Götzhäuser: On the Release of Hydrogen from the S-H groups in the Formation of Self-Assembled Monolayers of Thiols. *Langmuir* 25, 10435-10438 (2009).

[3] M. Schnietz, A. Turchanin, C. T. Nottbohm, A. Beyer, H. H. Solak, P. Hinze, T. Weimann, A. Götzhäuser, Chemically functionalized carbon nanosieves with 1 nm thickness. *Small* 5, 2651-2655 (2009).

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