Self-assembly of molecules into materials is an attractive materials construction strategy primarily due to its simplicity in application. By considering properly designed peptidic or synthetic polymer molecules in the bottom-up materials solution assembly process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. Two classes of molecules will be discussed: peptides and synthetic block copolymers.

The local nanostructure control of one-dimensional fibril growth with designed beta-hairpin peptides will be discussed. Changes in the assembling peptide molecules are manifested in the supramolecular fibril structure. If properly designed, hydrogel networks can be formed from the peptide assembly. Examples of nanostructure control as well as control of overall hydrogel network structure, and resultant viscoelastic and cell-level biological properties, will be presented. In addition, peptide fibrils can be used to template the growth of inorganic materials as well as the assembly of inorganic nanoparticles. Both long polypeptides, synthesized through recombinant techniques, as well as short peptides have also been designed for fibrillar assembly. On forming fibrils, the long polypeptides display chemistry at desired distances along the fibrils, thus allowing desired inorganic particle assembly with great fidelity.

Kinetic pathways and temporal stabilities of synthetic block copolymers in solution have been used to construct exotic nanoparticles. Due to low molecular chain exchange dynamics between block copolymeric aggregates and solvent, global thermodynamic equilibrium is extremely difficult, if not impossible, to achieve in block copolymer assembly. However, by taking advantage of this slow kinetic behavior of polymeric nanostructures in solution, one can purposely produce multicompartiment nanoparticles and multigeometry nanoparticles by forcing different block copolymers to reside in the same nanoscale structure through kinetic processing. While kinetically trapped in common nanostructures, local phase separation can occur producing compartments. This compartmentalization can be used within common micelle geometries to make complex spheres and cylinders or can be used to make new nanostructures such as multigeometry aggregates (e.g., hybrid cylinder-sphere aggregates, disk-cylinder nanoparticles). Other particle nanostructures such as toroids, disks, and helical cylinders have been constructed.

Cryo transmission electron microscopy (cryoTEM), transmission electron microscopy (TEM), small angle neutron or x-ray scattering (SANS, SAXS), atomic force microscopy, oscillatory rheology, spectroscopy, in vitro cell culturing and preliminary in vivo animal experiments have all been used to characterize the nano-through-microstructure and material properties of the above self-assembled systems.