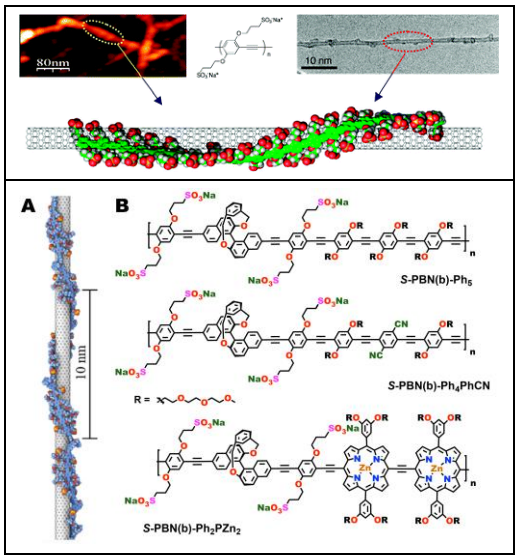
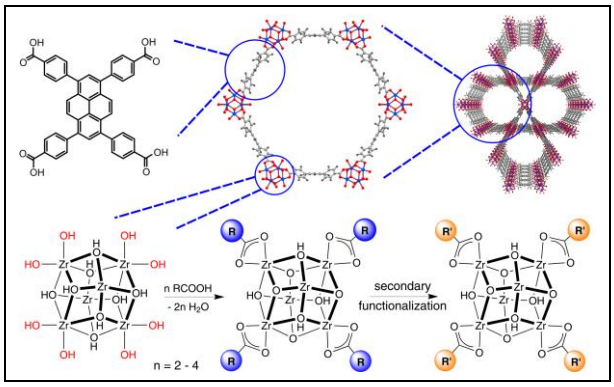
Surface Engineering: Evolution of Functional Materials Based on Nano-scale Tubular and Porous Structures

Inorganic and organic nanomaterials have emerged in the past decade as low-cost candidate materials for various optoelectronic devices, including solar energy harvesting systems. The size-dependent properties of semiconducting nanoparticles and nanotubes observed in these systems suggest new strategies to develop effective next generation materials for energy conversion and storage. Likewise, nanoporous crystalline structures known as porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) have recently sparked interest in applications such as catalysis, light harvesting, sensing, optical luminescence, ionic conductivity and non-linear optical behavior beyond their typical utility in gas capture, separation and storage purposes. Surface engineering (or functionalization) not only helps solubilizing and processing these materials but can incorporate new functionalities and modulate the excitonic and electronic properties of these nano-scale structures.

This presentation will focus on:



(*i*) Noncovalent surface engineering of single-walled carbon nanotubes (SWNTs) via helical wrapping of amphiphilic, linear conjugated poly(aryleneethynylene)s. Helical wrapping not only provides robust polymer-wrapped individualized SWNT superstructures in multiple solvents and high density solids with constant morphology but also helps studying various fundamental SWNT optoelectronic properties such as SWNT solvatochroism, optically excited SWNT-triplet state that could not have been studied otherwise. Development of polymers that wrap SWNTs with *fixed and controllable* helical chirality further offer preparation of bulk phase, hierarchical dense arrays of individualized, aligned SWNTs via ionic self-assembly. These studies also suggest that strongly interacting polymers can potentially modulate SWNT optoelectronic properties and play a key role as electron transport elements in excitonic solar cells and function as electron donors in electron transfer reactions involving photoactivatable redox centers anchored to the SWNT backbone.



(*ii*) Incorporation of functionality in MOFs is often not straightforward by using appropriately derivatized organic linkers during typical solvothermal syntheses due to limited linker solubility, chemical and thermal stability, or functional group compatibility. Therefore, metal-cluster containing nodes offer an opportunity to introduce a battery of new functionality through the replacement of charge balancing non-framework ligands. A new functionalization technique, solvent assisted ligand incorporation (SALI) was developed to efficiently incorporate various carboxylate-based functionalities in the Zr_6-based metal-organic framework, **NU-1000**. SALI relies on either acid-base or ligand exchange chemistry between the existing anionic ligand on the MOF node and the incoming anionic ligand. This technique not only proved to be versatile and tolerant of multiple functionalities, but also found to be robust and effective for a secondary functionalization.