

Biomaterial Interfaces

Room 117 - Session BI1-MoM

Biomolecules and Biophysics at Interfaces

Moderators: Christopher So, Naval Research Laboratory, Markus Valtiner, Vienna University of Technology, Austria

8:15am BI1-MoM-1 Molecular Modeling of Peptide and Protein-Based

Materials: Role of Surface and Interface on Structure and Function, Yaroslava Yingling, North Carolina State University **INVITED**

Borrowing the structure and function of proteins to design novel multifunctional materials offers a potential solution for pressing technological needs and various applications. However, integration of proteins or peptides with synthetic materials requires a deeper understanding of properties and processes at the bio-material interfaces. We use molecular modeling for the detailed examination of proteins or peptides as they interact with material surfaces or interfaces revealing critical insights into binding dynamics, structural changes, orientation shifts, and conformational alterations. These molecular interactions are key to engineering materials that are not only stable and biocompatible but also capable of retaining specific biological functions. We specifically examine the interaction of proteins and peptides with heterogeneous material interfaces, such as graphene oxide and silica, elucidating how these interactions impact the protein structure. We also incorporated functional peptides into supramolecular structures, such as micelles, that would mimic protein functions from natural metalloproteins and phosphate-binding functionalities and explore the role of core-corona interface by altering the chemical nature of the core on the retention of protein function and structure, the influence of molecular tails on properties and secondary structures, and the adsorption behaviors of phosphate and zinc ions. Overall, we show that atomic-level understanding of the properties and processes at the protein-material interface is crucial for designing advanced materials that enhance functionality and performance across diverse applications.

8:45am BI1-MoM-3 Crowding Accelerates Molecular Aging in Protein

Droplets, M. Brzezinski, P. Argudo, J. Michels, Max Planck Institute for Polymer Research, Germany; **Sapun Parekh**, University of Texas at Austin

Protein liquid-liquid phase separation (LLPS) is a process in which a homogeneous mixture of proteins in a solvent self-assembles, upon certain stimuli, into a protein-rich and protein-depleted phase. In a simple two-component system, the protein-rich phase is called a protein condensate or droplet phase, and the protein-depleted phase is the continuous phase. Recent work has shown that many intrinsically disordered proteins (IDPs) undergo two-component phase separation in vitro due to a myriad of weak interactions. LLPS can be further enhanced by crowding agents. Crowders help to tune effective volume fractions to more "convenient" ratios, which results in a broader window of suitable parameters for obtaining phase separation. Moreover, with use of crowding agents, LLPS has been shown to occur not only for IDPs, but also for folded proteins. So, how do crowding agents affect LLPS of proteins? Depending on the affinity of the crowder for the protein, segregative and associative phase separation can be distinguished. In the following work, we present a systematic approach to quantifying LLPS influenced by crowding agents for an IDP and folded protein. We use fluorescence recovery after photobleaching (FRAP) to quantify material properties and coherent anti-Stokes Raman spectroscopy (CARS) to quantify molecular composition and secondary structure, and theory to demonstrate molecular aging in crowded condensates. We find that crowding accelerates aging in condensates and that folded proteins can phase separate and show molecular aging as well. These results have implication for studying transitions from condensates to fibrils over time.

9:00am BI1-MoM-4 Self-Healing Nanotubes Consisting of Cyclic Peptides

Conjugated by Azobenzene Derivatives, **Olufolasade Atoyebi**, M. Beasley, W. Maza, M. Thum, C. Pyles, S. Tuck, A. Dunkelberger, M. Kolel-Veetil, K. Fears, US Naval Research Laboratory

Cyclic peptides are capable of self-assembling into supramolecular peptide nanotube structures, via hydrogen bonding along the backbone of the peptide rings. Research from our lab has improved upon the synthesis of the self-assembled peptide nanotubes by covalently linking the cyclic peptides into a linear polymer chain that transitions from the unfolded structure to the peptide nanotube by varying the pH of the solution. Here we present an alternate way to control the self-assembly from the linear polymer chain to the rigid peptide nanotube via photo-isomerization. We

capitalize on azobenzene's photo-actuable nature using a di-carboxylic acid azobenzene to covalently crosslink the cyclic peptide rings (KVVKVV) via the two primary amines displayed by each ring. When the azobenzene crosslinker is in its thermally-relaxed, *trans* conformation, the cyclic peptide polymer adopts a rigid, nanotube conformation. When excited by UV light (320 nm), the *trans* to *cis* transition of the azobenzene crosslinker disrupts hydrogen bonding between adjacent rings, causing the polymer to unfold. Atomic force microscopy (AFM) shows that the polymer chain re-fold into rigid nanotube when the azobenzene crosslinkers return to the *trans* conformation, either by stimulation by visible light (420 nm) or thermal relaxation. This work introduces a novel class of intrinsically self-healing nanomaterials that can be used as reinforcement agents for a wide variety of industrial and biological materials.

Author Index

Bold page numbers indicate presenter

— A —

Argudo, P.: BI1-MoM-3, **1**
Atoyebi, O.: BI1-MoM-4, **1**

— B —

Beasley, M.: BI1-MoM-4, **1**
Brzezinski, M.: BI1-MoM-3, **1**

— D —

Dunkelberger, A.: BI1-MoM-4, **1**

— F —

Fears, K.: BI1-MoM-4, **1**

— K —

Kolel-Veetil, M.: BI1-MoM-4, **1**

— M —

Maza, W.: BI1-MoM-4, **1**
Michels, J.: BI1-MoM-3, **1**

— P —

Parekh, S.: BI1-MoM-3, **1**
Pyles, C.: BI1-MoM-4, **1**

— T —

Thum, M.: BI1-MoM-4, **1**
Tuck, S.: BI1-MoM-4, **1**

— Y —

Yingling, Y.: BI1-MoM-1, **1**