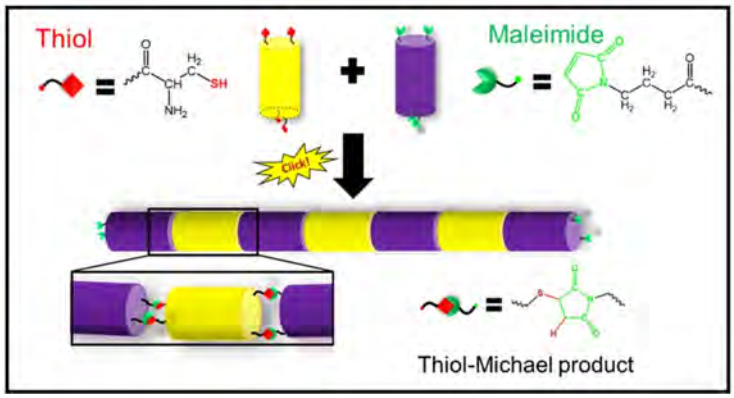
Exotic polymers of computationally designed peptide *Bundlemers* constructed via a new hybrid physical-covalent assembly pathway

Nairiti Sinha[1,2]*, sinha@udel.edu, Dongdong Wu*[1]*, Jeffery G. Saven*[4]*, Christopher J. Kloxin*[3,1]*, Darrin J. Pochan*[1]*.* (1) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States (2) NIST Center for Neutron Research, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, United States (3) Dept of Chemical Engineering, University of Delaware, Newark, Delaware, United States (4) Univ of Penn, Philadelphia, Pennsylvania, United States

Computational prediction of peptide sequences that assemble into predesigned nanostructures has emerged as a powerful avenue for new material construction. Applying this tool, we have identified short peptide sequences that form α-helical antiparallel homotetramers called coiled coils also known as bundlemers. The modular bundlemers are nanocylinders that are 4 nm in length and 2 nm in diameter as determined using small angle scattering (SAS) techniques and can be computationally designed to display various charge patterns via strategic placement of amino acid side groups. Taking advantage of the antiparallel packing of peptides within bundlemers, we have modified their N-termini to include complementary thiol or maleimide groups resulting in tetra-functional 'monomers' that can react via Thiol-Michael *click* reaction to form exotic polymers of alternating bundlemers. The polymer length can be controlled via stoichiometric considerations of step-growth polymerization and the resulting polymers are readily viewable under a Transmission Electron Microscope (TEM). Interestingly, the linker type between bundlemers impacts the polymer type: a propyl linker results in rigid rod-like polymers that display persistence lengths larger than a micron, whereas a tetra-thiol linker (PETMP) results in formation of semi-rigid fibers that have a persistence length of a few hundred nanometers, as characterized using end-to-end distance analyses of such worm-like polymers in TEM micrographs. These results are further corroborated by SAS measurements in which formation of 2 nm cross-section polymers displaying different persistence lengths is confirmed, proving the success of the hybrid physical-covalent assembly pathway. Rigid rod-like polymers of bundlemers also display tunable lyotropic liquid crystalline phases; formation of these phases are sensitive to the charge distribution along the rods as also to solution conditions such as pH and presence of salt.



Schematic of hybrid physical-covalent assembly pathway which results in rigid rod-like polymers via Thiol-Michael *click* reaction of bundlemers (cylinders) decorated with thiol (red) and maleimide (green) groups.