Thursday Morning, November 9, 2023

Surface Science Division
Room D136 - Session SS1+AS-ThM

Molecular Organization at Surfaces

Moderators: Eric Altman, Yale University, **Zdenek Jakub**, CEITEC

8:00am **SS1+AS-ThM-1 Supramolecular Self-assembly and Metal-Ligand Redox Assembly at Surfaces**, ***Steven Tait***, Indiana University **INVITED**

The selection and positioning of specific functional groups will direct packing and stacking of organic building blocks, which determine the electronic and chemical properties of molecular thin films and semiconductors. Design of molecular ligands for metal-organic complexation at surfaces can address the long-standing grand challenge of high selectivity in heterogeneous catalysis. Our group is working to develop principles of on-surface molecular self-assembly[1] and of metal-organic complexation[2] to gain new insight into molecular layers and new chemical activity at metal single-site catalysts.[3] This work involves close collaboration with multiple research groups to synergistically combine talent in design, synthesis, sample preparation, characterization, analysis, theory, and computational modeling. We use a range of surface characterization tools to interrogate these systems under well-controlled environments, including scanning probe microscopy, photoelectron spectroscopy, vibrational spectroscopy, and mass spectrometry. We investigate systems under a variety of conditions: solution/solid interface, ultra-high vacuum, and flow reactor conditions at high temperature and high pressure. Here, I will report on recent results in several aspects of this work. We have demonstrated the impact of conformational entropy in impeding self-assembly, but that this can be overcome with appropriate selection of co-solutes. Metal-organic complexes at surfaces can be designed to achieve single-site metal centers in which we can observe redox isomerism, control of metal oxidation state, transmetallation, and chemical spillover to the support. We have transferred this design concept for single-site catalysts to high-surface-area powder oxide supports and shown that these can operate as effective catalysts in solution and under gas flow conditions. Ongoing work will seek to extend understanding of these systems to achieve molecular thin films and single-site catalysts of greater complexity.

References

[1]D. L. Wisman, H. Kim, C. Kim, T. W. Morris, D. Lee, and S. L. Tait, Chemistry – a European Journal **27**, 13887-13893 (2021). DOI: 10.1002/chem.202101611 [https://doi.org/10.1002/chem.202101611]

[2]T. W. Morris, D. L. Wisman, N. Ud Din, D. Le, T. S. Rahman, S. L. Tait, Surface Science**712**, 121888 (2021). DOI: 10.1016/j.susc.2021.121888 [https://doi.org/10.1016/j.susc.2021.121888]

[3]E. Wasim, N. Ud Din, D. Le, X. Zhou, M. S. Pape, G. E. Sterbinsky, T. S. Rahman, S. L. Tait, Journal of Catalysis**413**, 81-92 (2022). DOI: 10.1016/j.jcat.2022.06.010 [https://doi.org/10.1016/j.jcat.2022.06.010]

8:40am **SS1+AS-ThM-3 Self-Assembly Controlled at the Level of Individual Functional Groups**, ***Benjamin Heiner***, *A. Pittsford, S. Kandel,* University of Notre Dame

Molecular self-assembly is a process that occurs when component molecules spontaneously organize into a specific arrangement due to the intermolecular interactions between them. These interactions are influenced by the functional groups present on the component molecules. By understanding the effects that different functional groups have on the self-assembly process, we can predict and control it. To do this, we study "families" of molecules that have a common backbone but differ in the functional groups they possess. We use a combination of experimental techniques, such as pulse deposition for scanning tunneling microscopy (STM), and a variety of computational methods to investigate the changes in self-assembly behavior that result from small modifications to the functional groups. In this talk/poster, I will present our work on a family of molecules with an indole backbone, including indol carboxylic acids, multiple isatin derivatives, and proline. By studying these molecules, we are able to gain a deeper understanding of the various intermolecular interactions that drive self-assembly in these systems.

9:00am **SS1+AS-ThM-4 Atomically-Defined, Air-Stable 2D Metal-Organic Frameworks on Graphene: How the Support Defines the System Properties**, ***Zdenek Jakub***, *A. Kurowska, J. Planer, A. Shahsavar, P. Prochazka, J. Cechal,* CEITEC - Central European Institute of Technology, Czechia

The functionality of 2D metal-organic frameworks (MOFs), crucially depends on the local environment of the embedded metal, and such details are best ascertained on 2D MOFs supported on atomically flat surfaces. Here, we present three systems which are well-defined at the atomic-scale, decoupled from the metal support and stable both in ultrahigh vacuum and in ambient conditions: M-TCNQ (M = Ni, Fe, Mn) supported on epitaxial graphene/Ir(111). We show that these systems are monophase with $M_1(TCNQ)_1$ stoichiometry, and we demonstrate their remarkable chemical and thermal stability. Furthermore, by a combined experimental and computational approach we study the differences between 2D MOF systems supported on graphene and on Au(111), the prototypical surface for on-surface synthesis. We show that the Fe-TCNQ on graphene is non-planar with iron in quasi-tetrahedral sites, but on Au(111) it is planarized by stronger van-der-Waals interaction. Combined with the distinct energy level alignment with the supports, this results in significant differences in the 2D MOF properties on these two surfaces. Our results outline the limitations of common on-surface approaches using metal supports and show that the intrinsic 2D MOF properties can be partially retained on graphene. The modular M-TCNQ/graphene system combines the atomic-scale definition required for fundamental studies with the robustness and stability needed for applications, thus we consider it an ideal model for research in single atom catalysis or spintronics.

9:20am **SS1+AS-ThM-5 Using 2D COFs to Stabilize Single-Atom Catalysts on Model Surfaces: From Ultra-High Vacuum System to Ambient Conditions**, ***Yufei Bai***, Indiana University; *D. Wisman,* NAVSEA Crane; *S. Tait,* Indiana University

Single-atom catalysts (SACs) combine the advantages of homogeneous and heterogeneous catalysts by limiting the reaction sites to isolated single metal atoms with well-defined chemical characters. Our group has developed a metal-ligand coordination method to stabilize SACs using 1,10-phenanthroline-5,6-dione (PDO) to coordinate with metal atoms such as Pt, Fe, and Cr. In order to further improve the stability of SACs and increase metal loading, we have synthesized single-layered covalent organic frameworks (SCOFs) on model surfaces under ultra-high vacuum (UHV) conditions or under ambient conditions. These two-dimensional (2D) networks with high thermal and chemical stability were used to confine single Pt atoms coordinated with ligands into SCOF pores. Under UHV conditions, the successful formation of the SCOF with regular hexagonal pores on the Au(111) surface was achieved by surface-mediated Ullmann radical coupling of 1,3,5-tris-(4-bromophenyl)benzene (TBB) and characterized by scanning tunneling microscopy (STM). Further sequential deposition of PDO ligand and Pt on the TBB-SCOF surface allowed the formation of single-site Pt catalysts by coordination interaction. STM images have proved the confinement of PDO in the SCOF pores, while X-ray photoelectron spectroscopy (XPS) has proven the oxidation state of Pt, which is an indication of the single atom character. Under ambient conditions, a 2D imine-linked SCOF was formed on the highly oriented pyrolytic graphite (HOPG) surface by a solid-vapor interface mechanism, which allows for a high quality SCOF with long-range order. STM characterization has shown that regular SCOF networks with negligible defects were formed on the HOPG surface with domain sizes greater than 1 µm × 1 µm. These systems which combine the COF and metal-ligand coordination strategy to stabilize SACs offer the possibility to achieve higher stability and greater loading in SACs.

9:40am **SS1+AS-ThM-6 Protein Adsorption on Mixed Self-Assembled Monolayers: Influence of Chain Length and Terminal Group**, ***Rebecca Thompson***, St. Edward's University

Mixed self-assembled monolayers (SAMs) are often used as highly tunable substrates for biomedical and biosensing applications. It is well documented, however, that mixed SAMs can be highly disordered at the molecular level and do not pack as closely or homogeneously, particularly when the chain lengths and head groups of the SAM thiol components are significantly different. In the current study, we explore the impact of SAM structure and mixing ratio on the weak physisorption behavior of bovine serum albumin (BSA), which adsorbs more readily to hydrophobic, methyl-terminated SAMs. Our results suggest that once the mixture includes 50% or more of the methyl terminus, mixing ratio alone is a relatively good predictor of adsorption, regardless of the relative chain lengths of the thiols used in the mixture. This trend persists at any mixing ratio for SAMs where methyl- and hydroxyl-terminated groups are the same length or where the hydroxyl-terminated thiol is longer. The only variance observed is at low mixing ratios (<50% methyl-terminated) for a mixed SAM where the methyl-terminated component has a longer chain length. Relative protein adsorption increases on these mixtures, perhaps due to the disordered exposure of the excess alkane backbone. Taken together, however, we do not find significant evidence that varying chain lengths for mixed SAMs prepared on polycrystalline substrates and analyzed in air have an outsized influence on nanoscopic adsorption behavior, despite molecular-level disorder in the SAM itself.

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